RED-SENSITIVE IMAGING SYSTEMS FOR HOLOGRAPHY

by

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A THESIS

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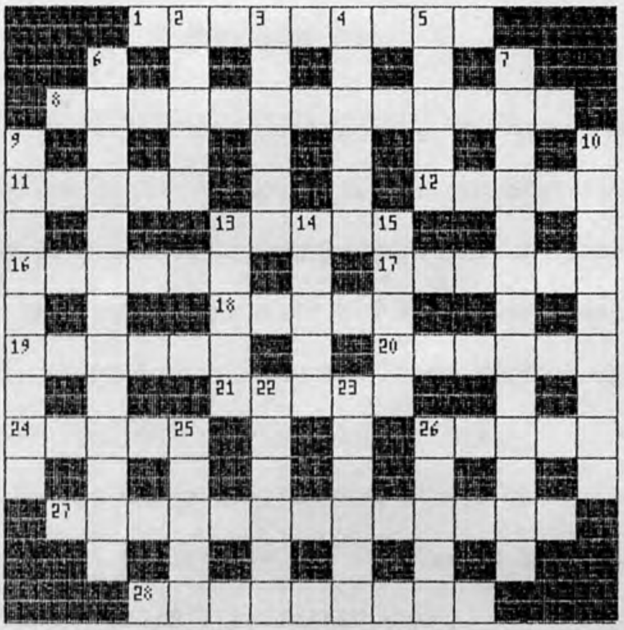
To my parents.



Thesis Crossword by M.J.Whitcombe

Across clues

1. Concerning deeds performed by chemists? (9)
8. Carbene unhappy with this dyestuff? (9,4)
11. This alternative can be a bit of a bother. (5)
12. Foreign currency Jo broke, thats how to take pleasure. (5)
13. Playful spirit of a gazelle? (5)
16. A whale secreted itself in a flower. (6)
17. Bill turned-up, seen at cove perhaps? (6)
18. Prepare for a fit of pique. (5)
19. Drinking vessel sounds like it's right on to me! (6)
20. Pen one thousand. That is to frustrate them. (6)
21. It's empty in a North-Easterly direction. (5)
24. Foul air maims badly. (5)
26. All play but make a disapproving noise when it returns. (5)
27. Like these resists, resembling America in the McCarthy Era. (3-10)
28. Brings about a reaction, causes a riot in it possibly. (9)

Down clues

2. There might be another solvent for organic material. (5)
3. Pass our paint. (6)
4. Noise I dispersed by going to make a small charge. (6)
5. Toff the French make into a peer. (5)
6. Have a cry after the event, covered in solvent and vinyl monomers. (13)
7. Topic of import not to the King but to one under him? (7-6)
9. Pictures of seemingly empty weights? (9)
10. Together with this volume we prepare the recipe. (9)
13. A study I made of someone from the Yemen. (5)
14. Elecampane was found in University, Los Angeles. (5)
15. Failure to listen to the way the cat drinks. (5)
22. Pole stern before becoming German chemist. (5)
23. There must be a little number in a group of deities. (6)
25. Particular claim by male offspring? (5)
26. Short thanks in love due to extinct West Indian. (5)

Solution on page 310.

Acknowledgments

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Abstract

The primary objective of the work described in this thesis was to devise a red-sensitive photoresist imaging process for use in the replication of diffraction optics.

In the introduction the chemistry of conventional photopolymer systems and photoresists used for holographic recording and the fabrication of diffraction gratings and diffracting optical elements is reviewed. The limitations of commercially available photoresist systems, particularly for applications requiring the use of red light are discussed.

A polymer system has been investigated which could be imaged by photochemically generated free radicals, followed by a simple aqueous development procedure as required by the original specification. The polymer chosen for study was a copolymer of methyl methacrylate, methacrylic acid and 2-hydroxyethyl methacrylate. This was derivatized using methacryloyl chloride or methacrylic anhydride in order to introduce cross-linkable units to the polymer backbone.

Polymers have been characterized by a number of techniques and the effect of varying composition on aqueous base solubility has been thoroughly studied. Various methods of derivatization have been employed. The ease of imaging has been found to be very sensitive to both the composition of the polymer and the extent of functionalization. High quality images have been obtained from this polymer using an organic solvent developer.

Imaging experiments have been carried out on thin films of the photopolymer coated on glass using phenylazotriphenylmethane (PATM) as photoinitiator. Good images of 100 lines per

millimetre (l mm^{-1}) have been recorded by contact printing. Interferometry has been used to demonstrate that interference patterns having 600 and 1200 l mm^{-1} can be recorded using this polymer with PATM as initiator, exposed to an argon ion laser operating at 458nm.

A number of two component photoredox initiator systems have been investigated, the light absorbing species of such systems being a dye such as methylene blue or certain cyanine dyes. The second component of these initiators may be an aryl sulphinate salt, a 1,3-diketone or some alkyl sulphides. The red light-initiated photopolymerization of acrylamide has been demonstrated using some of these initiators and a low resolution photopolymer image has been recorded using Azure A and perinaphth-1,3-indandione as the photoinitiator system.

This polymer can, in principle, produce images over a wide range of wavelengths depending on the nature of the initiator used.

CONTENTS

List of Abbreviations Used in This Thesis

A	acetone
AcAnh	acetic anhydride
AcCl	acetyl chloride
AIBN	azo-*bis*-isobutryonitrile
B	base
BN	*N*-methyl-2-benzoyl-β-naphthothiazoline
bp	boiling point
Bu^n-	normal butyl
Bu^t-	tertiary butyl
calc	calculated
COP	same as p(GMA-EA)
d	doublet
DMF	*N,N*-dimethyl formamide
DMSO	dimethyl sulphoxide
E	excitation
EA	ethyl acetate
Et-	ethyl
eV	electron volts
F	fluorescence
fig	figure
g	grams
gpc	gel-permeation chromatography
h	hours
HEMA	2-hydroxyethyl methacrylate
HOE	holographic optical element
HPLC	high performance (or high pressure) liquid chromatography
IC	internal conversion
ISC	inter-system crossing
$l\ mm^{-1}$	lines per millimetre
LSI	large scale integrated
lut	2,6-lutidine
m	medium, minutes, multiplet
M	monomer
MAA	methacrylic acid
MACl	methacryloyl chloride
MB	methylene blue
Me-	methyl
MEK	methyl ethyl ketone (butanone)
MG	methylene green
MHz	megahertz
MK	Michler's ketone
ml	millilitres
MMA	methyl methacrylate
mp	melting point
MV	methylene violet
NaTS	sodium *para*-toluenesulphinate
nmr	nuclear magnetic resonance (also NMR)
P	phosphorescence
PA	n-pentyl acetate
PATM	phenylazotriphenylmethane
p(GMA-EA)	copolymer of glycidyl methacrylate and ethyl acrylate
Ph-	phenyl
pic	2-picoline
PMMA	poly(methyl methacrylate)

p(MMA-MAA)	copolymer of methyl methacrylate and methacrylic acid
pNAT	*para*-nitrophenylazotriphenylmethane
ppm	parts per million
py	pyridine
q	quartet
R-	alkyl (generally)
reppt	reprecipitated
RHBNC	Royal Holloway and Bedford New College
RT	room temperature
R_4TS	tetra-n-butylammonium *para*-toluenesulphinate
s	singlet, strong
t	triplet
TB	toluidine blue
TEA	triethanolamine
THF	tetrahydrofuran
TMS	tetramethylsilane
TPP	triphenylpyrylium
TSA	*para*-toluenesulphinic acid
UV	ultra-violet
VLSI	very large scale integrated
w	weak
wt	weight
w/v	weight per volume (concentration)

INTRODUCTION

1. Introduction

This work was sponsored by the Division of Mechanical and Optical Metrology, The National Physical Laboratory, Teddington Middlesex. The aim was the development of a new photoresist material for holographic recording, sensitive to visible light at the red end of the electromagnetic spectrum, specifically 633nm, this being the wavelength of the output from the He-Ne laser. Work on the polymer system was carried out in consultation with polymer scientists at Ilford Ltd., Mobberley, Knutsford, Cheshire.

1.1 Photoresist

A photoresist[1-4] is an organic material which may be coated as a thin film on a substrate, the film so formed being capable of producing a photographic image on exposure to light of a suitable wavelength. The image consists of, after development, areas showing the presence or absence of an etch-resistant polymer coat derived from the original film.

The unexposed resist layer may consist of one, two, three or more components, one of which is generally polymeric in nature, deposited from an organic solvent. The latent image is created in the photoresist layer by photochemically initiated changes to the structure of the resist materials giving rise to a differential solubility between exposed and unexposed regions. A solvent, either aqueous or organic, is then used to develop the resist layer revealing the relief image. A wide variety of chemical strategies may be employed to achieve a difference in solubility, many of them involving the cross-linking of organic polymers.

A photoresist may be termed "negative-working" or "positive-working" depending on which areas of the coating remain after processing. Photochemical processes leading to the polymerization of monomers or to the cross-linking of pre-formed polymers give rise to negative tone images since it is the unexposed regions which are dissolved during development. A resist functioning in this manner is negative-working, (fig. 1.1a). In contrast, resists showing increased solubility of exposed regions are positive-working, (Fig. 1.1b).

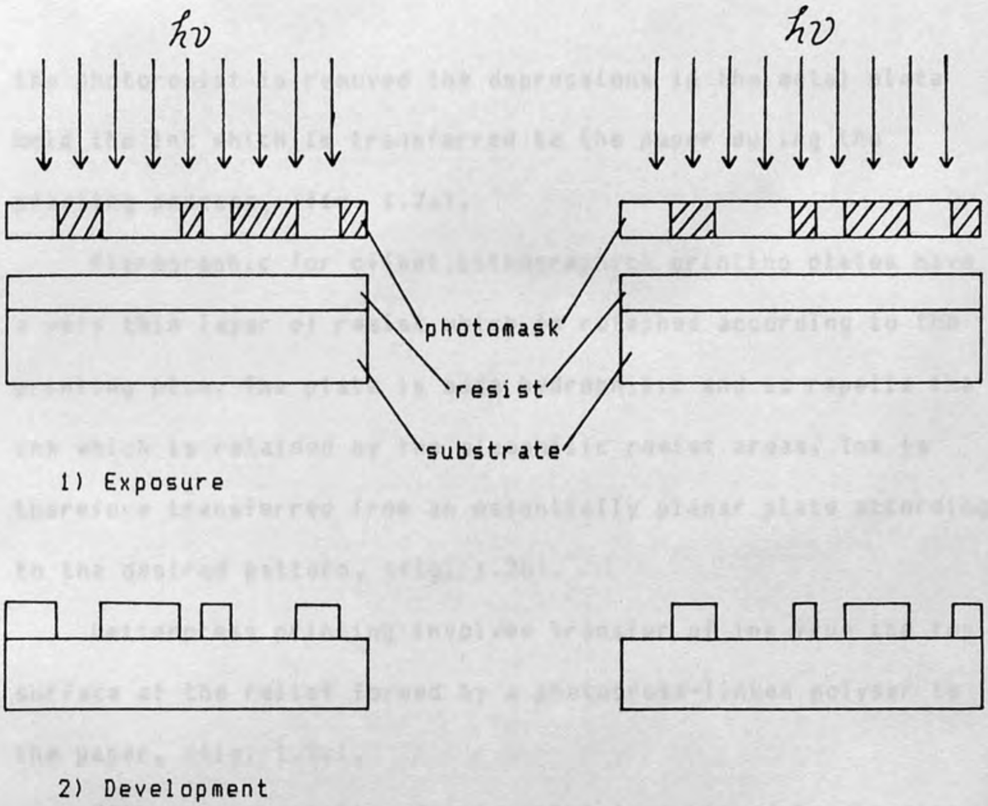
Historically, photoresists are among the oldest known photographic materials. The first permanent photographic image, taken by Nicéphore Niépce in 1826, was recorded in bitumen of Judea coated on a pewter plate.[5,6] His photograph, of the view from a window of his house in Châlon, Burgundy, took eight hours to expose. Unsaturated organic material in the bitumen cross-linked, rendering it insoluble in oil of lavender. William Henry Fox-Talbot, the inventor of the negative-positive process in conventional photography, patented a photoresist for printing plates in 1852. This material consisted of gelatine sensitized with dichromate.[5,7]

1.2 Applications of photoresist

Photoresist has a wide variety of industrial uses which include the preparation of printing plates, small component manufacture by electroforming, the preparation of printed circuit boards, semiconductor device fabrication (microelectronics) and optical devices such as video and compact audio laser disks. Related radiation-cured resins are used in other areas such as coatings, printing inks and dental fillings.

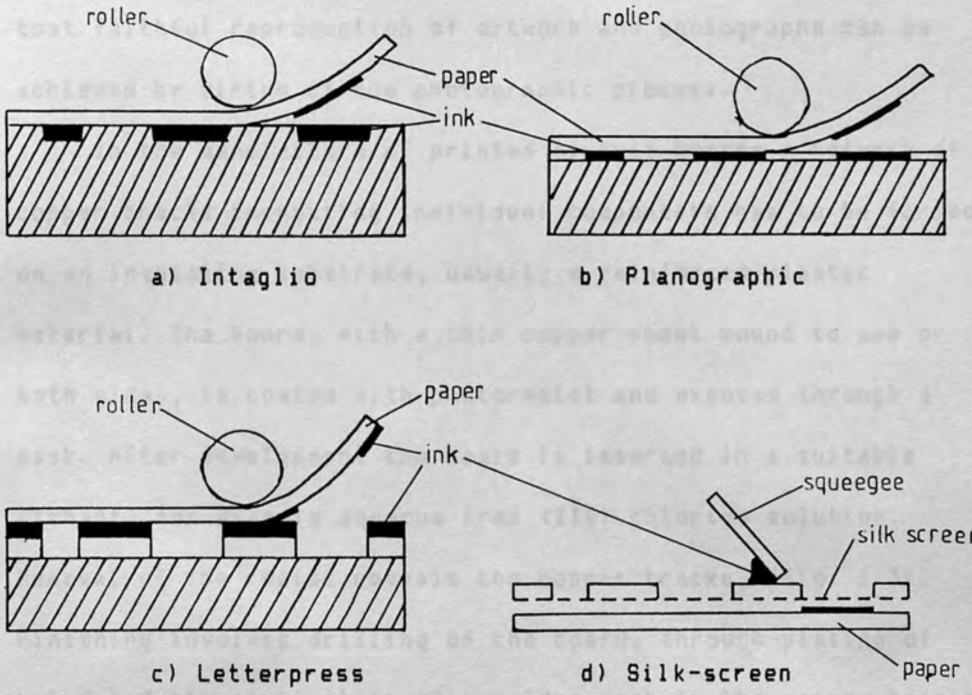
The four methods of industrial printing illustrate some of the ways in which photoresist may be used:

Intaglio (or Gravure) printing plates are made by etching into the metal substrate after forming a photoresist mask. When



a. Negative-working b. Positive working

Fig. 1.1 Negative- and Positive-working Photoresist



a) Intaglio b) Planographic

c) Letterpress d) Silk-screen

Fig. 1.2 The Four Main Types of Printing Plate the photoresist is removed the depressions in the metal plate hold the ink which is transferred to the paper during the printing process, (fig. 1.2a).

Planographic (or offset Lithographic) printing plates have a very thin layer of resist which is retained according to the printing plan. The plate is made hydrophilic and so repells the ink which is retained by the oleophilic resist areas. Ink is therefore transferred from an essentially planar plate according to the desired pattern, (fig. 1.2b).

Letterpress printing involves transfer of ink from the top surface of the relief formed by a photocross-linked polymer to the paper, (fig. 1.2c).

Silk-screen printing (serigraphy) is achieved by pressing ink through a mesh screen onto the receptive surface. Photoresist may be used to mask areas of the screen through which ink must not pass, (fig. 1.2d).

In all four instances the advantage of using photoresist is that faithful reproduction of artwork and photographs can be achieved by virtue of the photographic process.

In the manufacture of printed circuit boards a network of copper tracks connecting individual components has to be formed on an insulating substrate, usually a reinforced plastic material. The board, with a thin copper sheet bound to one or both sides, is coated with photoresist and exposed through a mask. After development the board is immersed in a suitable etchant, for example aqueous iron (III) chloride solution. Removal of the resist reveals the copper tracks, (fig. 1.3). Finishing involves drilling of the board, through-plating of holes and the application of a solder coat to the copper tracks.

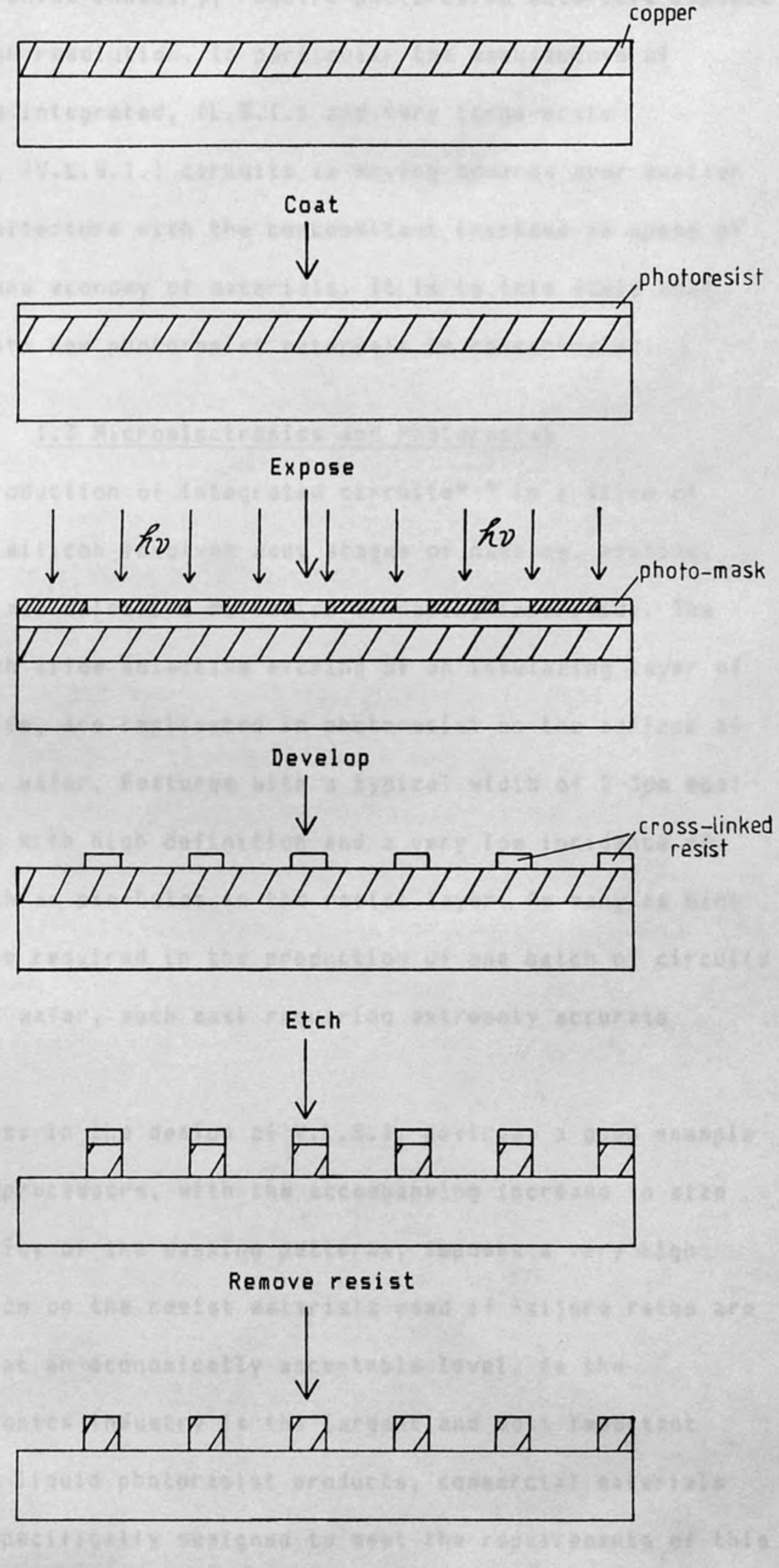


Figure 1.3 The Manufacture of a Printed Circuit Board

The manufacturers of semiconductor devices, the microelectronics industry, require photoresist materials capable of very high resolution. In particular the manufacture of large-scale integrated, (L.S.I.) and very large-scale integrated, (V.L.S.I.) circuits is moving towards ever smaller device architecture with the concommitant increase in speed of operation and economy of materials. It is in this field that research into new photoresist materials is concentrated.

1.3 Microelectronics and Photoresist

The production of integrated circuits[8,9] in a slice of ultra-pure silicon involves many stages of masking, etching, deposition and selective diffusion of doping impurities. The masks, which allow selective etching of an insulating layer of silicon oxide, are replicated in photoresist on the surface of the silicon wafer. Features with a typical width of 2-3μm must be recorded with high definition and a very low incidence of defects such as pin-holes in the resist layer. As many as nine masks may be required in the production of one batch of circuits on a single wafer, each mask requiring extremely accurate alignment.

Progress in the design of V.L.S.I. devices, a good example being microprocessors, with the accompanying increase in size and complexity of the masking patterns, imposes a very high specification on the resist materials used if failure rates are to be kept at an economically acceptable level. As the microelectronics industry is the largest and most important consumer of liquid photoresist products, commercial materials have been specifically designed to meet the requirements of this market.

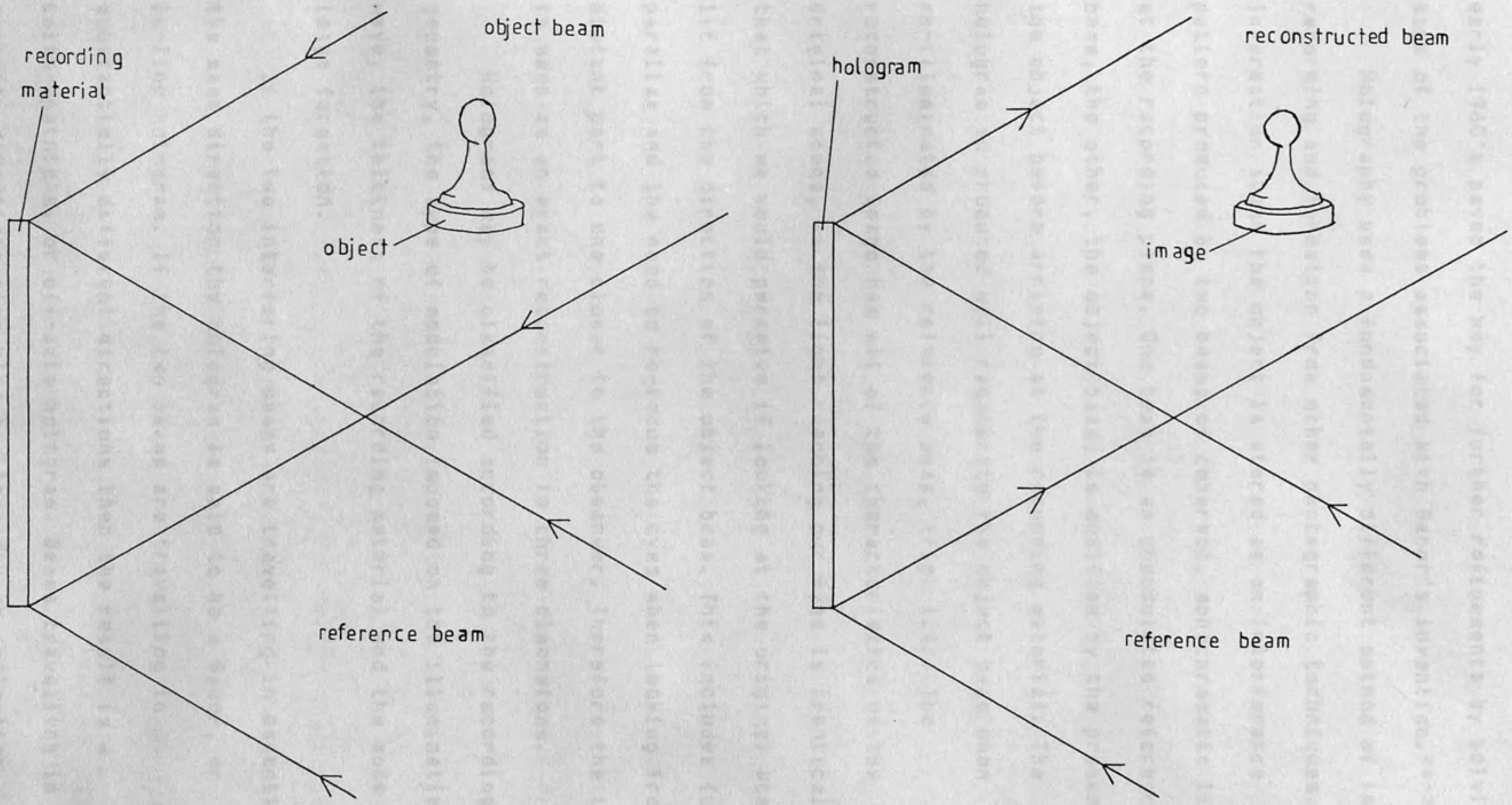
High purity of materials and solvents[10,11] and freedom from suspended particles[12] make the commercial materials particularly suitable for this market. In addition the materials are mainly sensitive to ultra-violet light with little or no sensitivity to visible light. This has a number of advantages over sensitivity to longer wavelength (visible) light: Sensitized materials may be handled under almost white-light conditions. Exposure times may be very short with high energy light sources and the high molar extinction coefficients of ultra-violet chromophores. The high photon energy may initiate a wider variety of chemical pathways than could be achieved with visible light. For any optical printing technique the maximum resolution obtainable is a function of the wavelength of light used to make the exposure, therefore mask replication with ultra-violet light has an intrinsically higher resolution capability than with visible light.

This last property of ultra-violet sensitive materials, namely their intrinsic resolution capability, also defines the limit of their usefulness. For higher resolution uses materials such as X-ray,[13-15] electron-beam[14-18] and ion-beam[19] resists have been developed.

1.4 Photoresist as a Holographic Recording Medium

A further use of photoresist is as a material for recording thin, relief, phase holograms.[20-23] One advantage of this over other holographic recording media is the possibility of mass-production by the technique of embossing;[24] a metal master is used to press further copies from a thermoplastic material such as vinyl.

Holography was first discussed as a technique applicable to microscopy in a series of papers by Gabor[25-27] in the late 1940's. Until the development of the laser, however, holography



a) Recording b) Reconstruction

Figure 1.4 Schematic Diagram of the Holographic Process remained a technique with little practical application due to the unavailability of a suitable light source. Advances in the early 1960's paved the way for further refinements by solving some of the problems associated with Gabor's invention.[28-30]

Holography uses a fundamentally different method of image recording and formation from other photographic techniques. Information about the object is stored as an interference pattern produced by two beams of coherent, monochromatic light at the recording plane. One beam is an unmodulated reference beam, the other, the object beam, is modified by the presence of the object before arriving at the recording material. The hologram so produced will regenerate the object beam when re-illuminated by the reference beam, (fig. 1.4). The reconstructed image has all of the characteristics of the original scene, as the light reaching our eyes is identical to that which we would perceive if looking at the original scene lit from the direction of the object beam. This includes full parallax and the need to re-focus the eyes when looking from a distant part to one closer to the observer. Therefore the image is seen as an exact reconstruction in three dimensions.

Holograms may be classified according to the recording geometry, the type of modulation imposed on the illuminating wave, the thickness of the recording material and the mode of image formation.

If the two interfering beams are travelling in essentially the same direction the hologram is said to be a Gabor, or in-line hologram. If the two beams are travelling in substantially different directions then the result is a Leith-Upatnieks, or off-axis hologram. Beams travelling in opposite directions give rise to Lippmann, or reflection holograms.

A further classification is possible according to the recording geometry. If the object is reasonably close to the recording plane, say less than ten object diameters, the diffraction pattern recorded at the hologram plane is the Fresnel diffraction pattern of the object, giving rise to a Fresnel hologram. If the separation between object and recording plane is large then Fraunhofer or far-field diffraction results and a Fraunhofer hologram is recorded. If a lens is used to produce the far-field diffraction pattern, with the lens a focal length distant from both the object and the recording plane, then a Fourier Transform hologram results, provided the reference beam is a plane wave. If the reference beam originates from a point the same distance from the recording plane as the object a Lensless Fourier Transform hologram results.

Depending on the recording medium, a thick or thin hologram may be produced. A thin, or plane hologram, is one for which the thickness of the recording medium is small compared to the fringe spacing. A thick, or volume hologram, is one for which the thickness of the recording medium is of the order of, or greater than, the fringe spacing. To determine whether a hologram is thick or thin a Q-parameter is defined as:

$$Q = 2\pi\lambda d/(n\Lambda^2)$$

where λ is the recording wavelength, n is the refractive index of the recording material, d its thickness and Λ the fringe spacing. A thick hologram results when $Q \gtrsim 10$.

A further distinction is made according to the mechanism by which the illuminating light is diffracted. An amplitude hologram records the interference pattern as a density variation in the recording material resulting in a modulation of the amplitude of the illuminating wave. A phase hologram is one in which a phase modulation is imposed on the illuminating wave. This phase modulation may be due to a variation of the refractive index of the material, or a surface distortion, or a combination of both.

1.4.1 Holographic Materials

To be useful as a holographic recording material a photographic material must fulfil some specific requirements: Firstly the material must be sensitive to the wavelength of the laser output used in the recording of the hologram. Secondly, the material must be capable of resolving the microscopic interference structure faithfully, that is have a suitably high spatial resolution capability. Thirdly, the material must exhibit a linear response over a wide range of exposures.

The spatial frequency resolution required in holographic materials can be shown by considering a limiting case. The frequency (ν), at which the image information is encoded is given by:

$$\nu = \frac{\sin\theta_o - \sin\theta_r}{\lambda} \quad m^{-1}$$

where λ is the recording wavelength and θ_o and θ_r are the angles between the direction of propogation of the object and reference beams to the recording plane normal. For a simple set-up typical values might be λ = 633nm (He-Ne laser), θ_o=0°, θ_r= 45° giving ν = 1120 mm^{-1}. For shorter wavelengths and the larger angles used in alternative recording geometries higher carrier frequencies will result.

Silver halide emulsions,[31] long known as photographic materials, have the highest sensitivities of any materials used for holographic or photographic recording. Photographic emulsions[32] consist of microscopic crystals of a light sensitive silver salt, usually the bromide, suspended in gelatine. Absorption of a photon by a silver halide crystal causes a silver ion to be reduced to a silver atom. The absorption process may occur anywhere throughout the body of the crystal, liberating an electron which may move through the crystal lattice until it encounters a silver ion at a crystal defect, (Scheme 1.1). The sensitivity of individual crystals is therefore dependent on their volume.

$$Br^- \xrightarrow{h\nu} Br^\circ + e^-$$

$$e^- + Ag^+ \longrightarrow Ag^\circ$$

Scheme 1.1 Photoreduction of Ag^+ in AgBr

Each silver atom so produced provides a site at which subsequent silver atoms are deposited as further photons are absorbed. It is this speck of metallic silver that forms the latent image and, provided it is of critical size, catalyses the conversion of the entire crystal to silver during the development process.

Holographic emulsions must have an extremely fine grain, that is very small silver halide crystals, in order to achieve the required resolution. This, however, results in a reduction in sensitivity of the the emulsion as this is related to crystal size. Silver halide emulsions, on the other hand, may be sensitized to the whole of the visible spectrum by the addition of suitable dyes and into the infra-red region so compatability with light sources is not a problem.

The interference pattern is recorded in photographic emulsion as a variation in the transmission characteristic due to the distribution of developed silver grains in the emulsion. This gives rise to an amplitude hologram. Because of the grain inherent in photographic emulsions, holograms recorded in this manner are subject to noise, due to scattering of light from the silver particles, which generally degrades the image. Phase holograms have a much higher theoretical efficiency than amplitude holograms and these may be created by further processing. The silver in the gelatine layer may be bleached out by one of a number of techniques leaving a refractive index variation in the gelatine or a surface relief effect. Such bleached photographic emulsions, as well as producing phase holograms with higher diffraction efficiencies than the silver image, although not completely grainless, are less prone to noise from scattering.

Dichromated gelatine,[33-35] as well as behaving as a resist, may be used to record phase holograms of very high diffraction efficiency. Gelatine is a polypeptide mixture derived from collagen, a protein from animal tissue, capable of forming a rigid gel when aqueous solutions are cooled. Potassium or ammonium dichromate, when added to the gelatine layer, sensitizes the material to light of wavelengths of 520nm or less. This sensitivity may be extended to longer wavelengths by the addition of sensitizing dyes.[36]

The imaging process in dichromated gelatine films is due to a photoinitiated reduction of the chromium (VI), in the presence of oxidizable gelatine, to chromium (III). This coordinates strongly to polar groups in the gelatine producing a local hardening effect. The degree of swelling when immersed in water will then depend on the exposure since hardened areas take up less water and dissolve less readily than normal gelatine. Pre-hardening[37] of the gelatine results in differential swelling of the imaged material with no dissolution, subsequent rapid dehydration by treatment with isopropanol results in a permanent record in the gelatine film as a large refractive index change.

Dichromated gelatine is capable of producing high efficiency, thick phase holograms with low noise levels, but considerable care must be taken with this material to achieve its potential due to the problems of distortions of the photosensitive layer which may be introduced during processing. In addition to gelatine, a range of colloids may be sensitized by the addition of dichromate including polyvinyl alcohol, albumen, shellac, fish glue and gum arabic.

Thermoplastic-photoconductive materials may also be used to record holograms,[38-40] in this case thin phase holograms are created by a surface deformation giving rise to a relief image. A photoconductive thermoplastic film is coated on a conductive substrate, (fig. 1.5), the thermoplastic is uniformly charged with static electricity before exposure. Exposure causes charge to leak away due to photoconduction, lowering the charge density in areas of high exposure. Heating, softening the thermoplastic, causes a deformation of the surface due to electrostatic pressure. The image is fixed by cooling.

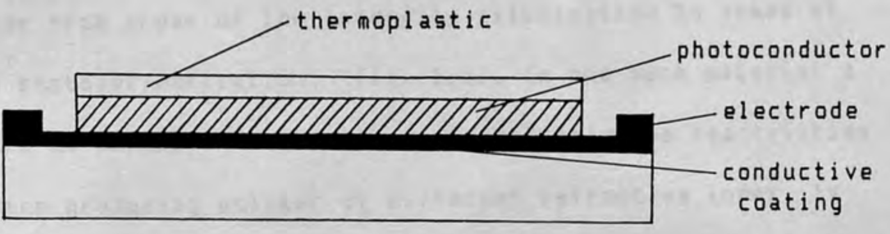


Figure 1.5 Structure of a thermoplastic-photoconductor plate

A modification of this method is possible whereby a synthetic hologram[41] may be produced by writing on the surface of a thermoplastic film with an electron beam.[42]

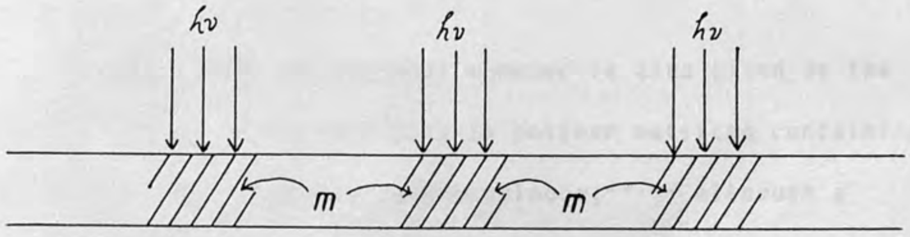
High sensitivity and high resolution are possible with this technique and the material may be easily thermally erased and re-used. Disadvantages include the complex apparatus required to produce uniform charging and development, the soft surface of thermoplastic devices and the problems of dust which may adhere to the surface, especially when electrostatically charged.

Other materials which may be used for reversible recording of holograms include ferroelectric crystals and photochromics.

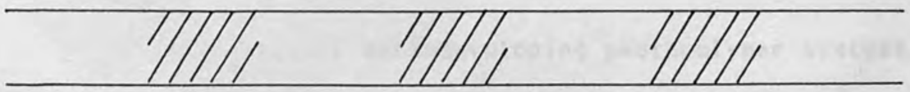
1.4.2 Photopolymers as recording materials

Photoresists are organic polymers exhibiting a solubility change on irradiation. Other polymeric materials have been found to be useful holographic recording materials, the diffraction pattern being recorded other than by a surface modulation produced by solvent action. A number of systems employing photopolymerization of vinyl monomers with a suitable initiator have been reported.[43-59] In general these systems give rise to a refractive index modulation in the photopolymer film, although a surface modulation is also found in some instances.[44]

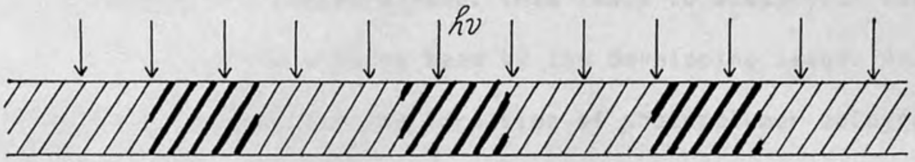
The refractive index modulation is due to a variation in density of the imaged material caused by the diffusion of monomer from areas of low intensity illumination to areas of rapid photopolymerization, (fig. 1.6). In one such material a mixture of monomers, each with different relative reactivities and each producing polymer of different refractive index, is employed in order to amplify the diffusion controlled index variation.[48] A number of papers giving details of the processing and applications of some photopolymer holographic recording materials have appeared in the literature.[51-57]



a) Monomer diffusion during exposure.



b) Unfixed image.



c) Optical fixing by uniform exposure.

Figure 1.6 Monomer diffusion in photopolymer materials

In general photopolymer materials use simple vinyl monomers such as acrylamide with difunctional monomers such as *N,N'*-methylene-*bis*–acrylamide[44,50] and the acrylates of Ba^{2+}, Pb^{2+} [43,44] and Zn^{2+} [50] included in the mixture in order to produce a cross-linked polymer image.

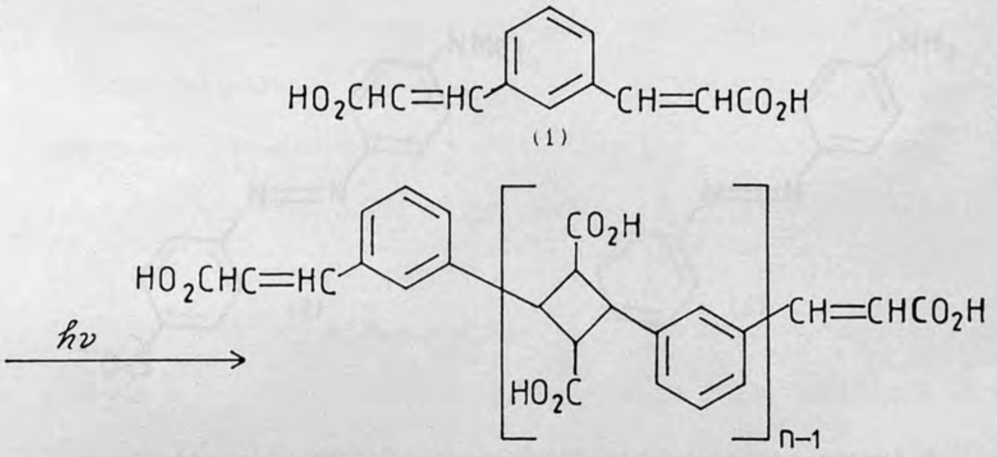
In addition to the direct photopolymerization of mixtures of monomers or monomer solutions, residual monomer trapped in a polymer matrix has been photopolymerized giving rise to an index change. This explanation has been proposed[58] for the index varation observed when partially oxidized polymethyl methacrylate (PMMA) was irradiated with ultra-violet light at 325nm, (He-Cd laser).[59] Cross-linking was rejected as the imaging mechanism as no insolublization occurred. In contrast, cross-linking has been shown to occur in *para*-benzoquinone sensitized PMMA films on exposure to 488nm light with a corresponding index change.[60,61]

Polymerization of residual monomer is also given as the explanation for index recording in polymer matrices containing α-diketones, particularly camphorquinone,[62,63] although a non-polymeric host matrix, sucrose benzoate[64] may also be used, with dimerization of sucrose benzoate radicals giving rise to the image.

One disadvantage of self-developing photopolymer systems is that the index variation produced on irradiation begins to develop during the exposure step. This leads to distortion due to scattering of the writing beam by the developing image. An alternative strategy for the formation of photopolymer holograms designed to overcome this problem involves the formation of a latent image on a receptive surface which is later brought into contact with the polymerisation mixture. In an example of this type[65] a sensitizer, benzoin, is adsorbed onto the surface of a microporous glass by immersion in a suitable solution. The surplus is removed by a solvent wash and a latent image is recorded by exposure to an argon ion laser operating at 364nm. The pores in the glass are small compared to the wavelength of light used so scattering is minimal. Irradiation destroys initiator in areas of high intensity exposure such that when the surface is flooded with a monomer solution and exposed to uniform illumination the rates of initiation of polymerization across the surface will depend on the previously recorded latent image.

This process produces an image which is negative in tone compared to the direct photopolymerization system described above, that is the index variation is opposite in sign to that obtained when using the same monomer mixtures.

The use of *meta*-phenylene diacrylic acid (1), which polymerizes via a [2+2] cycloaddition reaction in the crystalline state, (Scheme 1.2), is also reported as the basis of a material capable of producing holographic gratings.[66,67]



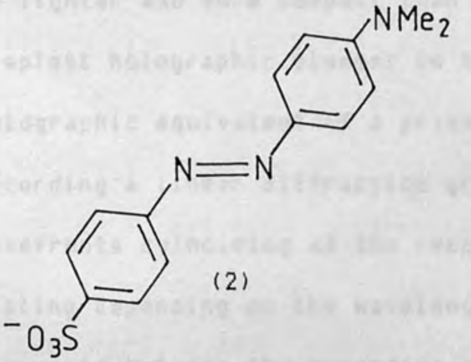
Scheme 1.2 Photochemical polymerization of (1)

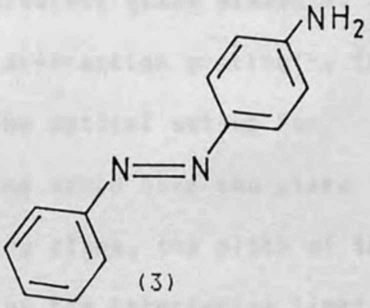
A solution containing (1) and a large amount of picramide as sensitizer is spin-coated to form an inhomogeneous layer containing crystals of the phenylene diacrylic acid.[66] In a variation on this technique polymethyl methacrylate is used as a binder in the film.[67] After exposure the plate is heated to develop the image.

The use of negative photoresist as a variable index recording material has been reported.[68,69] In this case a commercially available negative photoresist produced by Kodak, Kodak Microresist 747, was exposed to a grating pattern of 100 lines/mm and heated for one to two hours at 80°C. An index variation of up to 2% was reported, no index variation was seen in exposed materials at room temperature.

Variable index materials, including photopolymers, are the subject of a recent review by Thompson and Chandross.[70]

A number of other organic materials used in holographic applications use the photoisomerization of unsaturated molecules, for example azo dyes, in a polymer matrix.[71-75] Such systems are essentially reversible, being erased optically or on standing in the dark. Methyl orange (2)[71] and 4-amino azobenzene (3)[75] have both been used.


(2)


(3)

In the case of methyl orange[71] and a plastic material containing an unspecified red dye,[72,73] the hologram is recorded as a photoinduced birefringence giving rise to a polarization hologram.

1.4.3 The Formation of Holographic Optical Elements

In principle any conventional optical element can be replaced by its holographic equivalent and in practice holographic optical elements (HOEs) may be produced for applications where it would be difficult or impossible to use conventional optics. One disadvantage of HOEs, particularly those recorded as thick holograms, is that the optical element will only perform well at the wavelength at which it was recorded, aberrations being introduced as the wavelength changes. Thick holograms may be thought of as layers of discrete thin holograms recorded in parallel planes, the planes corresponding to constructive interference of the recording wavefronts. The diffracted beam obeys the Bragg condition:

$$\lambda = 2n\Lambda \mathrm{Sin}\,\theta$$

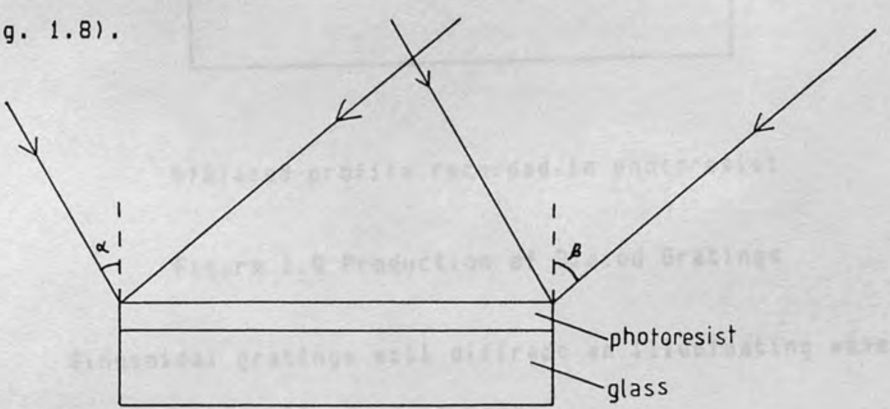
Diffraction efficiency will fall off as the angle θ of the read-out beam or its wavelength λ deviates from the recording conditions. Λ is the fringe spacing.

HOEs have the advantage of possible mass production and may be lighter and more compact than equivalent glass elements. The simplest holographic element is the diffraction grating[76], the holographic equivalent of a prism. The optical set-up for recording a linear diffraction grating would have two plane wavefronts coinciding at the recording plane, the pitch of the grating depending on the wavelength of the interfering light and the angle between the recording beams. Holograms of points, one spherical wavefront and one plane wavefront, can be used as the equivalent of a lens, the diffraction pattern being similar to a ruled zone plate or Fresnel lens. For practical reasons it is more usual to record holographic zone-plates as the interference of two spherical wavefronts[77], the focal length f of such an element is related to the distances a and b of the centres of interfering wavefronts from the recording plane by:

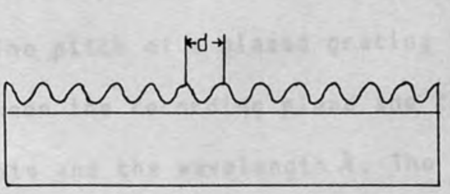
$$\frac{1}{f} = \frac{1}{a} - \frac{1}{b}$$

Such a zone plate , when used in transmission, will act as a lens. A reflecting zone plate will mimic a concave mirror. Reflecting elements of this type can be made using photoresist or similar material giving rise to a surface relief hologram which can be coated with a reflective coating such as aluminium. The manufacture of holographic optical elements and the suitability of a range of materials is discussed by Stevens and Hutley[78].

As has already been stated, gratings are the simplest holographic elements, being the result of interference of two plane waves, (Fig. 1.7). The generalised hologram is a grating that has further modulation imposed upon it. Before the advent of holographic techniques which can "write" thousands of lines on an optical surface with a single exposure, gratings were produced mechanically by very precise ruling engines. Optical gratings have applications in spectroscopy and integrated optics. As it is a convenient measure of the performance of a holographic recording material, a linear grating is often presented as evidence of the achievable resolution of a new system. In addition to the sinusoidal modulation characteristic of the gratings described above, a blazed grating may also be recorded by exposing photoresist to the standing wave pattern produced by a beam of light passed back along its own path, (Fig. 1.8).

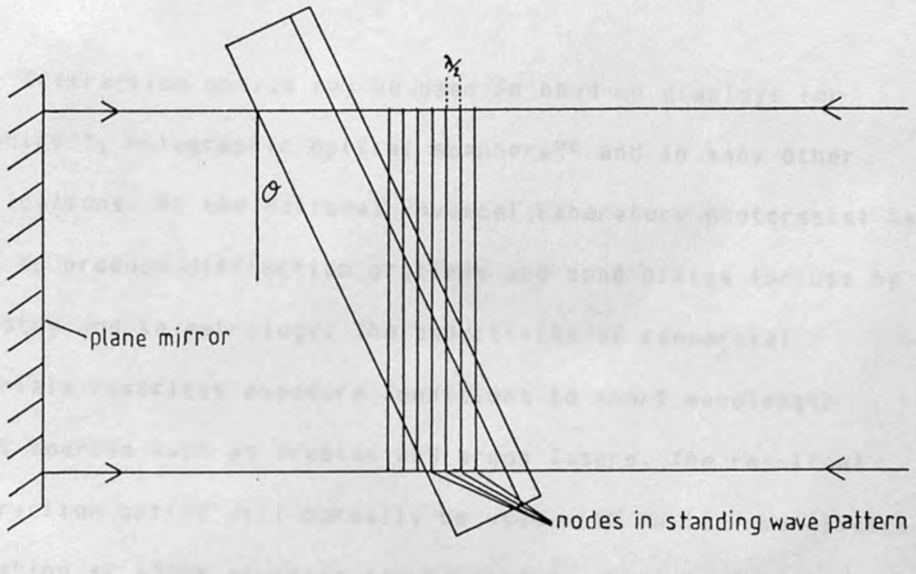


a) Exposure

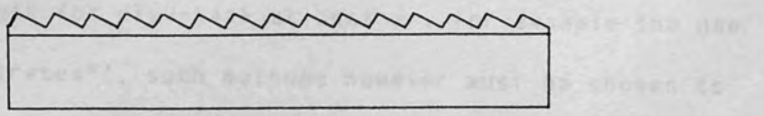


b) Sinusoidal grating in photoresist

Figure 1.7 Diffraction Grating Produced by Interference of Two Plane Waves



a) Exposure



b) Blazed profile recorded in photoresist

Figure 1.8 Production of Blazed Gratings

Sinusoidal gratings will diffract an illuminating wavefront according to the following relation:

$$d\ (\text{Sin}\,\alpha + \text{Sin}\,\beta) = n\lambda$$

where d is the period of the grating, α and β are the angles between the exposing wavefronts and the normal to the recording plane. The pitch of a blazed grating is dependant on the angle, θ, between the recording plane and the plane of the standing wavefronts and the wavelength λ. The period of the grating is given by:

$$d = \frac{\lambda}{2\ \text{Sin}\,\theta}$$

the nodes of the standing wave pattern being spaced by $\lambda/2$.

Diffraction optics may be used in head-up displays for avionics[79], holographic optical scanners[80] and in many other applications. At the National Physical Laboratory photoresist is used to produce diffraction gratings and zone plates for use by industry and in metrology. The sensitivity of commercial materials restricts exposure conditions to short wavelength light sources such as krypton and argon lasers. The resultant diffraction optics will normally be used with helium-neon lasers operating at 633nm as these may be readily obtained and are low cost, portable units. Photoresist optical elements, when played-back with light of different wavelength to that at which they were recorded, are subject to aberrations[78]. Techniques have been developed whereby optical elements may be fabricated at one wavelength for play-back at another, for example the use of curved substrates[81], such methods however must be chosen to suit the type of optical element being made and the application. It would be much easier from the point of view of fabrication, to record the grating, zone plate or hologram in photoresist sensitive to light of the same wavelength as that used in reconstruction, hence the need for a red-sensitive holographic photoresist material.

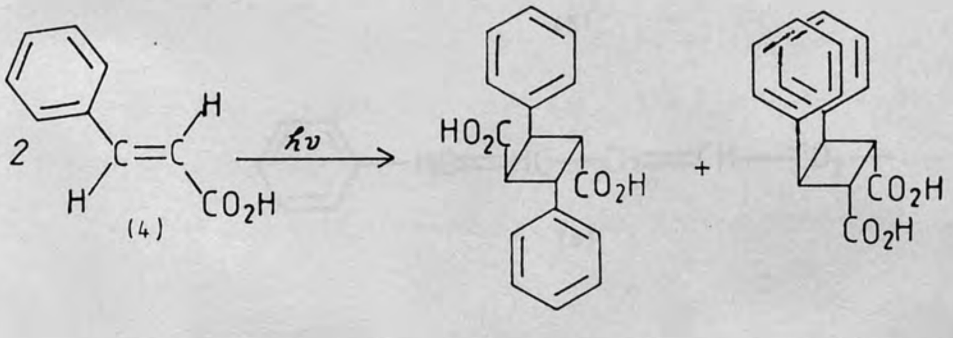
1.5 Negative Photoresist

The photo-induced insolubilization of organic materials has been utilized for over 150 years from the early experiments of Niépce and W.H. Fox Talbot with bitumen and dichromated gelatine, through materials used for printing and printed circuits to modern high-resolution materials used in integrated circuit technology. A short history of the development of a number of these materials is the subject of an article by Hepher[82] and a number of the early patents are given as references in Ostroff's "History of Photomechanical Reproduction"[7].

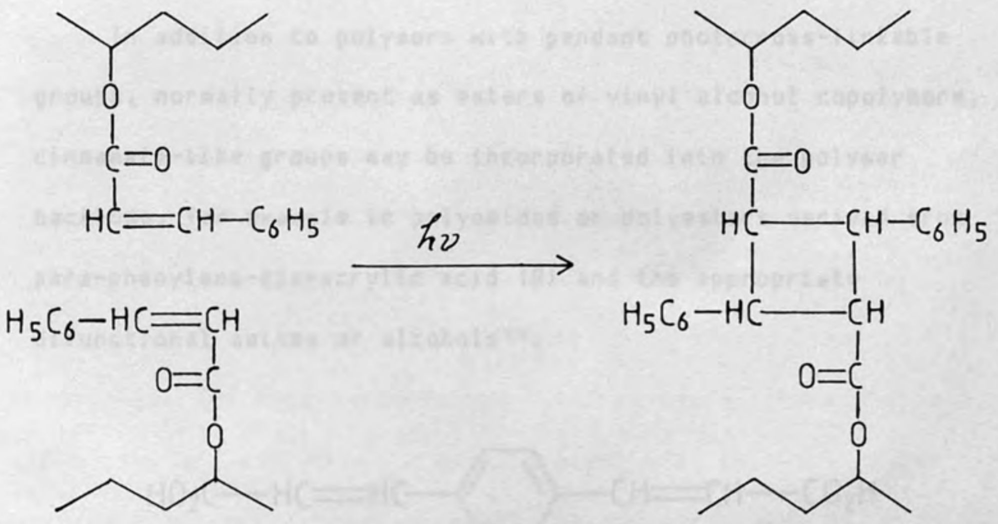
Insolubilization of organic films may be achieved by reactions leading to the polymerization of monomers, or a monomer/polymer mixture or to the cross-linking of pre-formed polymers. Because of the superior film-forming properties and the wide variety of organic groups which may be attached, most negative photoresists involve cross-linking of polymers. A comprehensive review of photocross-linkable resin systems by Green, Stark and Zahir[83] covers photoresist chemistry as well as radiation cured resins used in other areas. In a series of articles on photoresist technology, Clark describes some commercial negative photoresists employing photopolymerization[84] and photocross-linking[85].

1.5.1 Cross-Linking by Cycloaddition Reactions

Cinnamic acid (4) and its derivatives, in particular cinnamate esters, undergo a photochemical cyclodimerization, (Scheme 1.3), on irradiation with short wavelength light. Cinnamate esters of polymeric alcohols, for example polyvinyl cinnamate, will therefore form cross-links under similar conditions, (Scheme 1.4).

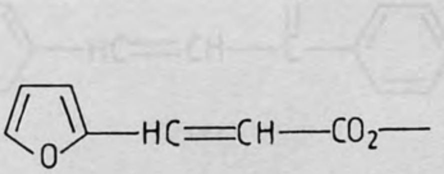


Scheme 1.3 Photodimerization of cinnamic acid

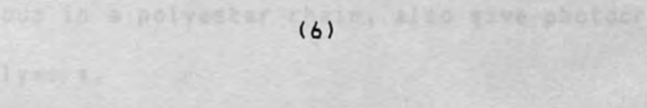


Scheme 1.4 Cross-Linking of Polyvinyl Cinnamate

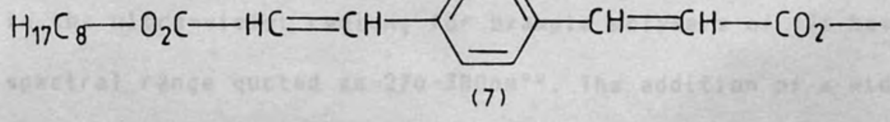
Polyvinyl cinnamates derived from polyvinyl alcohol or vinyl alcohol copolymers esterified with cinnamoyl halides formed the basis of the first photoresists based on this cross-linking mechanism[86-89], followed by systems employing substituted cinnamic acid derivatives. Alternative light sensitive groups analogous in reactivity to cinnamates include 2-furfurylacrylate (5)[90], cinnamylideneacetate (6)[91] and *p*-[2-(2-ethylhexyloxycarbonyl) vinyl] cinnamate (7)[92].



(5)

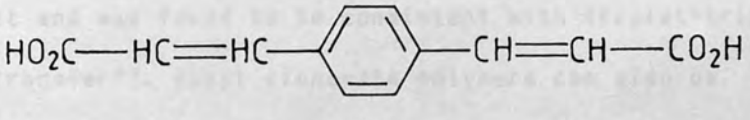


(6)



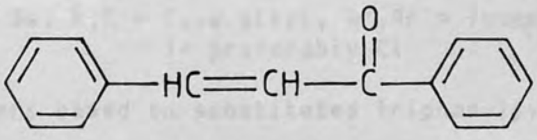
(7)

In addition to polymers with pendant photocross-linkable groups, normally present as esters of vinyl alcohol copolymers, cinnamate-like groups may be incorporated into the polymer backbone, for example in polyamides or polyesters derived from *para*-phenylene-*bis*-acrylic acid (8) and the appropriate difunctional amines or alcohols[92].



(8)

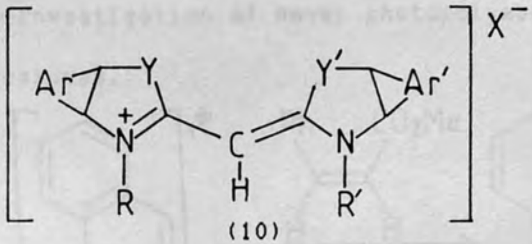
Groups whose structure is based on benzylideneacetophenone (chalcone), (9), also have light sensitivity, forming cyclobutane dimers. These groups may be incorporated in a light sensitive polymer composition by a Friedel-Crafts acylation of polystyrene or styrene copolymers with cinnamoyl chloride[93-95] or by grafting of a substituted chalcone to a polyamide chain[96].



(9)

As with the cinnamate-like polymers, structural variations in the chalcone moiety, for example the substitution of aromatic heterocycles for the phenyl groups[97] and incorporation of the chalcone group in a polyester chain, also give photocross-linkable polymers.

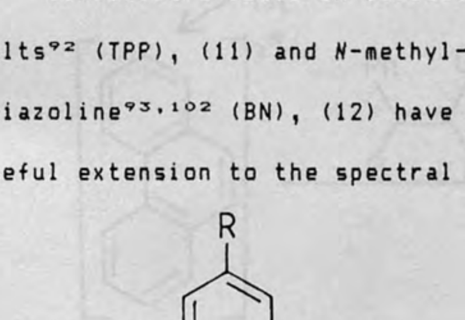
Vinyl cinnamates and chalcones have intrinsic sensitivities in the ultra-violet region, for example polymers of (7) have a spectral range quoted as 270-380nm[92]. The addition of a wide range of sensitisers can increase both the spectral range and photographic speed of polyvinyl cinnamate and its analogues. Polyvinyl cinnamate has been sensitized with, among others: polynuclear aromatics, nitrobenzenes, nitroanilines, phenol, nitrophenols, aromatic aldehydes and ketones, quinones and anthrones[98]. The mechanism of sensitization of polyvinyl cinnamates has been investigated for a number of compounds in this list and was found to be consistent with triplet-triplet energy transfer[99]. Vinyl cinnamate polymers can also be sensitized with triphenylmethane[88] and trimethine cyanine dyes[100]. The use of monomethine cyanines (10) in combination with aromatic nitro compounds is also reported as giving enhanced sensitivity[101].



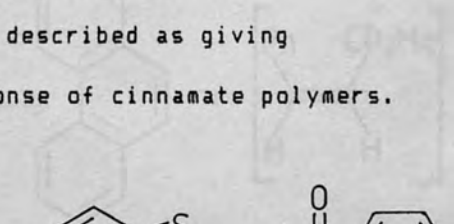
(10)

Y,Y'= S or Se, R,R'= C_{1-5} alkyl, Ar,Ar'= fused aromatic
X= preferably Cl

Sensitizers based on substituted triphenylpyrylium salts[92] (TPP), (11) and *N*-methyl-2-benzoyl-β-naphthothiazoline[93,102] (BN), (12) have been described as giving useful extension to the spectral response of cinnamate polymers.

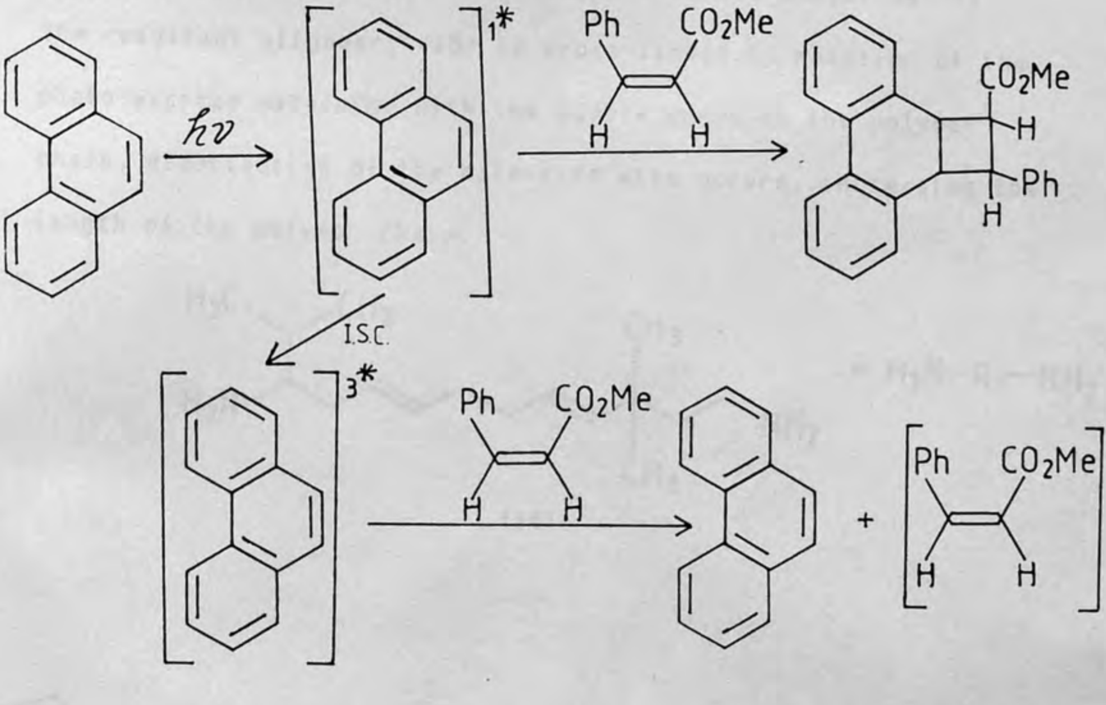


(11)



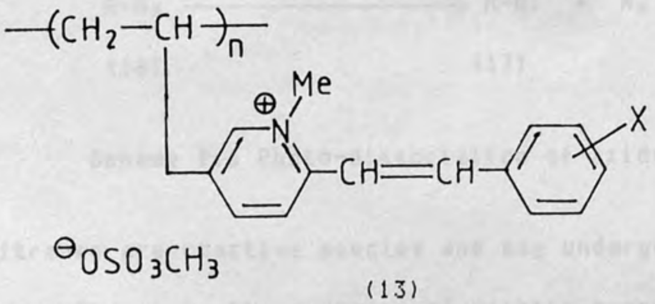
(12)

Williams *et al*[72] have re-examined the mechanism of sensitization following the discovery of anomalies in the fluorescence and phosphoresence spectra of combinations of TPP and stilbene, and the photostationary state achieved in the sensitized *cis-trans* isomerism of stilbene. They proposed that another mechanism was operating in addition to triplet energy transfer, the observation that TPP salts can initiate vinyl polymerization led them to suggest the involvement of excited state electron-transfer reactions. It was also shown that the photo-excited state of polynuclear aromatics, exemplified by phenanthrene, in addition to activating the triplet state of methyl cinnamate, reacts directly with both *cis* and *trans* methyl cinnamate in its singlet excited state, (Scheme 1.5). This led to the investigation of novel photopolymers containing phenanthroate residues.



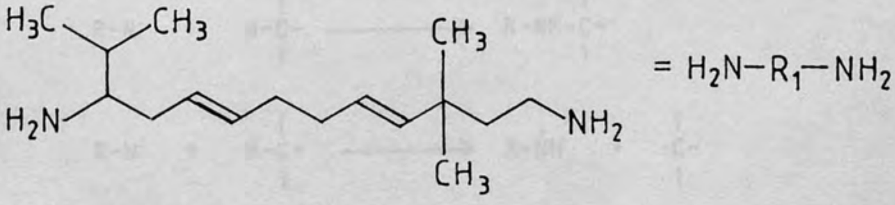
Scheme 1.5 Reactions of Photo-excited Phenanthrene and Methyl Cinnamate

Styrylpyridinium groups on photosensitive polymers, (13) are not amenable to sensitization by triplet sensitizers, photocross-linking occuring via the singlet excited state. The sensitivity and spectral response of such polymers is enhanced by careful choice of substituents on the phenyl group. Useful spectral coverage from 270-630nm is possible[92].

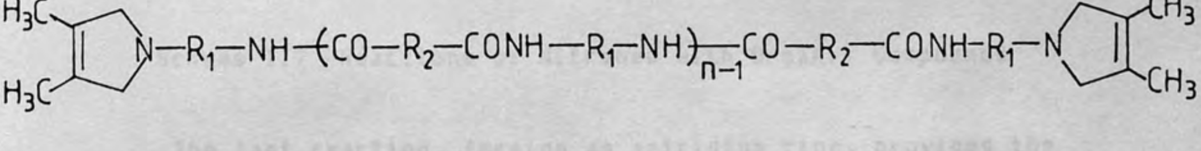


(13)

A number of other groups containing unsaturated linkages have been used to sensitize polymers to cross-linking involving photocycloaddition, for example maleic acid derivatives such as maleimides. A polyamide chain derived from a dicarboxylic acid and an unsaturated diamine, (14), may be sensitized by reacting the terminal amine groups with dimethyl maleic anhydride[103]. The resultant oligomer, (15) is cross-linked by reaction of the photo-excited maleimide with the double bonds on the polymer chain, dimerization of the maleimide also occurs, increasing the length of the polymer chain.



(14)



(15)

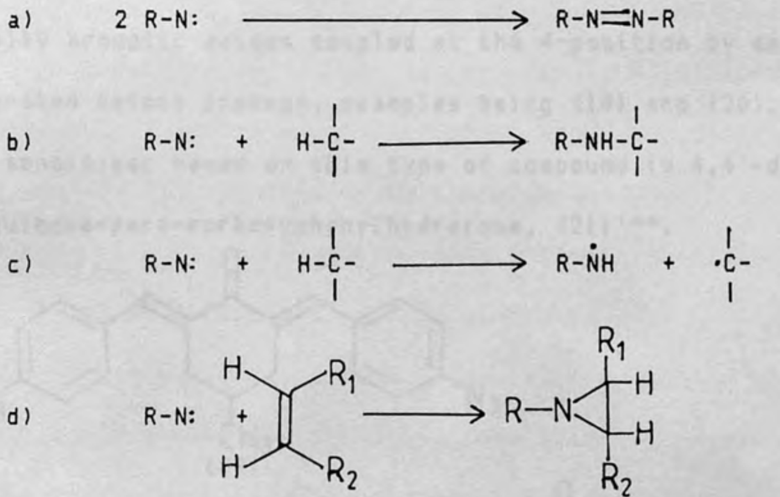
1.5.2 Azide Sensitized Resists

Azides, (16), undergo photodissociation forming nitrenes (17) and molecular nitrogen, (Scheme 1.6).

$$\underset{(16)}{R\text{-}N_3} \xrightarrow{h\nu} \underset{(17)}{R\text{-}N:} + N_2$$

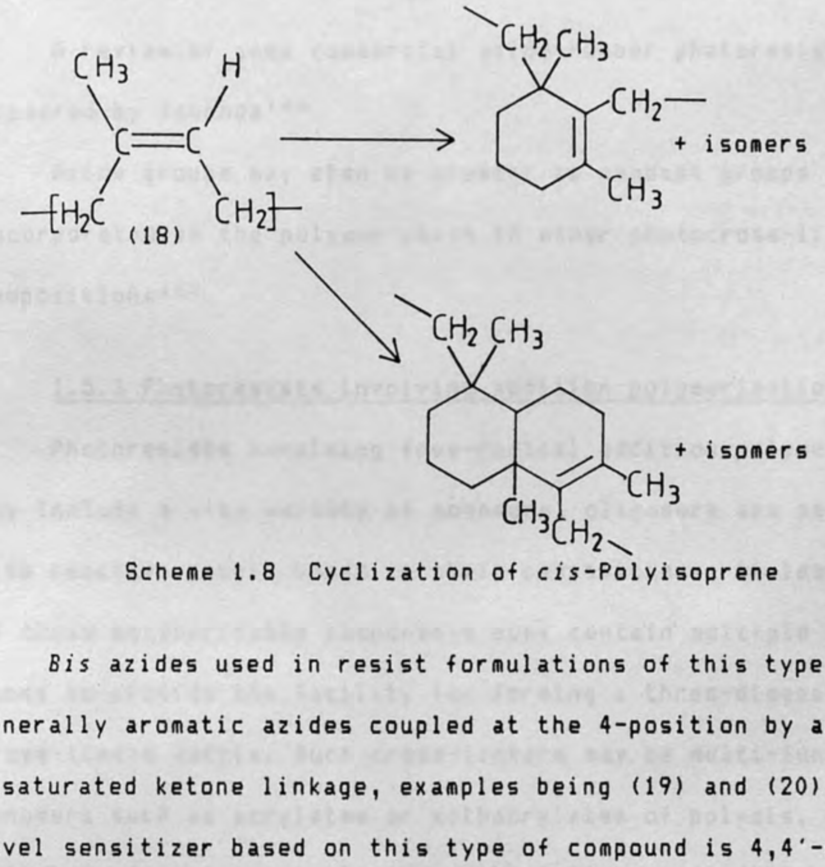
Scheme 1.6 Photo-dissociation of azides

Nitrenes are reactive species and may undergo a variety of reaction pathways in the presence of organic compounds, as with carbenes the reactions of singlet and triplet nitrenes take a different course. Possible reactions include dimerization, singlet or triplet, (Scheme 1.7a), C-H bond insertion, singlet only, (Scheme 1.7b), hydrogen abstraction, triplet only, (Scheme 1.7c) and addition to double bonds, singlet or triplet, (Scheme 1.7d). In some instances the products formed in these reactions are themselves reactive and will undergo further reactions until stable products are formed.



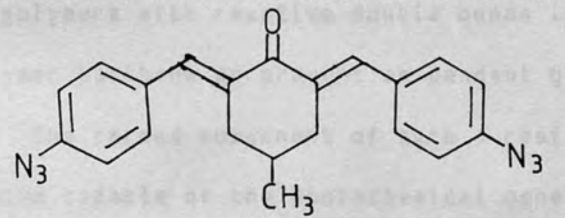
Scheme 1.7 Reactions of Nitrenes with Organic Compounds

The last reaction, forming an aziridine ring, provides the mechanism for cross-linking of polymers containing double bonds by *bis* azides. Photoresists utilizing this reaction are generally based on rubbers, either natural rubber or synthetic materials such as *cis*-polyisoprene, (18), or polybutadiene. These elastomers have to be modified in order to provide a more rigid polymer for resist purposes, this is achieved by a partial cyclization of the polymer resulting in some loss of unsaturation, (Scheme 1.8).

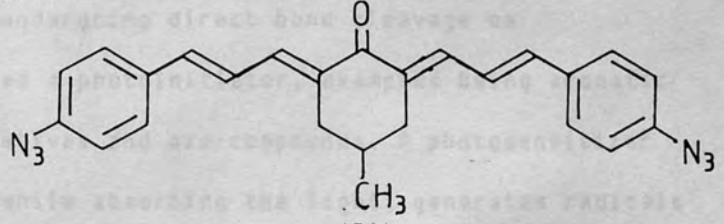


Scheme 1.8 Cyclization of *cis*-Polyisoprene

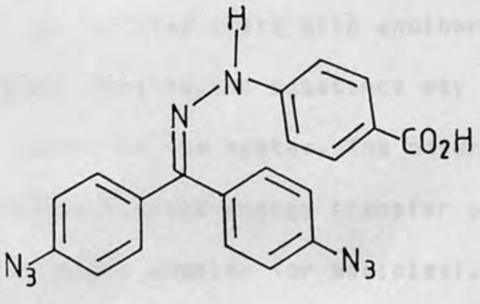
Bis azides used in resist formulations of this type are generally aromatic azides coupled at the 4-position by an unsaturated ketone linkage, examples being (19) and (20). A novel sensitizer based on this type of compound is 4,4′-diazido-benzoquinone-*para*-carboxyphenylhydrazone, (21)[104].



(19)



(20)



(21)

A review of some commercial azide-rubber photoresists has appeared by Tsunoda[105].

Azide groups may also be present as pendant groups or incorporated in the polymer chain in other photocross-linkable compositions[106].

1.5.3 Photoresists involving addition polymerization

Photoresists involving free-radical addition polymerization may include a wide variety of monomers, oligomers and polymers with reactive double bonds in their compositions. At least one of these polymerizable components must contain multiple double bonds to provide the facility for forming a three-dimensional cross-linked matrix. Such cross-linkers may be multi-functional monomers such as acrylates or methacrylates of polyols, or amides derived from acrylic or methacrylic acid and bis amines, or polymers with reactive double bonds incorporated into the polymer backbone or present as pendant groups.

The second component of such a resist formulation will be a system capable of the photochemical generation of free-radicals. A single substance undergoing direct bond cleavage on irradiation is termed a photoinitiator, examples being aromatic ketones, keto-derivatives and azo-compounds. A photosensitizer on the other hand, while absorbing the light, generates radicals by the interaction of its excited state with another substance and not by its breakdown. This second substance may be monomer or another molecule present in the system. The nature of this interaction may be triplet-triplet energy transfer or the formation of an excited-state complex (or exciplex). In addition to free-radicals other reactive intermediates such as anions, cations and strong acids can initiate addition polymerization and may be employed in some circumstances in photopolymerizable systems.

A general overview of imaging systems employing photopolymerization[107,108] and a discussion of photoactive catalyst systems[109] may be found in the photographic literature. A review by Oster and Yang[110] covers the general subject of photopolymerization of vinyl monomers.

Oster has reported a method of photopolymerization[111-113] employing a photosensitizer consisting of an organic dye and a mild reducing agent capable of reducing the photoexcited state of the dye but not its ground state. Several classes of dye and a wide variety of reducing agents have been reported as suitable. In a further patent[114] a number of examples of conventional photoresist techniques are described employing the new sensitizing system and monomers such as acrylamide, *N,N'*-methylene-*bis*-acrylamide and calcium acrylate polymerized in visible light.

Free-radical photopolymerization is a chain process and may be described by initiation, propogation, chain transfer and termination steps, (Scheme 1.9).

Initiation

$$\underset{\text{(Photoinitiator)}}{I} \xrightarrow{h\nu} R\cdot + R'\cdot$$

Propagation

$$R(M)_n\cdot + M \longrightarrow R(M)_{n+1}\cdot$$

Chain transfer

$$R(M)_n\cdot + R'H \longrightarrow R'\cdot + R(M)_nH$$

Termination

$$R(M)_n\cdot + R(M)_m\cdot \longrightarrow \text{polymer}$$

Scheme 1.9 Photopolymerization Reaction Steps

The extent of polymerization for a constant rate of initiation is shown in the graph below, (fig. 1.9), the induction period is due to the presence of inhibitors in the polymerization mixture. Inhibitors are substances which react with the initiating and propagating radicals faster than the propagation step forming inactive species and must all be consumed before polymerization can continue. In addition to inhibitors, retarders may be present, slowing the overall rate of polymerization. Retarders may either act in the same way as inhibitors (chain terminators) but at a much reduced rate or react forming radical intermediates (through chain transfer for example) of low reactivity towards monomers.

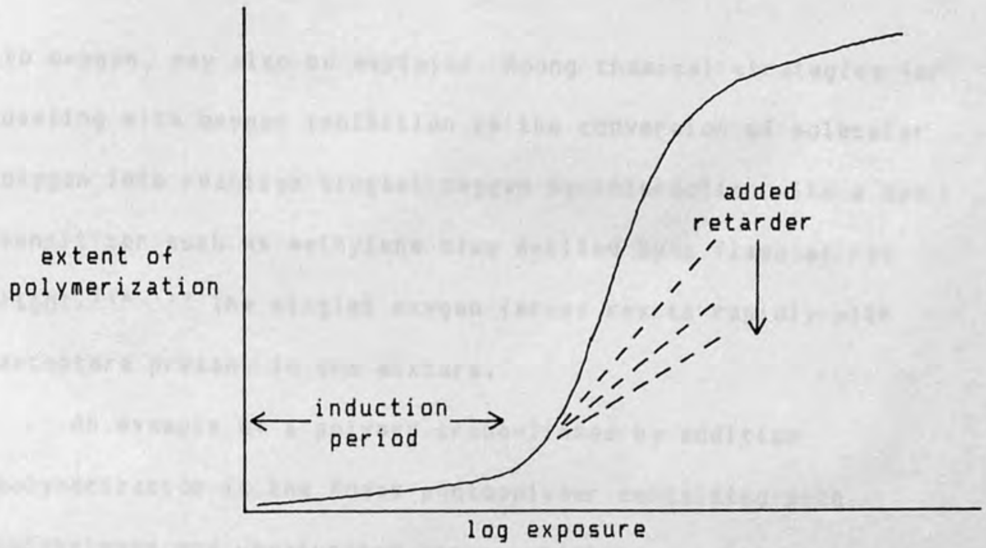
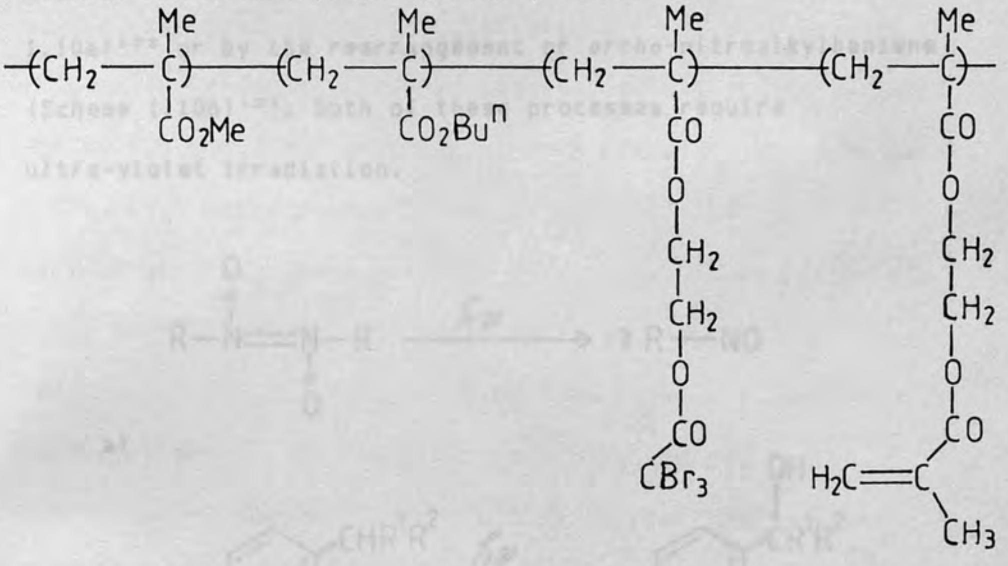


Figure 1.9 Generalized graph of the photopolymerization process

Inhibitors may be added to polymerizable compositions in order to extend shelf-life, hydroquinone and its derivatives are frequently used, as are some phenols. Molecular oxygen is also an inhibitor of polymerization and with acrylic monomers no polymerization occurs until all of the oxygen present is consumed, either in photosensitized oxidations of suitable species or by conversion to peroxides. Diffusion of oxygen from the atmosphere may continue to interfere with polymerization once the induction period is over, this may be quite likely with materials coated as thin layers. The consequence of oxygen diffusion during exposure is that the photographic speed of the system will depend on the intensity of the illuminating light and hence exposure times will show reciprocity failure when changing light sources.

Oxygen inhibition in practical systems is dealt with in a number of ways, oxygen-free atmospheres of nitrogen or carbon dioxide are used, as are gas impermeable coatings[115] which prevent diffusion of oxygen into the polymerizing layer. Polymeric binders such as gelatine, which has a low permeability to oxygen, may also be employed. Among chemical strategies for dealing with oxygen inhibition is the conversion of molecular oxygen into reactive singlet oxygen by interaction with a dye sensitizer such as methylene blue excited by a flash of red light.[116,117] The singlet oxygen formed reacts rapidly with acceptors present in the mixture.

An example of a polymer cross-linked by addition polymerization is the Kodak photopolymer containing both polyhalogen and unsaturated groups which is sensitized by a transition metal carbonyl compound,[118,119] typically benzene chromium tricarbonyl. In an example of a polymer of this type, a copolymer of methyl methacrylate, butyl methacrylate and 2-hydroxyethyl methacrylate is esterified with tribromoacetyl bromide and methacryloyl chloride, (22).



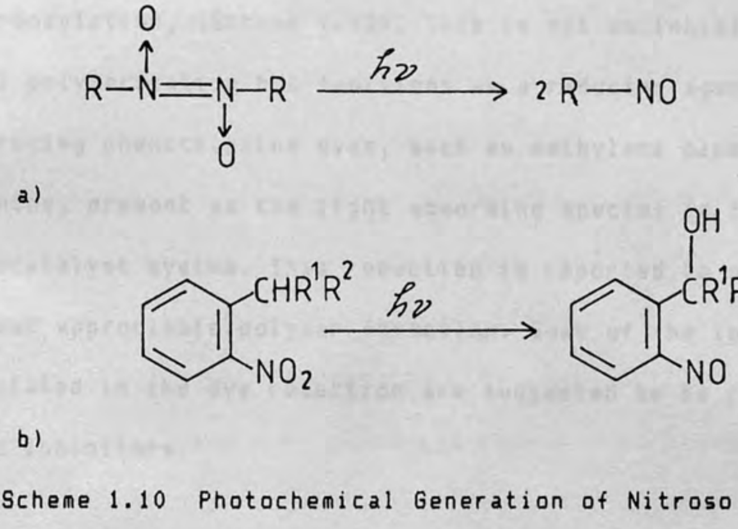
(22)

Sensitization of such a system is possible by incorporation of pyrylium salts or cyanine or xanthene dyes.[120] An oxygen-impermeable barrier layer is also recommended.

In a variation on the technique of imaging by photopolymerization a positive image may be recorded by including a photo-inhibitor in a photopolymerizable layer.[121]

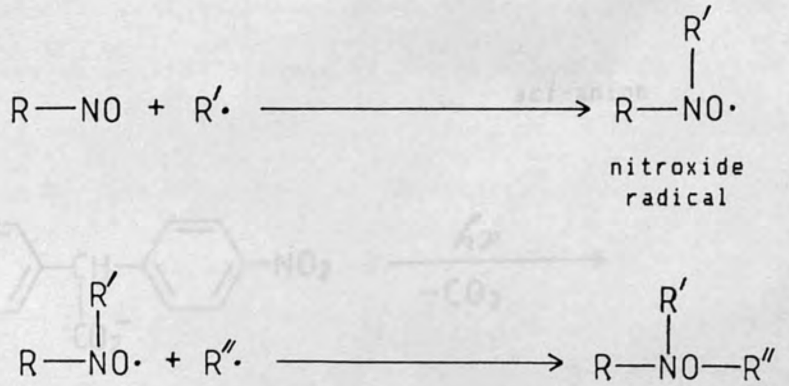
An initial imaging exposure produces a latent image in the form of polymerization inhibitors in the coating. A uniform exposure polymerizes monomer rapidly except in areas of high inhibitor concentration. Solvent development reveals a resist image which is positive in tone. In order for such an imaging system to work the wavelength of the light absorbed by the photo-inhibitor must not initiate polymerization, similarly polymerization must be initiated by light of a wavelength at which no further inhibitor is produced. Such a material is still capable of forming negative images by exposing at the photopolymerization wavelength.

Photo-inhibitors are substances which, on irradiation, produce compounds capable of inhibition of free-radical polymerization, for example nitroso compounds. Nitroso compounds may be formed by the decomposition of nitroso dimers (Scheme 1.10a)[122] or by the rearrangement or *ortho*-nitroalkylbenzene (Scheme 1.10b)[121]. Both of these processes require ultra-violet irradiation.



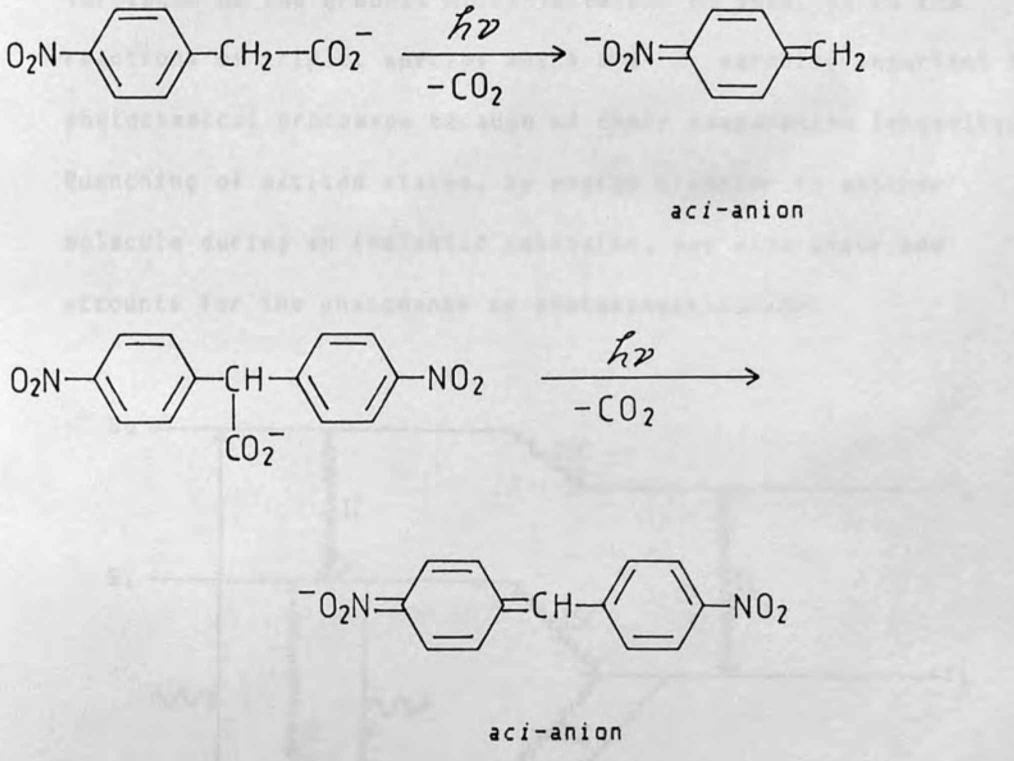
Scheme 1.10 Photochemical Generation of Nitroso Species

Nitroso compounds are particularly effective as inhibitors, having the ability to react with two propagating radical chains, initially forming a nitroxide radical which is inactive as a chain propagator, (scheme 1.11).



Scheme 1.11 Chain Termination by Nitroso Compounds

The possibility of tone reversal in a photopolymer system was also suggested by Margerum *et al* using a nitrophenyl acetic acid salt as the photoinhibitor.[123] This is normally present in their photopolymer material as a means of optically fixing the image. On irradiation with ultra-violet light *para*-nitrophenyl acetate anion forms an *aci*-anion by decarboxylation, (Scheme 1.12). This is not an inhibitor of vinyl polymerization but functions as a reducing agent, destroying phenothiazine dyes, such as methylene blue or thionine, present as the light absorbing species in the photocatalyst system. This reduction is reported to occur without appreciable polymer formation. Some of the intermediates postulated in the dye reduction are suggested to be radical chain inhibitors.



Scheme 1.12 Photodecarboxylation of *para*-Nitrophenyl Acetate

1.5.4 Photoinitiators for Negative Resists

The energy states and transitions characteristic of organic molecules[124] are represented in the Jablonski diagram, (figure 1.10). Excitation (E) occurs by the absorption of a photon, raising the molecule from its singlet ground state to some excited singlet state. Internal conversion (I.C.) is a radiationless process allowing the molecule to relax to a lower energy state of the same multiplicity. Inter-system crossing (I.S.C.) is a radiationless process allowing the molecule to relax to a lower energy state of different multiplicity. Singlet excited states have very short lifetimes; undergoing internal conversion, fluorescence (F) or inter-system crossing. Triplet lifetimes are much longer compared to those of singlet excited states because transitions to the singlet ground state, for example phosphorescence (P) (the radiative process) are forbidden on the grounds of conservation of spin. It is the reactions of triplet species which are normally important in photochemical processes because of their comparative longevity. Quenching of excited states, by energy transfer to another molecule during an inelastic collision, may also occur and accounts for the phenomenon of photosensitization.

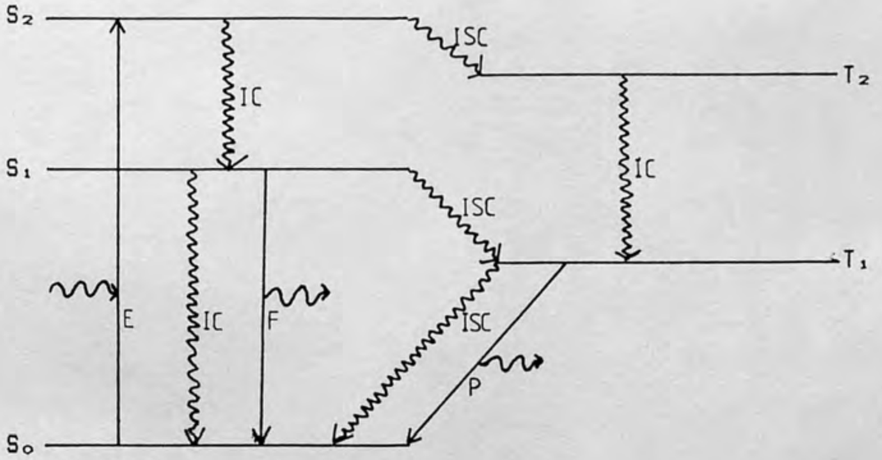


Figure 1.10 A Jablonski Diagram

The absorption spectra of organic molecules are due to transitions between electronic states, the probability of each transition determining the strength of the absorbance at each wavelength. The electronic configuration of a carbonyl compound may be represented using molecular orbital theory (figure 1.11). The σ-framework is assumed to make a negligible contribution to the π-bond and only the highest occupied and lowest unoccupied molecular orbitals are considered. The ground state is shown as having a doubly occupied π-bonding orbital and a doubly occupied n (non-bonding) orbital localized on oxygen, corresponding to an atomic p-orbital. The next highest in energy is the anti-bonding π^*-orbital. The lowest energy transition is the $n \rightarrow \pi^*$ which will be of low intensity, being forbidden on the grounds of symmetry and/or overlap. The $\pi \rightarrow \pi^*$ transition is a higher energy process and will normally be of much greater intensity than $n \rightarrow \pi^*$, being fully allowed. Conjugation has the effect of lowering the energy gap between the frontier orbitals, shifting the spectrum to longer wavelength.

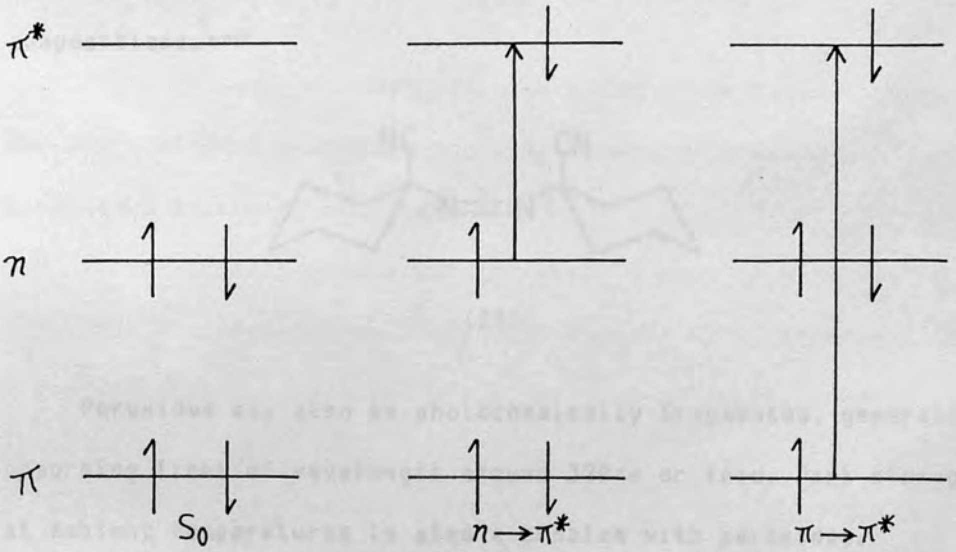
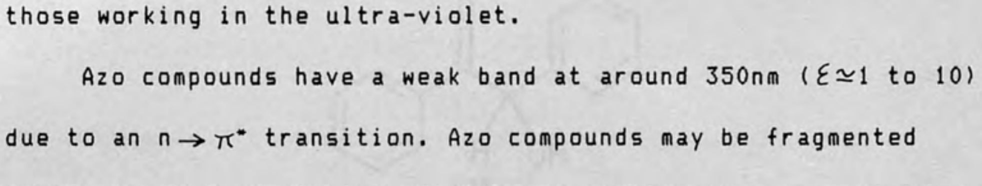


Figure 1.11 Electronic Transitions of Carbonyl Compounds

Initiators for photographic processes must be selected such that the maxima in their absorption spectra coincide with the maximum emissions of commonly used light sources, generally those working in the ultra-violet.

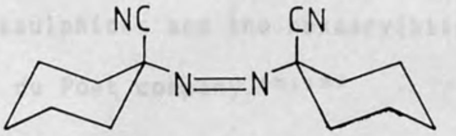
Azo compounds have a weak band at around 350nm ($\mathcal{E} \simeq 1$ to 10) due to an $n \rightarrow \pi^*$ transition. Azo compounds may be fragmented either on photochemical excitation or by thermal means, (scheme 1.13), yielding two radicals capable of initiating polymerization, and molecular nitrogen.



$$H_3C-\underset{CH_3}{\overset{CN}{C}}-N{=}N-\underset{CH_3}{\overset{CN}{C}}-CH_3 \;(23) \xrightarrow[\text{or } \Delta]{h\nu} 2\; H_3C-\underset{CH_3}{\overset{CN}{C}}\cdot + N_2$$

Scheme 1.13 Fragmentation of Azo-*bis*-isobutyronitrile

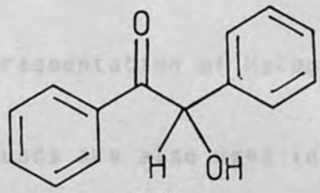
Azo compounds such as azo-*bis*-isobutyronitrile (23) decompose thermally at a significant rate at normal room temperatures, severely limiting their use in photosensitized compositions. α-Azo-1-cyclohexanecarbonitrile (24) does not have a high decomposition rate due to thermal dark reaction and is reported as being more suitable for use in resist compositions.[125]



(24)

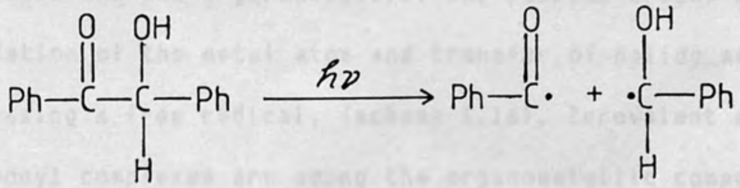
Peroxides may also be photochemically fragmented, generally absorbing light of wavelength around 320nm or less. Dark storage at ambient temperatures is also a problem with peroxides.

A very important class of initiator undergoing direct photofragmentation is represented by benzoin (25) and its derivatives, benzoin ethers or esters, benzoin thioesters or benzil alkyl ketals.



(25)

Photofragmentation of benzoin produces a benzoyl radical and a benzyl alcohol radical, (scheme 1.14) which may react in a number of ways: by recombining to form benzoin, benzil or 1,2-dihydroxy-1,2-diphenylethane, by disproportionation to two molecules of benzaldehyde, by hydrogen abstraction, by initiating polymerization or by termination of a growing polymer chain.



Scheme 1.14 Photofragmentation of Benzoin

Other classes of compounds undergoing photofragmentation include dialkyl disulphides and the hexaarylbiimidazoles initiators of the du Pont company.[45,121]

Direct photofragmentation can also be seen in halogenated compounds, represented by structure (26) and (27), (scheme 1.15) where R is the chromophoric group and X is chlorine, bromine or iodine.

$$R\text{-}CH_2\text{-}X \xrightarrow{h\nu} R\text{-}CH_2\cdot \;+\; X\cdot$$

(26)

$$R\text{-}SO_2\text{-}X \xrightarrow{h\nu} R\text{-}SO_2\cdot \;+\; X\cdot$$

(27)

Scheme 1.15 Photofragmentation of Halogenated Compounds

Halogenated compounds are also used in combination with organometallics, examples being 2-halomethyl-5-aryl-1,3,4,-oxadiazoles[126] (28) and the Kodak photopolymers[118,119] (22) described above.

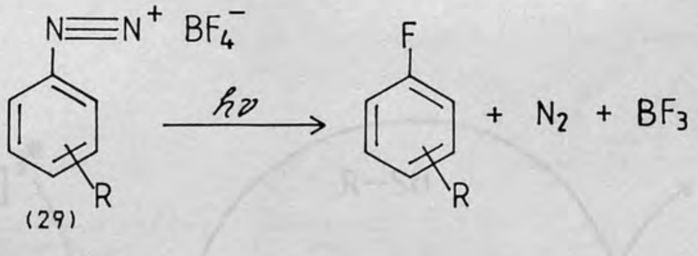
(28)

On excitation a complex is formed between the halogenated compound and the organometallic. The complex breaks down with oxidation of the metal atom and transfer of halide anion, releasing a free radical, (scheme 1.16). Zerovalent metal carbonyl complexes are among the organometallic compounds acting in this manner. These organometallic complexes are coloured and have sensitivities extending into the visible spectrum.

$$\mathrm{R\text{-}CX_3 + ArM(CO)_n \xrightarrow{h\nu} [complex]^{*} \longrightarrow R\text{-}\dot{C}X_2 + ArM^{+}(CO)_nX^{-}}$$

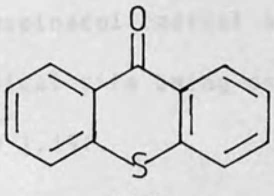
Scheme 1.16 Metal Carbonyl Sensitized Loss of Halogen

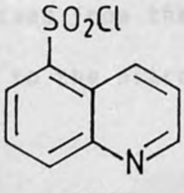
The release of Lewis acids, boron trifluoride for example, may also be accomplished photochemically. Lewis acids are catalysts for epoxide polymerization and are generated by the photo-decomposition of the appropriate diazonium compound (29), (scheme 1.17).



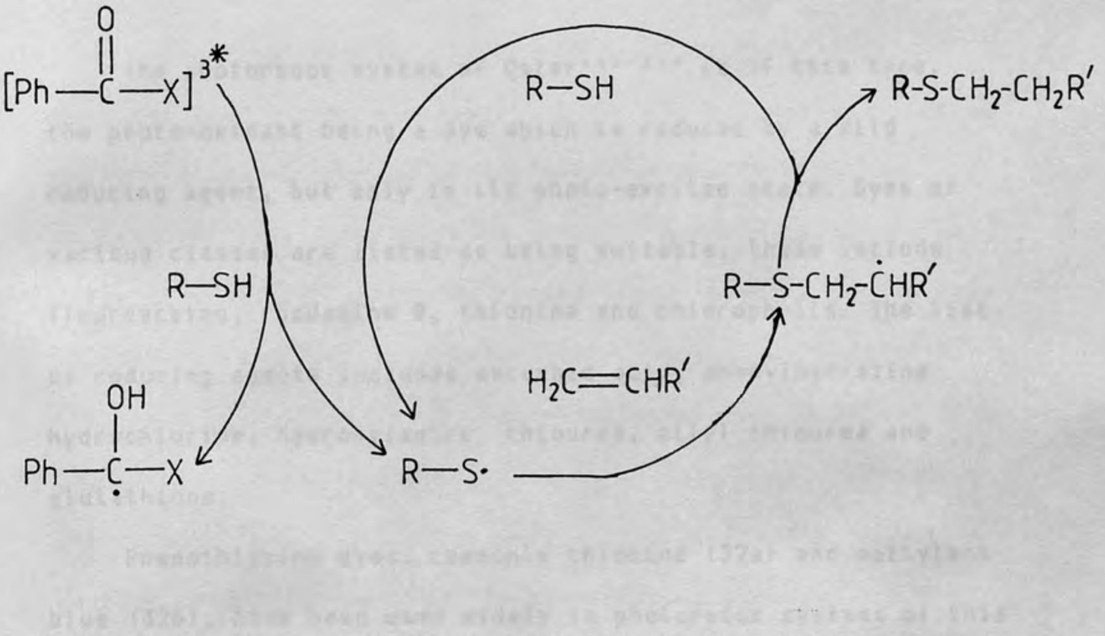
Scheme 1.17 Photo-decomposition of Diazonium Tetrafluoroborates

In addition to the direct photo-excitation of initiator and its subsequent dissociation, a photosensitized pathway may also be possible whereby the absorbing species, the sensitizer, transfers energy to the initiator which then dissociates. For this to be a viable pathway the triplet excited state of the sensitizer must be close in energy to a triplet state of the initiator. That this process is taking place can be shown by exposing at a wavelength at which the sensitizer absorbs but the initiator does not. An example of this energy-transfer process is provided by the thioxanthone (30) sensitized decomposition of quinoline-8-sulphonyl chloride (31).


(30)

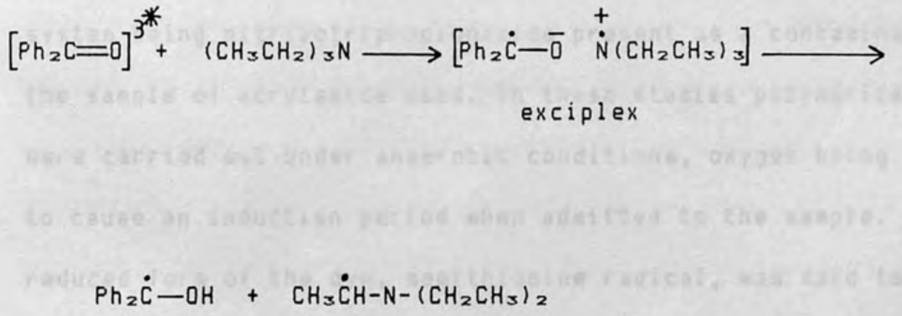

(31)

Hydrogen abstraction by excited-state carbonyl compounds from suitable donors is also a method used for the photochemical generation of free radicals. Mercaptans are particularly labile substrates yielding reactive radicals which readily add to ethylenically unsaturated materials, (scheme 1.18). This is employed in the formation of network polymers in photo-cured systems using polymercaptans and polyenes. The unpleasant smell of mercaptans tends to limit the applications of such materials however.



Scheme 1.18 Mercapto Radicals Generated by Hydrogen Abstraction and Their Addition to Alkenes

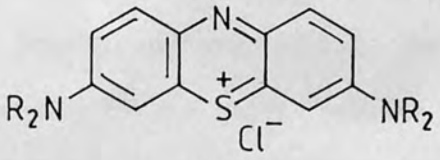
Photoinitiated electron transfer processes may also lead to free-radical intermediates. The triplet excited state of benzophenone forms an exciplex (or encounter complex) with triethylamine. Electron transfer followed by proton transfer leads to breakdown of the complex with the formation of a semibenzpinacol radical and a radical derived from the amine, the radical site being on a carbon atom α to the nitrogen, (scheme 1.19).



Scheme 1.19 Photo-electron Transfer Between Benzophenone and Triethylamine

The photoredox system of Oster[111-114] is of this type, the photo-oxidant being a dye which is reduced by a mild reducing agent, but only in its photo-excited state. Dyes of various classes are listed as being suitable, these include fluoresceins, rhodamine B, thionine and chlorophylls. The list of reducing agents includes ascorbic acid, phenylhydrazine hydrochloride, hydroxylamine, thiourea, allyl thiourea and glutathione.

Phenothiazine dyes, commonly thionine (32a) and methylene blue (32b), have been used widely in photoredox systems of this type.



(32)
a) R = H, b) R = Me

The photopolymerization of acrylamide, reported to be sensitized by thionine,[127] was later shown in fact to be a photoredox-initiated process,[128] the second component of the system being nitrilotripropionamide present as a contaminant in the sample of acrylamide used. In these studies polymerizations were carried out under anaerobic conditions, oxygen being found to cause an induction period when admitted to the sample. The reduced form of the dye, semithionine radical, was said to be the initiating species. Triethanolamine has also been used, in combination with thionine or methylene blue, to initiate the photopolymerization of acrylamide,[129] with similar inhibition by oxygen being noted.

These observations differ from those of Oster[130] who reported that oxygen was essential for the photopolymerization of acrylamide to proceed when riboflavin was used as the photosensitizer. Riboflavin is somewhat unusual in having an internal reducing agent, the ribose group, present in the same molecule as the dye functionality and requires no second component to function as a photoredox initiator. A method of maintaining the oxygen concentration at something approaching the optimum level, using cobalt(II) as a reversible oxygen carrier, has been reported,[131] oxygen being required for the initiation step but also inhibiting polymerization. The role of oxygen in the initiation is to re-oxidize the reduced form of the dye, this regenerates dye and produces peroxy species which initiate polymerization. This was shown by photoreduction of dye in the presence of monomer where no polymer was produced until the admission of oxygen.[130] The peroxy species was reported by Delzenne and co-workers[132] to be hydrogen peroxide. They also found general agreement with Oster on the mechanism of photopolymerization of acrylamide and methacrylic acid by eosin (tetrabromofluoresein) and ascorbic acid or thiourea.[133]

In another study of the photopolymerization of acrylamide in aqueous solution, using methylene blue and triethanolamine, the dye was shown to be a photosensitizer but the associated (dimeric) form is a chain terminator.[134] The rate of photopolymerization could be increased by methods which reduced the concentration of the associated form present in solution. Combinations of an anionic and cationic dye[135] and the use of ethylene glycol as solvent[136] were both successfully employed. Similar results were reported for two other phenothiazine dyes investigated.[137]

Some dicarbonyl compounds have also been shown to reduce the photo-excited state of phenothiazine dyes, initiating the polymerization of acrylamide in the process.[138,139] 2,4-Pentanedione (acetylacetone) and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) acted as photoinitiators when used in conjunction with thionine or methylene blue. The extent of enolization of these β-diketones is suggested as being significant. This was supported by the observation that 2,3-butanedione and 2,5-hexanedione did not show any similar activity. Photoactivity was also seen for a number of metal acetylacetonates.

The photopolymerization of acrylamide and *N,N'*-methylene *bis*-acrylamide sensitized by methylene blue and 2,4-pentanedione or triethanolamine has been used for the recording of holograms in a variable index photopolymer material.[49] The observation that aryl sulphinic acids may be used with phenothiazine dyes to initiate photopolymerization[140] has been exploited in the formation of photopolymer images[123] and in some holographic recording materials. Methylene blue or thionine was used to polymerize mixtures of metal acrylates and acrylamide with *para*-toluene sulphinic acid,[44] or its sodium salt,[43] producing a variable index polymer image. The reaction of the triplet state of the dye and various *para*-substituted benzene sulphinates has been studied,[141] with the conclusion that the oxidised form of the sulphinate is likely to be the active initiator rather than the reduced form of the dye.

The shelf-life of solutions of arylsulphinates and vinyl monomers is limited by an ionic dark reaction[142-144] leading to sulphone formation, (scheme 1.20). Sulphones are inactive in dye-activated photopolymerizations.

$$\mathrm{X{-}C_6H_4{-}SO_2^-} + \mathrm{CH_2{=}CHY} + \mathrm{H_2O} \longrightarrow \mathrm{X{-}C_6H_4{-}SO_2\,CH_2CH_2Y} + \mathrm{OH^-}$$

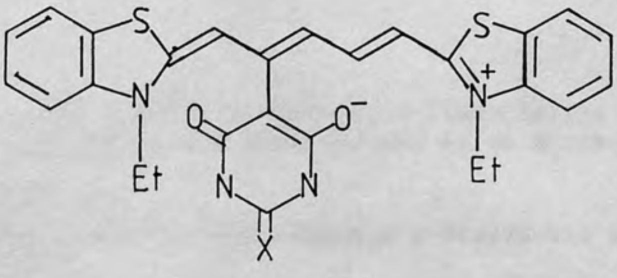
Scheme 1.20 Addition of Arylsulphinates to Vinyl Compounds forming Sulphones

Eosin (tetrabromofluorescein) is reported to interact directly with acrylamide (via an exciplex with water) to photopolymerize that monomer in the absence of any reducing agent or oxygen,[145] (scheme 1.21).

$$D + H_2O \xrightarrow{h\nu} (D \text{ --- } HOH)^{*} + M \longrightarrow DH\cdot + HOM\cdot$$

Scheme 1.21 Direct Photosensitization of Acrylamide by Eosin (D)

The ability of a range of dyes to directly sensitize the photopolymerization of acrylonitrile,[146] and the photobleaching of acridine yellow in a variety of vinyl monomers and the polymerization initiated thereby,[147] have also been investigated. The photopolymerization of styrene by a selection of simple cyanine dyes has been reported in a series of papers by Watanabe.[148-150] Changing the halogen counter-ion was found to affect the activation energy for the process in experiments carried out on dyes with identical cations, indicating the participation of halide ion in the initiation step. Cyanine dyes of the structures shown below (33 a-b) have also been shown to photopolymerize acrylonitrile in visible light.[151]



(33)

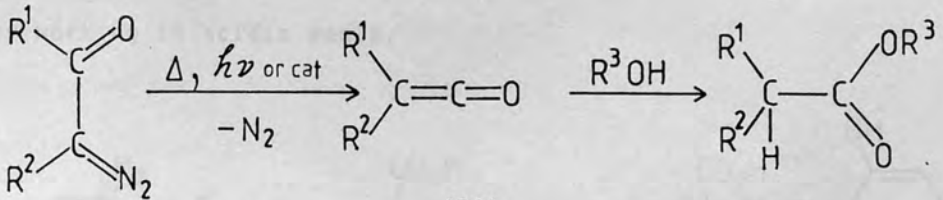
a) X = O, R = Me. b) X = S, R = Et.

1.6 Positive Photoresists

In contrast to the wide range of available mechanisms for the photocross-linking and insolubilization of organic materials, the scope for engineering an increase in solubility on exposure to light is more severely limited. Outside of resists for use with high energy radiation sources (electron beam and X-ray resists) which can function by bond scission, only one type of positive-working photoresist has found successful application. All of the commercial positive photoresists are based on this same process, the photochemical decomposition of an α-diazo ketone, the Wolff rearrangement.

1.6.1 The Wolff Rearrangement

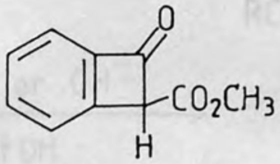
α-Diazo carbonyl compounds may undergo a thermal-, photochemical- or metal ion-catalysed rearrangement, with the loss of molecular nitrogen, to form a ketene (34).[152] This is a reactive intermediate and, with alcohols for example, will be trapped as an addition product, in this case an ester, (scheme 1.22).



Scheme 1.22 Wolff Rearrangement of α-Diazo Ketone and Trapping of the Ketene Intermediate by an Alcohol

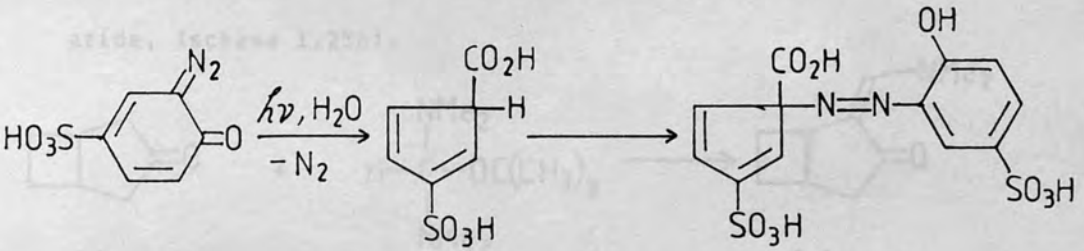
The photochemical rearrangement proceeds via a singlet excited state of the diazo ketone, triplet sensitization leading to suppression of ketene formation and to products derived from reactions more typical of carbenes.[153]

The Wolff rearrangement of cyclic diazo ketones leads to ring-contracted products and has been used as a synthetic route to strained ring systems. The benzocyclobutenone derivative (35) was made by a thermal Wolff rearrangement, the product itself being photolabile, a photochemical conversion was ruled out in this case.



(35)

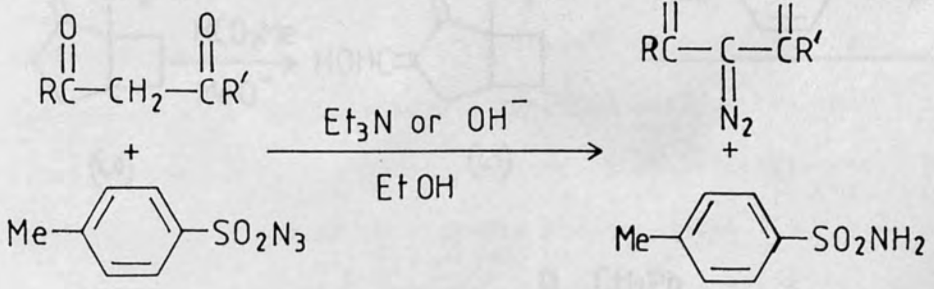
With *ortho*-quinone diazides the Wolff rearrangement leads to ring-contraction with the formation of cyclopentadienes. This was first noted by Süs[155-157] and is sometimes referred to as the Süs reaction as a specific example of the general Wolff rearrangement. Quinone diazides have been used in a diazotype photocopying process. An increase in the pH promotes coupling of the acid product with unreacted quinone diazide forming an azo dye, (scheme 1.23). Coupling reactions of this type are avoided by working in acidic media.



Scheme 1.23 Azo Dye Formation in the Süs Reaction

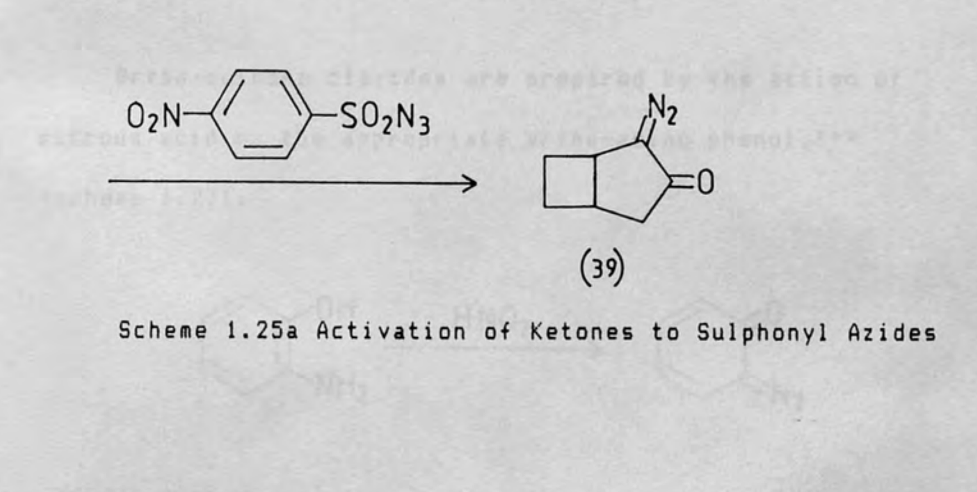
α-Diazo ketone derived from β-diketones and similarly activated α-methylene groups may be synthesized by the action of base and *para*-toluene sulphonyl azide (tosyl azide),[158] (scheme 1.24).

A polymer bound sulphonyl azide, derived from a polystyrene/divinyl benzene copolymer resin, derivatized with chlorosulphonic acid followed by sodium azide, has been reported to carry out the same conversion.[159] The advantages are a cleaner product and avoiding the use of the potentially shock-sensitive tosyl azide.

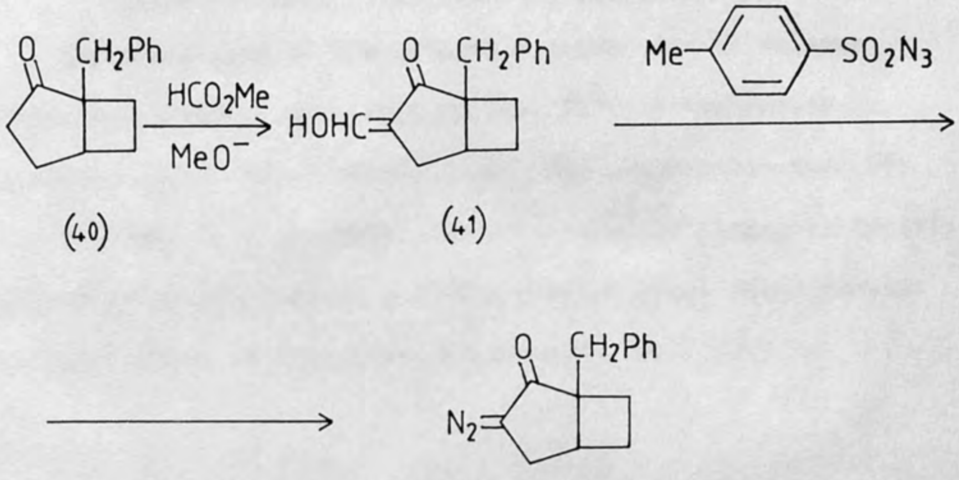


Scheme 1.24 Tosyl Azide in Diazo Ketone Synthesis

Ketones with less reactive ∝-methylene groups may be activated by various means. In the synthesis of bicyclo[2,2,0]hexane derivatives,[160] the enamine (38) produced by the reaction of the ketone (36) with *bis*-(dimethylamino)-*tert*-butoxy methane (37) was converted to the diazo ketone (39) with *para*-nitrobenzene sulphonyl azide, (scheme 1.25a). The reaction of methyl formate with a related ketone (40) activated the formylated product (41) to reaction with tosyl azide, (scheme 1.25b).



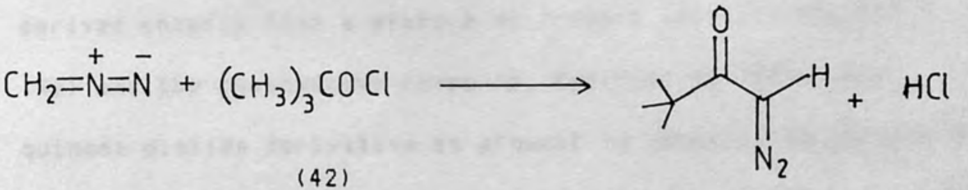
Scheme 1.25a Activation of Ketones to Sulphonyl Azides



(40) (41)

Scheme 1.25b Activation of Ketones to Sulphonyl Azides

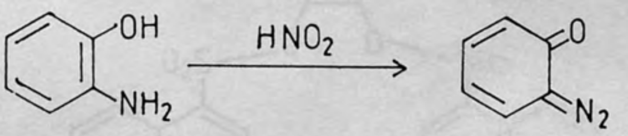
Acyclic diazo ketones may be prepared by the reactions of diazo alkanes with an acid chloride, for example the reaction of diazomethane with trimethylacetyl chloride (pivaloyl chloride), (42),[161] (scheme 1.26)



(42)

Scheme 1.26 The reaction of Diazomethane with an Acyl Chloride

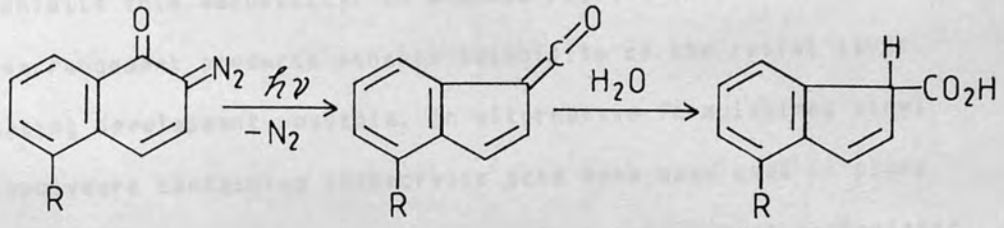
Ortho-quinone diazides are prepared by the action of nitrous acid on the appropriate *ortho*-amino phenol,[162] (scheme 1.27).



Scheme 1.27 The Action of Nitrous Acid on *ortho*-Amino Phenols

1.6.2 Positive Photoresist (Shipley AZ 1350)

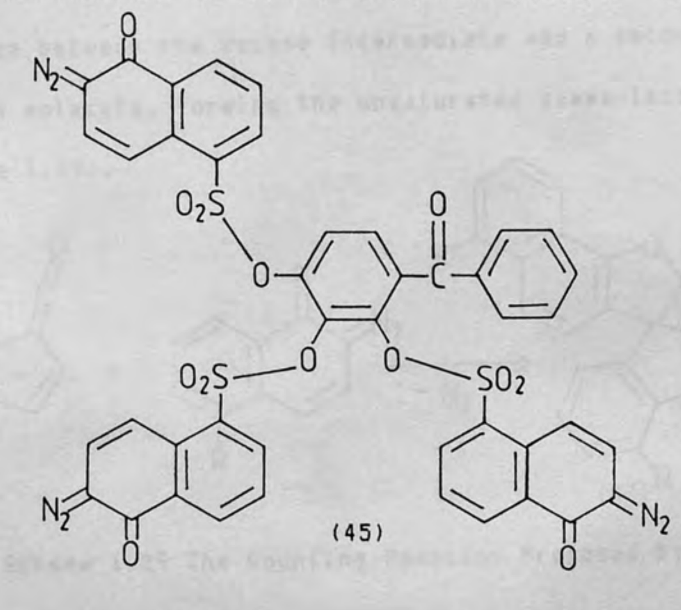
The photolysis of the quinone diazide (43) in aqueous acidic media would, according to Süs,[155-7] give the indene-1-carboxylic acid (44), (scheme 1.28). The observation that the rearrangement of a non-polar compound to an ionizable carboxylic acid could be achieved in a simple photochemical step leads to the development of photoresists employing this reaction.



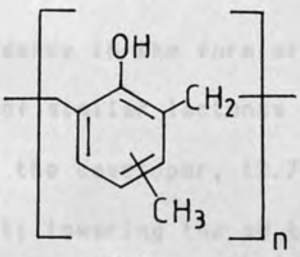
(43) (44)

Scheme 1.28 The Photolysis of a Quinone Diazide

A typical resist formulation of this type consists of a low molecular weight novolak resin (a phenol-formaldehyde resin derived chiefly from a mixture of cresols and xylenols)[163] (46) and the photoactive compound, typified by (45). This quinone diazide derivative is present in about 15-20 percent by weight of solids. The resist is coated from a mixture of xylene and acetate solvents to inhibit crystallization of the diazide.



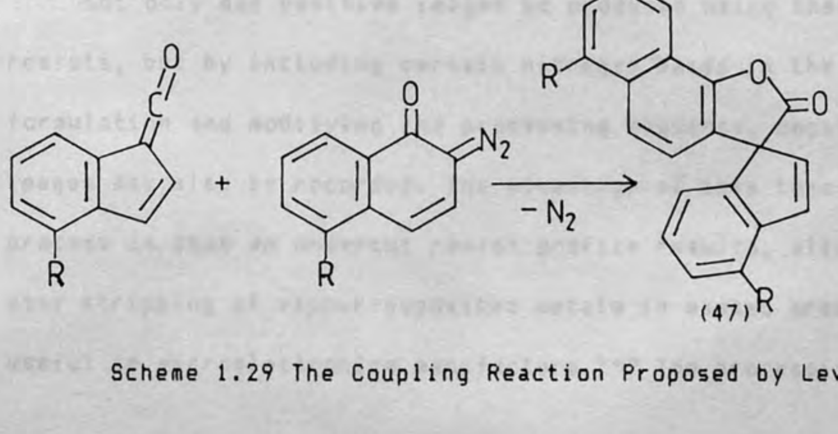
(45)



(46)

The novolak resin is soluble in aqueous alkalis used as developers for the resist, but the presence of the diazide (45) inhibits this solubility. In exposed regions however the rearrangement products enhance solubility of the resist layer making development possible. In alternative formulations vinyl copolymers containing methacrylic acid have been used in place of novolak resins. The basic materials on which most mechanistic studies have been carried out are the Shipley photoresists such as AZ 1350. A review of some commercial positive photoresists is given in the series of articles by Clark,[164] the spectral sensitivities of materials reviewed lies between 300 and 500nm.

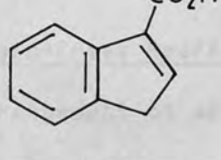
It has been noted that, in a layer cast from an organic solvent, there would be insufficient water to allow for total conversion of photolysed quinone diazide to indene carboxylic acid, as seen in the studies by Süs, (scheme 1.28). Levine[165] attempts to explain this observation by proposing a coupling reaction between the ketene intermediate and a second quinone diazide molecule, forming the unsaturated *gamma*-lactone (47), (scheme 1.29).



Scheme 1.29 The Coupling Reaction Proposed by Levine

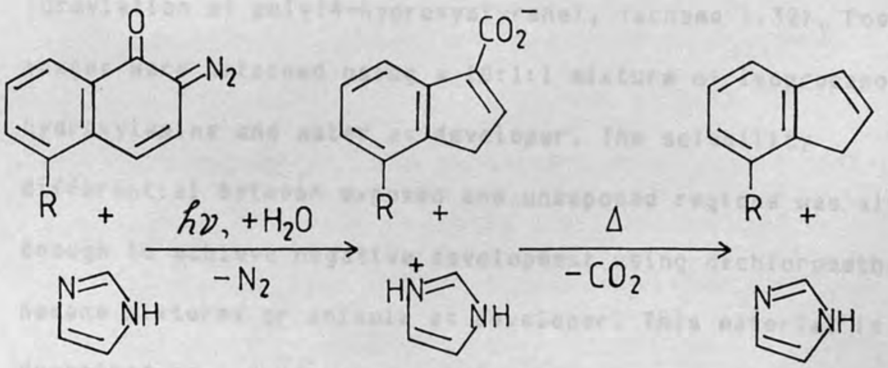
Levine produces evidence in the form of infra-red spectra and cites the formation of similar lactones in diazo ketone photolyses.[161] The pH of the developer, 12.7-12.8, has to be this high for development; lowering the pH to 12.0 results in loss of developing activity. This is taken to imply the hydrolysis of an intermediate being relevant to the development process.

Pacansky and Lyerla[162] suggest that lactone formation would be a minor pathway and that the formation of an ester with the phenolic groups of the novolak resin, along with some acid formation, would be more likely. The invocation of base-catalysed azo coupling reactions between unexposed quinone diazide and novolak phenols, effectively cross-linking unexposed areas, as suggested by DeForrest,[3] is not seen as necessary by these authors. They also point out that indene-1-carboxylic acid (44) may not be the final product of the Süs reaction, as it has been shown to rearrange readily to the isomeric indene-3-carboxylic acid (48).[167]



(48)

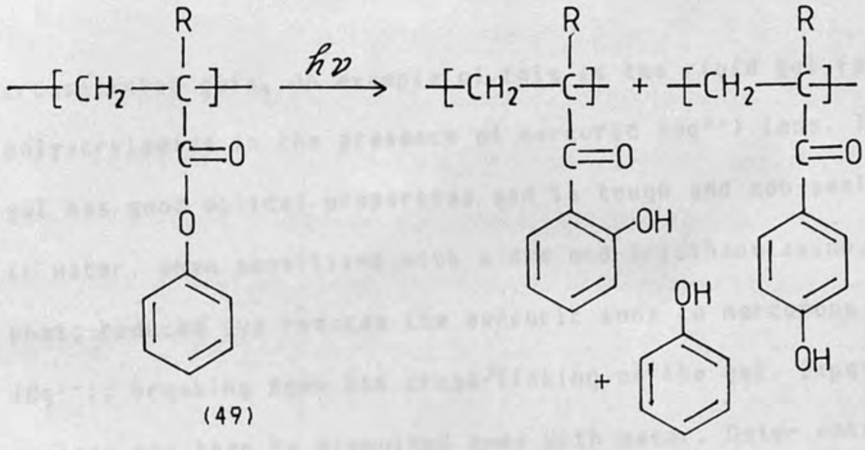
Not only may positive images be produced using these resists, but by including certain nitrogen bases in the formulation and modifying the processing sequence, negative images may also be recorded. The advantage of this tone-reversal process is that an undercut resist profile results, allowing easy stripping of vapour-deposited metals in masked areas, useful in microelectronics manufacture.[168] The processing sequence consists of exposure to ultra-violet light through a negative mask in a moist environment, a post-bake at 100°C for 30 minutes, then a flood exposure followed by normal development. The moist environment ensures the formation of indene carboxylic acid which forms a salt in the presence of imidazole. Post-baking causes decarboxylation of the acid to neutral indene which is not soluble in the developer. The unreacted quinone diazide in the unexposed areas is then rendered soluble by the second exposure and washed-out in development. This is summarized in scheme 1.30.



Scheme 1.30 The Image Reversal Process

1.6.3 The Photo-Fries Rearrangement

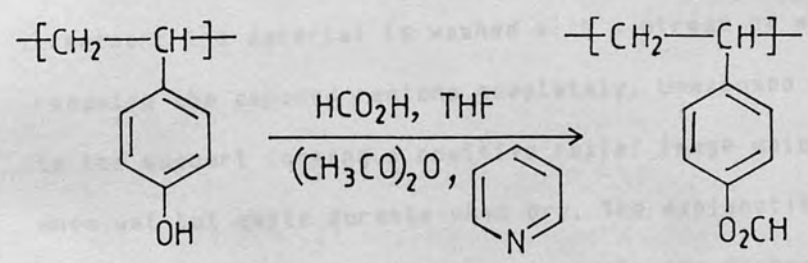
The Photo-Fries rearrangement of an aromatic ester has been used as the basis of an experimental resist.[169] Ultra-violet irradiation of polyacrylic acid esterified with phenol (49) produces some 2-substituted and some 4-substituted rearranged product along with a little phenol, (scheme 1.31). The polymer, bearing phenolic groups, should now have increased solubility in basic solvents. This was the starting point for the investigation of a series of poly(aromatic esters) as lithographic materials.



(49)

Scheme 1.31 The Photo-Fries Rearrangement

Poly(4-formyloxystyrene) (50) was the best of the experimental formulations tried. The polymer was prepared by the formylation of poly(4-hydroxystyrene), (scheme 1.32). Positive images were obtained using a 10:1:1 mixture of isopropanol, hydroxylamine and water as developer. The solubility differential between exposed and unexposed regions was also good enough to achieve negative development using dichloromethane/hexane mixtures or anisole as developer. This material is described as a deep U.V. resist.



(50)

Scheme 1.32 The Synthesis of Poly (4-formyloxystyrene)

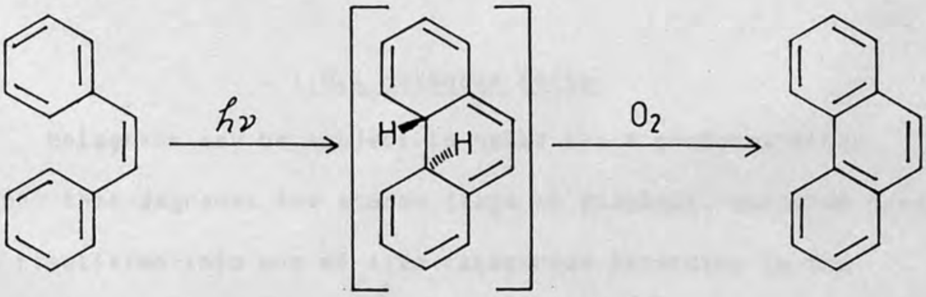
1.6.4 Positive Processes Involving Organic Colloids

Oster[170] notes that many water soluble polymers form complexes with metal ions with the possibility of forming cross-linked gels. An example of this is the rigid gel formed by polyacrylamide in the presence of mercuric (Hg^{2+}) ions. This gel has good optical properties and is tough and non-swelling in water. When sensitized with a dye and triethanolamine, the photo-reduced dye reduces the mercuric ions to mercurous (Hg^{1+}), breaking down the cross-linking of the gel. Exposed regions may then be dissolved away with water. Oster notes the possibility of forming a positive colour printing system employing three layers sensitized with cyan, magenta and yellow dyes. A range of metal ions[171] has been investigated including Fe^{3+}, Ti^{4+}, Cu^{2+} and Ag^{+}. This is similar to processes employing the direct photoreduction of ferric ions in organic colloids.[172].

Dichromated colloids containing an aqueous dispersion of a water-insoluble, soft synthetic resin may be used as the basis of a positive system.[173] On drying a continuous film is produced which is exposed through a positive mask. Development consists of immersion in warm water containing a small amount of ammonia to swell the exposed areas. After a few seconds of this treatment the material is washed with a stream of warm water, removing the exposed regions completely. Unexposed areas adhere to the support forming a positive relief image which is delicate when wet but quite durable when dry. The explanation for this behaviour is that the imaging process in the dichromated material disrupts the continuous film of synthetic polymer, allowing the ingress of water. Suitable colloids are as for dichromated gelatine and its alternatives. Resins used include polystyrene, natural rubber latex, vinylacetate copolymers and acrylamide copolymers.

1.7 Miscellaneous Processes

Stilbene undergoes photoisomerization between its *cis* and *trans* forms on photolysis. In addition phenanthrene may be formed[174] via a transient dihydro intermediate, oxidized by molecular oxygen or other suitable oxidant present in the solution,[175] (scheme 1.33).



Scheme 1.33 Phenanthrene Formation in the Photolysis of Stilbene

This reaction has been used in a number of resist formulations,[176] the conversion to the aromatic phenanthrene providing sufficient alteration in physical properties to allow solvent discrimination between exposed and unexposed regions. Negative or positive images may be obtained depending on the identity of the stilbene compound used. The photosensitivity is said not to be limited to the ultra-violet but to cover "practically the whole of the visible spectrum".

1.8 Processing Considerations

Both negative- and positive-working photoresists have been used to record holograms[23,24] and holographic gratings.[20,22] Photoresist in its major application, photomasking, is only required to produce a high contrast image, that is either resist or no resist (a binary process). In holographic applications the build-up of resist (in the case of a negative-working material) must be proportional to the intensity of the exposing radiation at any particular point (an analogue process). This means that a graph of depth of resist against exposure should approximate linearity over a significant portion. This would define the useful range of the material. The shape of this exposure characteristic curve will also be influenced by the development conditions.

1.8.1 Hologram Noise

Holograms may be subject to noise which produces stray light that degrades the stored image on playback. Hologram noise is classified into one of five categories according to the mechanism of its origin as follows:

Granularity: when the image consists of particles of material in a transparent binder, the obvious example being silver halide emulsions, stray light will be produced by scattering from these grains. The degradation is evident as a veiled glare around the holographic image due to this non-directional scatter. Thermoplastic and photoresist materials are essentially grainless and so do not scatter light in this manner. Other materials such as photochromics have "grain" of molecular dimensions, too small to act as scattering centres.

Scattering from support and/or binder: scatter to some extent is always present due to the support and binder and their interfaces. Anti-halation layers* may reduce some of this type of noise in the recording step.

Phase noise: this is intrinsic to phase holograms, but only occurs in the case of diffuse objects. Self-interference of

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*An anti-halation layer is a coating of a dye containing material at the base of a photographic film. Its purpose is to absorb photons which have passed through the emulsion without contributing to the imaging process. The term "halation" refers to the halo of scattered light seen around highlights when such layers are not used.

the object light is recorded as a low-frequency pattern on the hologram. Noise is then due to additional unwanted diffraction in and around the holographic image.

Non-linearity distortion: this arises when the amplitude transmittance of the hologram is not strictly proportional to the recording exposure. This results when the range of exposures is outside the dynamic range of the recording material. Second and higher order diffractions also degrade the holographic image.

Speckle noise: this is a result of diffuse, coherent illumination limited by the apertures of the system. It is degrading to the image but not dependent on the nature of the recording material.

1.8.2 Development of Photoresist

Development of photoresist is normally achieved by either a spray treatment or immersion in solvent. Spray development is generally preferred as it ensures fresh solvent is continually being used and is gentler on the image.

In a negative-working (photocross-linking) resist, only light cross-linking is needed to form a three-dimensional network polymer, insoluble in the developer. However such network polymers are still substantially swollen by solvents which dissolve the uncross-linked portions. In narrow, linear features swelling may lead to the relief of strain by a snake-like oscillation of the resist tracks.[178] Adjacent swollen features may adhere to each other, drying with the formation of "bridges" between them due to a transference of material.[178] This distortion is similar in appearance to the "frost" seen in thermoplastic materials.[40] An analogous distortion of holographic gratings may be due to the high molecular weight polymers present in some types of photoresist, the chains forming links between areas of the image.[179]

The effects of swelling in negative materials may be reduced by a series of rinses, following development, designed to reverse the swelling process. Shock-rinsing, a rapid quenching of swollen resist, gives rise to a "swiss cheese" effect surface due to the rapid contraction of swollen features.[180] Resists have also been reported which are non-swelling in their developers, the polystyrene bound tetrathiafulvalene (PSTTF) and related charge-transfer resists[14,15,181] show excellent resistance to swelling but require high energy exposures (X-ray, e-beam or actinic radiation).

Positive resists such as Shipley AZ 1350 contain very low molecular weight novolak polymers which dissolve with minimal swelling in a layer by layer manner. This is the main reason for the high resolution capability of these materials.[180] The exposure characteristic of these materials may be modified to give a suitable linear response for the recording of holograms by controlled dilution of the developer.[21] Negative resists require cross-linking throughout the resist layer and at the resist-substrate interface to ensure adhesion, if this is not so solvent may penetrate this layer and cause a lifting-off of the image. Positive resists are rendered soluble by exposure from the surface into the bulk, in the same way that the developer penetrates the resist, therefore similar adhesion problems do not occur.

For all these reasons, positive resists such as Shipley AZ 1350 are preferred for holographic applications, giving high resolution (>1500 l mm^{-1}),[21] low noise and a recording wavelength range extending from the ultra-violet to around 500nm.[21] There remains however, no photoresist material suitable for the recording of thin relief phase holograms at the wavelength of the helium-neon laser.

RESULTS AND DISCUSSION

2 Photopolymers for the Formation of Relief Images

The aim of this project was the development of a photoresist material capable of forming high resolution relief images using Helium-Neon (633nm) laser light. Such a system will necessarily include a polymer in its formulation to allow for the formation of stable thin films, the photochemical modification of which will lead to a change in its solubility characteristics.

2.1 The Requirements for a Holographic Photoresist

The starting point for our investigations was a list of preferred specifications for a photoresist material for use in holography. These requirements are summarized below:

1) The material must be tough and durable and adhere well to a range of substrates. Physical strength is necessary in the final relief image if further copies are to be produced by embossing techniques.

2) The resolution of the material should be as high as possible, in the case of a negative resist this will be about 1000 lines per millimetre (1 mm^{-1}) but for positive resists >3000 1 mm^{-1} may be achieved.

3) While no suitable material is available for the 633nm region, sensitivity from 450 to 700nm would provide a useful working range. Any sensitivity at longer wavelengths would be a bonus. Photochemical speed is not critical but the limiting factor is the exposure time required, too long an exposure would be impractical and would risk problems caused by vibration.

4) Aqueous development would be preferable. Organic solvents require special precautions to be taken, against fire

and spillage for example, and the use of a fume hood is advised.

In the light of these requirements, and considering the higher resolution capability, coupled with the aqueous alkaline development, positive resists appear particularly attractive. The commercial positive photoresists, as exemplified by Shipley AZ 1350, are the materials of choice for holographic recording in photoresist at short wavelength but have little sensitivity at 633nm.

2.2 Possible Strategies

Possible strategies for the development of a red-sensitive resist may be arrived at by a review of the commercially available materials and their chemistry. These may be divided into four mechanisms for discussion: azido-sensitized materials, photocycloaddition, photopolymerization and Wolff-rearrangement (positive) resists.

In many azido-sensitized materials (excepting those in which the azide group is polymer-bound) the polymer system is essentially the same, being derived from natural or synthetic rubbers. The development of new materials would therefore rely on the development of new azido sensitizers. Azides used in existing systems generally have maximum sensitivity at around 360 to 400nm and are virtually transparent above 450nm so there is little possibility of extending sensitivity to around 633nm.

Photocycloaddition is a versatile strategy, being employed in polymeric systems leading to cross-linking with a wide variety of structural variations. Many of these materials are readily sensitized by a wide range of triplet sensitizers, increasing both the sensitivity at a particular wavelength and spectral coverage. Materials are rarely sensitized at wavelengths greater than about 400nm although some styryl pyridinium salts have been reported with sensitivities extending to 630nm,[92] and this may mark the limit of such systems.

Photopolymerization offers an attractive field of investigation; a wide variety of monomers and substituted polymers may be used as the basis for a resist.[83] Initiating radicals may be derived from the fragmentation of ketones and azo compounds, by photoredox processes or by other means.[109] A given photopolymerizable composition may be "tuned" to a target wavelength by careful selection of the initiating system used. The major drawback of free radical-initiated systems is their sensitivity to oxygen. For this application a polymeric system has advantages over those involving monomers and monomer mixtures due to the ease of casting rigid thin films from solutions of polymer.

Photinitiated ionic polymerization is also possible, with alkyl vinyl ethers or cyclic ethers such as epoxides, polymerization may be initiated cationically. Cations may be photochemically generated from typical free radical photoinitiators in the presence of a suitable oxidant. These give an amplification of the rate of initiation with exposure in comparison with free radical initiation alone.[182,183] Cationic polymerization of epoxides is also initiated by Lewis acids generated by the photodecomposition of diazonium salts of counterions such as BF_4^- or PF_6^-. Diazonium salts have low thermal stability and this has led to the appearance of diaryliodonium and triarylsulphonium salts as cationic photinitiators.[109] It is also possible in principle to initiate polymerizations anionically with monomers such as styrene[184] and the cyanoacrylates, their value may be limited in photoimaging applications however because of the lack of a facile termination mechanism in such processes. The products of anionic polymerizations are termed "living polymers" because the reactive anions survive at the chain termini and can polymerize further monomer when it is introduced.[185]

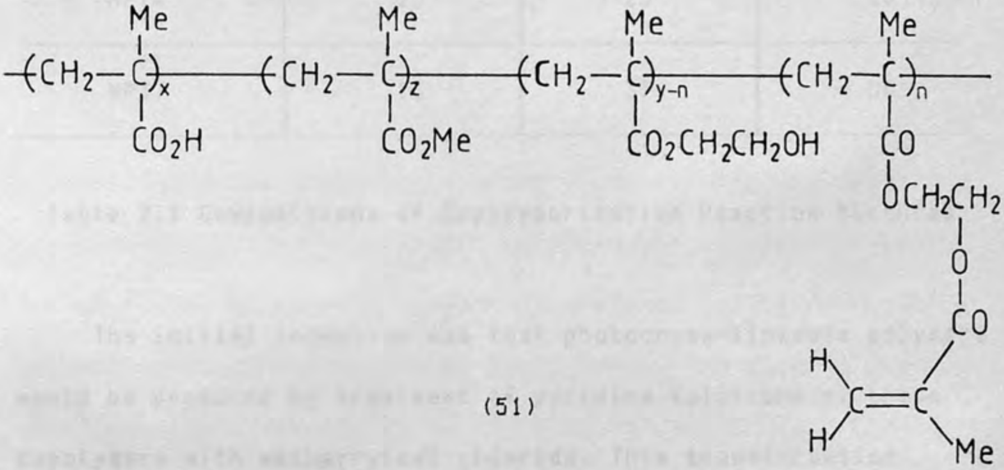
Positive photoresists are based on *ortho*-quinone diazides and generally phenol-formaldehyde (novolak) polymers. The sensitivity of such materials is highest at about 350-380nm although they have been used successfully in holographic applications at 458 and 488nm.[186] In common with decompositions of azides and azo compounds, loss of molecular nitrogen provides an entropic driving force for the reaction. This suggests that photolysis at long wavelength may be possible.

2.3 Methacrylate Copolymers as Photopolymers

Discussions with Ilford Limited resulted in the adoption of a strategy based on a methacrylate copolymer with pendant vinyl groups, cross-linked by free radical addition polymerization. Phenylazotriphenylmethane (PATM) was chosen as the model initiator in the evaluation of polymerizable coatings. PATM is decomposed to free radicals capable of initiating the polymerization of vinyl monomers by irradiation with light of 488nm (argon ion laser).[187]

The proposed copolymer would be prepared by polymerizing a mixture of methacrylic acid (MAA), methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA). As a starting point the molar ratios 2:3:5 (MAA:MMA:HEMA) were used. The role of the acid residues was to render the polymer soluble in aqueous sodium carbonate solution, chosen as the developing system.

Methyl methacrylate would act as a spacer group and give mechanical strength to the coating. The hydroxyethyl groups would provide functionality on the polymer backbone allowing for the attachment of polymerizable groups, principally the methacrylate ester, (51).



(51)

2.3.1 The Preparation of Copolymers

The methacrylate copolymers and the products of their reactions with reagents such as methacryloyl chloride are referred to by a number preceeded by the letters MP. The number refers to chronology only and does not convey any information about composition, the composition of polymer batches may be found by reference to the tables presented in the experimental section and given below. The first polymer prepared was a copolymer designated MP1 which, after esterification, gave products MP2 to MP9.

Four copolymers of the three monomers were prepared as described in the previous section. All preparations were on the scale of 0.8 moles of monomer. The concentration, temperature, method of initiation and reaction time were kept constant but the composition of the polymerization mixture was adjusted in accordance with the following table, (Table 2.1).

polymer	molar percentage MMA	MAA	HEMA
MP1	30	20	50
MP10	30	20	50
MP14	25	25	50
MP37	13	37	50

Table 2.1 Compositions of Copolymerization Reaction Mixtures

The initial intention was that photocross-linkable polymers would be produced by treatment of pyridine solutions of these copolymers with methacryloyl chloride. This transformation proved to be not as straightforward as it first appeared.

2.3.2 Esterification of Copolymers with Methacryloyl Chloride

The conditions for the esterification of initial batches of polymer, namely MP2-9, MP13 and MP15-18, were varied in order to optimize the conversion. Addition of the reagent to a warm solution of the polymer in pyridine resulted in the rapid formation of an insoluble gel (MP2). Room temperature preparations produced polymers (MP3, MP4) which were swollen by polar organic solvents but insoluble in any tried. The preparation of MP5, in which the reagent was added to an ice-cold solution in a foil-wrapped flask, gave material of acceptable solubility but this only weakly imaged using 5% aqueous sodium carbonate as developer. A repeat of this preparation, MP6, failed to reproduce this result.

Experiments with alternative acyl transfer agents, triethylamine, 2-picoline and 2,6-lutidine did not improve the reliability of the method. Triethylamine caused an immediate gel to form when the reagent was added. The addition of extra solvent did nothing to improve this state of affairs and the preparation was abandoned. The sterically hindered 2,6-lutidine gave a soluble product (MP8) but an insoluble material when the preparation was repeated on a larger scale (MP9).

A milder set of conditions was finally established for the conversion in the preparation of MP18. A mixture of pyridine and *N,N*-dimethyl formamide (DMF) was used, sufficient pyridine being present to react with the HCl produced by the reaction of the methacryloyl chloride with the polymer. The reagent was added to a solution cooled to ice-bath temperature and the mixture was stirred for only 30 minutes before precipitation of the crude polymer pruduct. The flask was wrapped in foil to exclude light from the reaction.

The reaction of methacryloyl chloride carried out in a pyridine containing solvent is difficult to monitor as methacryloyl chloride, when brought into contact with pyridine vapour, produces a dense white solid. This tends to block the dropping funnel used for the addition and it is not easy to maintain efficient mixing of the reactants. Due to the viscosity of polymer solutions coupled with this problem it is impractical to stir reaction mixtures magnetically and a mechanical stirrer must be used.

Some possible mechanisms were proposed for the cross-linking which led to the insolubilization of early batches of esterified polymer. As well as polymerization by reactive intermediates such as radicals, anions or cations, three other mechanisms could be operating. In each case the cross-link would be equivalent to an ethylene glycol *bis*-methacrylate polymerized into two polymer chains. In the first instance this could arise by direct esterification of a hydroxyethyl residue by a polymer-bound carboxyl group. Secondly a methyl methacrylate and hydroxyethyl methacrylate residue could react via a transesterification with the release of methanol. Thirdly transesterification occurring between two hydroxyethyl methacrylate residues (a disproportionation reaction) would form a cross-link with the release of a molecule of ethylene glycol. None of these three mechanisms seem likely to occur to any great extent although it must be said that an average of only one cross-link per polymer molecule is required to link all the polymer molecules in a solution into a three-dimensional network.

Whatever the mechanism of cross-linking in early preparations the adoption of the reaction conditions exemplified by MP 18 made premature cross-linking much less likely although samples were found to be insoluble after long-term storage at room temperature in the dark.

The esterification of polymers leading to products soluble in organic solvents such as DMF and methanol highlighted another problem: the products were generally not soluble in 5% aqueous sodium carbonate solution. A batch of copolymer with a higher acid content, MP14, was prepared to improve the chance of a base soluble esterified polymer being produced. The copolymers themselves, MP1, MP10 and MP14 were all acceptably soluble in sodium carbonate solution but the solubility characteristics are modified by esterification. In order to investigate the effect of reaction conditions on base solubility (and degree of esterification) a series of preparations was undertaken varying the total solvent volume and the volume of reagent used. These experiments were all carried out along the lines of MP18 using MP14 as starting material.

The conclusion from this series of experiments was that, for the polymer used in these conversions, base soluble products were only produced in dilute solution or when the volume of reagent used was small, with the correspondingly low conversion of hydroxyl groups to the methacrylate ester. Clearly some further work was necessary to establish the relationship between polymer composition and solubility characteristics.

2.3.3 The Acid Content of Copolymers

Following experiments which varied the esterification conditions it became evident that conversion to the methacrylate ester lowers the solubility of this polymer to the chosen developer, 5% aqueous sodium carbonate. Two factors may be responsible for this observation: esterification increases the molecular weight of the polymer chains but, perhaps more importantly, esterification lowers the polarity of the polymer molecules by converting hydroxyl groups to non-polar ester groups, thereby markedly reducing the ability of the polymer to form hydrogen bonds with solvent water.

In order to investigate the effects of copolymer composition on base solubility a series of copolymers of methyl methacrylate and methacrylic acid were prepared using the same conditions as MP1, MP10 and MP14 but on half the scale. These binary copolymers were coded using a new system. Each polymer was referred to by the letters MPX followed by the molar percentage of methacrylic acid present in the polymerization mixture. Five of these polymers were prepared in all; MPX10, 20, 30, 40 and 25.

A number of assumptions were made when comparing these polymers with a hypothetical fully esterified photopolymer. In such a polymer the only groups of high polarity would be the methacrylic acid residues. It was assumed that methyl methacrylate residues and esterified hydroxyethyl methacrylate residues would have a similar effect on the aqueous solubility of the polymers, both being relatively non-polar ester groups. It was also assumed that the molecular dimensions of the MPX series of copolymers would be similar to that of the base copolymers prepared under the same conditions of initiator, time, temperature and total monomer concentration. In order to make the comparison on the basis of these assumptions a new parameter must be specified. The most convenient quantity by which the polymers can be compared is the number of free acid groups per gram of polymer. Not only can this quantity be calculated from the known copolymer compositions but it can be determined experimentally by titration. The major source of error introduced by comparing polymers would be due to the disparity in the mass of methyl methacrylate residues compared to esterified hydroxyethyl methacrylate residues. Basing the comparison on weight is an attempt to overcome this problem.

Prepared samples of the MPX series of polymers were examined for solubility in organic solvents, water and 5% aqueous sodium carbonate solution. MPX10 was insoluble in water, 5% sodium carbonate solution and methanol (swelling only) but soluble in DMF. MPX20 was insoluble in water but soluble in methanol and DMF and formed swollen particles in sodium carbonate solution which dissolved after 24 hours. Both MPX30 and MPX40 were completely soluble in methanol, DMF and 5%

sodium carbonate solution but insoluble in water. Finally MPX25 was prepared and found to be soluble in methanol, DMF and 5% sodium carbonate and insoluble in water. The theoretical carboxylic acid content per gram is given in the table below (Table 2.2) for each of these polymers.

polymer	molar ratios (%) MMA	MAA	moles $-CO_2H$ per gram
MPX10	90	10	1.013×10^{-3}
MPX20	80	20	2.055×10^{-3}
MPX25	75	25	2.588×10^{-3}
MPX30	70	30	3.128×10^{-3}
MPX40	60	40	4.233×10^{-3}

Table 2.2 Theoretical Numbers of Acid Groups Per Gram for MPX Copolymers

A composition equivalent to MPX25 was taken as the target for a copolymer with enhanced solubility in 5% sodium carbonate solution, MPX25 being around the lowest acid content still showing complete solubility in that developer. The acid content per gram of polymer was calculated for a number of monomer ratios assuming a constant 50 molar percent of fully esterified hydroxyethyl methacrylate in the final product, (Table 2.3).

monomer ratios			moles $-CO_2H$ per gram
MMA	MAA	HEMA	
11	39	50	2.714×10^{-3}
12	38	50	2.642×10^{-3}
13	37	50	2.570×10^{-3}
14	36	50	2.498×10^{-3}
15	35	50	2.426×10^{-3}

MMA= methyl methacrylate, MAA= methacrylic acid, HEMA= hydroxyethyl methacrylate.

Table 2.3 Numbers of Acid Groups Per Gram of Hypothetical Fully Esterified Copolymers

From the above table it can be seen that the nearest composition to the target in terms of acid groups per unit mass is that with monomer ratios of 13:37:50, MMA:MAA:HEMA. This led to the preparation of MP37 using exactly these initial monomer ratios. This polymer was indeed more soluble in aqueous media: precipitation into dilute hydrochloric acid following polymerization gave a swollen gummy solid which dried into brittle glassy lumps. This polymer was rendered in a more manageable form by reprecipitation into either ethyl acetate or diethyl ether from a solution in methanol. The latter proved to be the better non-solvent.

2.3.4 Esterifications of MP37

The enhanced solubility of MP37 also proved troublesome in the precipitation of polymer following conversion to the ester with methacryoyl chloride in a DMF/pyridine cosolvent mixture.

Conditions which had been successful for esters of polymers with a lower acid content failed with MP37 because the products would not precipitate with the normal aqueous work-up. It was thought important to keep the conditions of the initial precipitation aqueous in nature in order to remove ionic impurities such as pyridinium hydrochloride. Aqueous conditions would also serve to hydrolyse any anhydride groups formed by the reaction of methacryloyl chloride with polymer-bound carboxylate groups which could lead to the subsequent formation of unwanted cross-links.

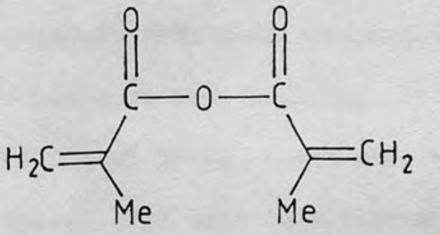
The first successful precipitation of a polymer based on MP37 was carried out using brine in the work-up step in place of some of the water. Unfortunately this polymer, MP46 was swollen by water used to wash the precipitate which made filtration very slow, and it was subsequently found to have dissolved when left in contact with the water. When this preparation was repeated (MP49) the crude material was dried over phosphorus pentoxide in a vacuum desiccator while still wet with brine. The glassy solid produced was dissolved in methanol and the solution was filtered through fine filter paper before precipitation into ether. A small quantity of *para*-benzoquinone was added to this preparation as a free-radical inhibitor in order to reduce the possibility of premature cross-linking. When these conditions were repeated in the absence of *para*-benzoquinone (MP57) an insoluble crude product was obtained. This result may not be very significant as the crude product appears prone to cross-linking if left for more than a day or two before reprecipitation. The evidence of the small number of experiments conducted does seem to suggest that the presence of an inhibitor during this conversion does give a better chance of obtaining soluble polymers. One or more reprecipitation steps using ether as the non-solvent stabilizes the polymer to long-term storage provided samples are kept in a refrigerator. Reprecipitation does however lead to a significant loss of material.

Despite having an acceptable degree of conversion to the methacrylate ester, MP49 was not an ideal polymer for imaging. Some inorganic material was still present in the polymer sample which gave a somewhat rough-looking film when coated on glass. Development with 5% aqueous sodium carbonate also was not showing acceptable differentiation between exposed and unexposed regions. At this stage it was thought that the milder conditions of using the anhydride of methacrylic acid as the reagent for the esterification might improve matters. To investigate the conditions for this proposal, model conversions were carried out using acetyl chloride and acetic anhydride, the latter both in the presence and absence of an acyl transfer agent (pyridine).

The product MP43, acylated using acetyl chloride, appeared to be almost 100% esterified by inspection of its high field proton nuclear magnetic resonance spectrum, a higher conversion than had ever been achieved using methacryloyl chloride under the same conditions. This product, derived from MP37, was insoluble in water and precipitated well in an aqueous work-up. It was soluble in DMF, slow to dissolve in methanol and soluble in an excess of 10% potassium carbonate solution. This solubility behaviour is reasonably similar to MPX25 showing our approach to be valid at least in the case of an acetylated polymer. The acetic anhydride derivatized polymer, MP45, was found to show negligible conversion in 30 minutes at ice-bath temperatures whereas when pyridine was present a moderate conversion was achieved, MP47. Double the molar quantity of acetic anhydride was used in these preparations relative to acetyl chloride.

2.3.5 Methacrylic Anhydride as Reagent

The results of the acetylations of MP37 suggest that moderate conversion to the ester may be achieved using methacrylic anhydride (52) as the reagent when similar conditions to preparations using methacryloyl chloride are employed. Higher conversions may be made possible by increasing reaction times. Methacrylic anhydride was not available commercially when these experiments were undertaken so it was prepared by the reaction of methacryloyl chloride with sodium methacrylate in refluxing ether in the presence of *para*-benzoquinone.



(52)

The initial preparation using this reagent, MP48, produced a polymer of very low conversion and in subsequent preparations reaction times of 1 and 2 hours were employed (MP50 and MP51 respectively). The excess anhydride caused some problems in the precipitation step. So much of it was left at the end of the reaction times (one molar excess was also being used) that it formed an oily layer on top of the aqueous precipitation mixture. Much of it was also found to be occluded in the gummy particles of precipitated polymer. Methacrylic anhydride is a severe lachrymator and apparently not very readily hydrolysed under the conditions of the work-up. An improvement in the precipitation step was the addition of some ether to the non-solvent mixture. This helped to extract methacrylic anhydride from the product as did washing the polymer with the same solvent following collection of the sticky solid by filtration. Reprecipitations were carried out using ether alone as the non-solvent.

Extension of the reaction time to 4 hours at 0°C or to 2 hours at room temperature both gave polymers of moderately good conversion. The 4 hour/0°C product, MP54, was different from any previous batch of esterified polymer in that it was completely soluble in 2-methoxyethanol at room temperature but dissolved in a similar quantity of methanol only on warming; cooling to room temperature caused two phases to separate.

In imaging experiments MP51 gave encouraging results although only coarse patterns were produced. It was noticed that the cross-linked portions of these images swelled considerably in the aqueous developer. MP54 gave no discernable image when 5% aqueous sodium carbonate was used as the developer. Sodium hydroxide (10%) did reveal the image however but removal of unexposed areas was incomplete and exposed areas were severely affected by swelling. It was clear that the intended cross-linking was taking place but that the aqueous developer was incapable of doing its job. Experiments with some common organic solvents arrived at mixtures containing acetone as acceptable developers for MP54 in high resolution imaging.

The conditions of MP51 were repeated in the preparations of MP56 and MP58, and those of MP54 in the preparation of MP60. This last product was used to produce gratings of 600 l mm^{-1}.

Samples prepared under the same conditions as MP60 but using MP10 and MP14 as the starting materials (MP59 and MP63 respectively) were of similarly high conversion but not as efficient at imaging as MP60 using the same conditions of development. The time for the reaction of MP37 with methacrylic anhydride was further extended to 8 and 12 hours in the preparations of MP62 and MP63. MP62 has been used to prepare gratings of 1200 l mm^{-1}.

2.4 Characterization of Polymers

The characterization of these polymers has been concerned with establishing their chemical structure. Information about composition was obtained by analysis of the nmr spectra of samples and by a titration technique. Some information about the molecular weight of products has been inferred from viscometry measurements and the molecular weight distribution has been monitored by gel-permeation chromatography.

2.4.1 Nuclear Magnetic Resonance Spectra of Copolymers

Nuclear magnetic resonance spectra of polymers may be used to make inferences about composition and structure. The sequence distribution and tacticity of methyl methacrylate-methacrylic acid copolymers[188] and the monomer ratios in butyl methacrylate-glycidyl methacrylate copolymers[189] are examples from the literature. In the copolymers of this investigation there are three monomers to be assayed and a method had to be found to isolate information about each of them from the integrals of peaks in the proton nmr spectrum. An analysis of the high-field (400MHz) spectrum of MP1 (fig. 2.1) and the structure of the copolymer (53) led to the following assignments: The peaks labelled "a" are due to the methyl and methylene protons on the polymer backbone. Since each monomer makes the same contribution to this region of the spectrum, one fifth of this integral corresponds with one proton on each of the monomer units present. The peak labelled "b" is due to the methyl group of the methyl methacrylate residues and the two peaks labelled "c", of equal intensity, are due to the hydroxyethyl methylene protons.

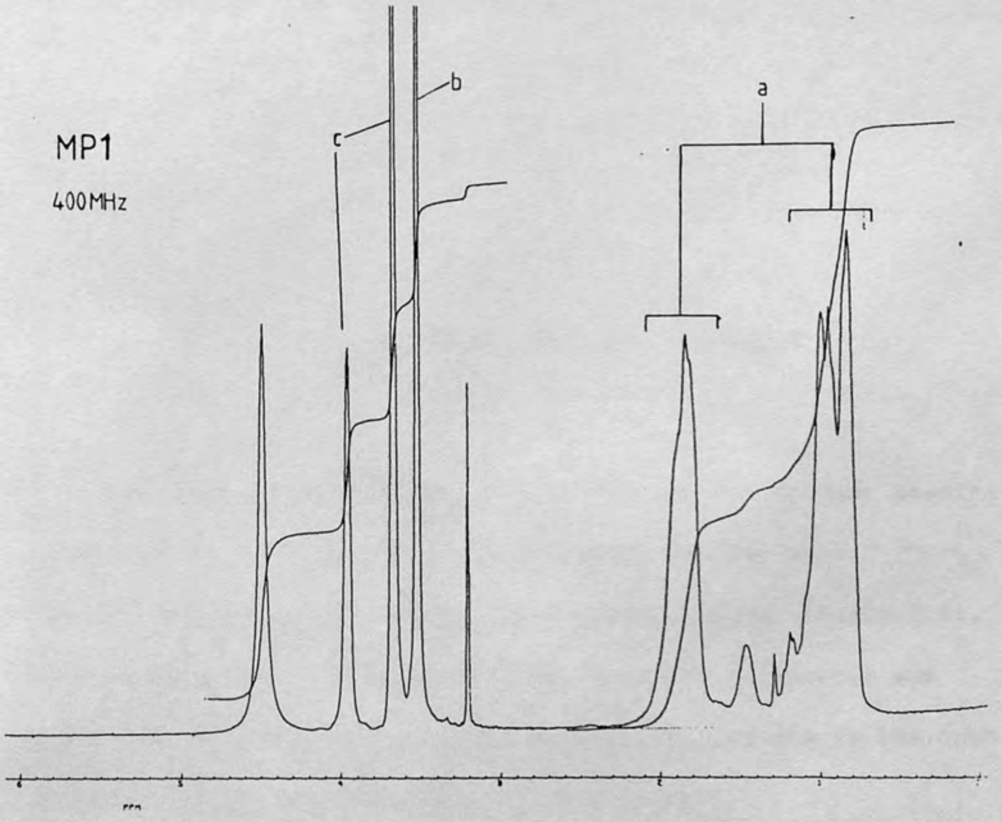
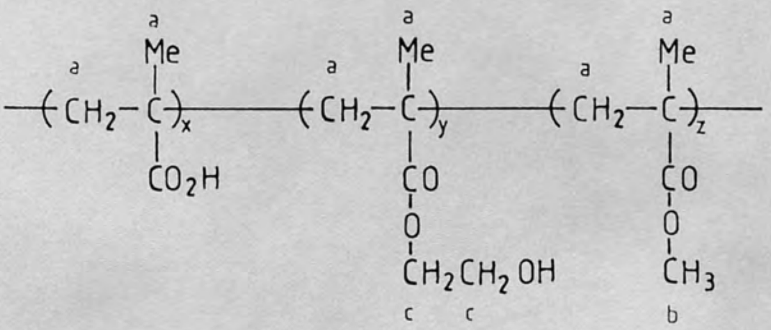


Figure 2.1 400MHz nmr Spectrum of MP1



$-(CH_2-C(Me)(CO_2H))_x-(CH_2-C(Me)(CO-O-CH_2CH_2OH))_y-(CH_2-C(Me)(CO-O-CH_3))_z-$

(53)

From these assignments equations were arrived at for the molar ratios of methyl methacrylate and hydroxyethyl methacrylate present in a sample of copolymer. The methacrylic acid content may then be calculated by difference. The equations are given below where $X_{(MAA)}$, $Y_{(HEMA)}$ and $Z_{(MMA)}$ are the mole fractions of each monomer present in the polymer and a,b and c are the integrals of the peaks designated thus in Figure 2.1:

$$Y_{(HEMA)} = \frac{5}{4} \cdot \frac{c}{a}$$

$$Z_{(MMA)} = \frac{5}{3} \cdot \frac{b}{a}$$

$$X_{(MAA)} = 1 - [Y_{(HEMA)} - Z_{(MMA)}]$$

Applying these equations to the 250 and 400 MHz nmr spectra of MP1, MP10, MP14 and MP37 gives figures for the molar compositions of these polymers as presented below, (Table 2.4). Spectra were run in deuteromethanol, dimethyl sulphoxide was tried initially but spectra were poorly resolved due to the high viscosity of polymer solutions in this solvent.

polymer	percentage compositions					
	250 MHz			400 MHz		
	MMA	MAA	HEMA	MMA	MAA	HEMA
MP1	32	13	55	30	20	50
MP10	30	21	49	27	25	48
MP14	25	25	50	25	23	52
MP37	15	27	58	12	32	56

MMA= methyl methacrylate, MAA= methacrylic acid, HEMA= hydroxyethyl methacrylate.

Table 2.4 Compositions of Copolymers Determined by High-Field nmr Spectroscopy.

It can be seen from this table (Table 2.4) that although there is general agreement between the two sets of data, discrepancies can be quite large in some instances. This is particularly true of the figure for the methacrylic acid content as errors in the calculations of the hydroxyethyl methacrylate and methyl methacrylate figures may be added, giving twice the uncertainty. Ideally spectra should be recorded several times and the mean result calculated but this would place an unreasonable demand on spectrometer time. In general more reliance will be placed on the results determined by analysis of spectra run at 400MHz as these spectra are better resolved than those run at 250MHz.

Similar calculations were performed on the spectra of the MPX series of copolymers and the results are tabulated below, (Table 2.5). It appears from these results that the methacrylic acid content of the polymers is generally lower than that of the polymerization mixtures from which they were prepared. These results should be compared to those obtained by titration, (Section 2.4.3).

polymer	250 MHz		400 MHz	
	MMA	MAA	MMA	MAA
MPX10*	85	15	90	10
MPX20	83	17	87	13
MPX25	75	25	81	19
MPX30	76	24	80	20
MPX40	59	41	66	34

MMA= methyl methacrylate, MAA= methacrylic acid, HEMA= hydroxyethyl methacrylate.
* MPX10 spectra were recorded in d_5-pyridine.

Table 2.5 Compositions of the MPX Series of Copolymers Determined by High-Field nmr Spectroscopy

2.4.2 Nuclear Magnetic Resonance Spectra of Derivatized Copolymers

A measure of the efficiency of the esterification reaction is the percentage of available hydroxyl groups which have been converted to the methacrylate ester. This quantity can also be calculated by analysis of the nmr spectra of polymers, although a knowledge of the base copolymer composition is required.

The conversion of some of the hydroxyethyl groups to the methacrylate ester produces changes in the proton nmr spectrum of the polymer, as can be seen in the spectrum of MP5 below, (Figure 2.2).

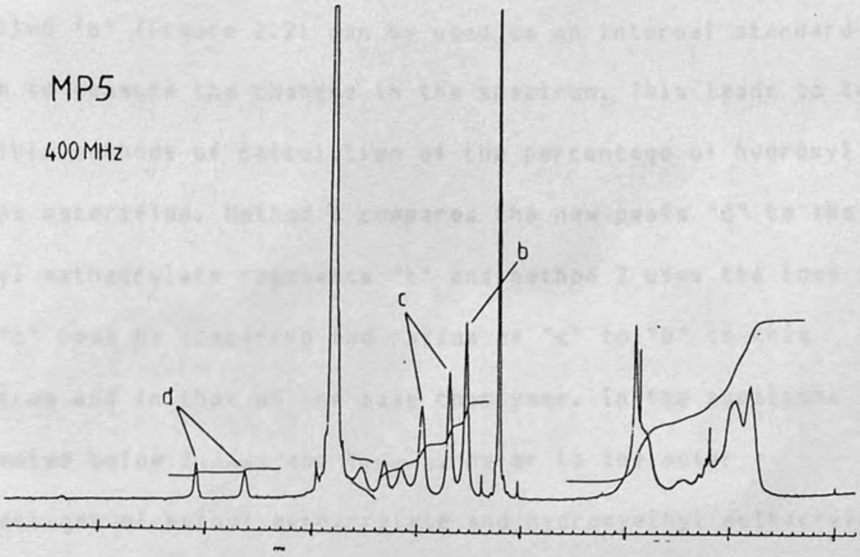
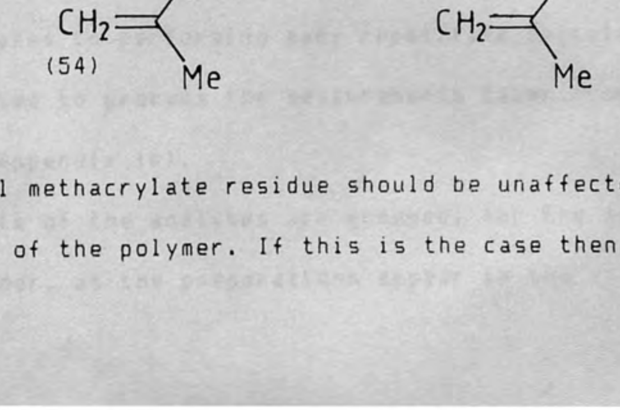


Figure 2.2 400 MHz nmr Spectrum of MP5

The principal changes seen in the spectrum are the two new peaks (labelled "d") due to the vinyl protons of the newly introduced methacrylate group, a loss in intensity of the peaks due to the unesterified hydroxyethyl methylene protons (marked "c") and the appearance of new peaks in the region between 4.0 and 5.0 ppm. The isobutyrate ester of hydroxyethyl methacrylate (54) was prepared as a model compound for part of the polymer structure in order to confirm possible assignments of these peaks.



(54)

The methyl methacrylate residue should be unaffected by derivatization of the polymer. If this is the case then the peak labelled "b" (Figure 2.2) can be used as an internal standard by which to measure the changes in the spectrum. This leads to two possible methods of calculation of the percentage of hydroxyl groups esterified. Method 1 compares the new peaks "d" to the methyl methacrylate resonance "b" and method 2 uses the loss of the "c" peak by comparing the ratios of "c" to "b" in this spectrum and in that of the base copolymer. In the equations presented below $Z_{(MMA)}$ and $Y_{(HEMA)}$ refer to the molar percentages of methyl methacrylate and hydroxyethyl methacrylate in the particular base copolymer, as previously determined by nmr and b,c and d represent the integrals of the peaks labelled thus in Figure 2.2:

Method 1

$$\%\ \text{HEMA groups esterified} = \frac{3}{2} \cdot \frac{d}{b} \cdot \frac{Z_{(MMA)}}{Y_{(HEMA)}} \times 100$$

Method 2

$$\%\ \text{HEMA groups esterified} = \frac{\dfrac{4Y_{(HEMA)}}{3Z_{(MMA)}} - \dfrac{c}{b}}{\dfrac{4Y_{(HEMA)}}{3Z_{(MMA)}}} \times 100$$

The data derived from the analysis of spectra by both methods, and at 250 and 400MHz are give in the following tables. Consistency of data has been maintained; that is 400MHz spectra have been analysed using the copolymer compositions derived from 400MHz spectra, and similarly for 250MHz spectra. To save time and avoid mistakes in performing many repetitive calculations, a computer was used to process the measurements taken from the spectra, (see Appendix 1b).

The results of the analyses are grouped, for the most part in the same order, as the preparations appear in the

Experimental Section. Where there is no entry in a table it was not possible to obtain a spectrum on that sample, generally this was because a cross-linked product was obtained.

	250 MHz		400 MHz	
polymer	method 1	method 2	method 1	method 2
MP3	22	27	21	30
MP4	44	57	37	49
MP5	33	40	33	26
MP6	42	64	42	49
MP8	38	32	31	25
MP15	45	69	48	58
MP17	41	64	39	76
MP18	21	24	21	24

Table 2.6 Estimates (by nmr) of the Percentage of -OH Groups Esterified, Initial conversions of MP1.

For this set of data (Table 2.6) agreement is generally very good between the figures arrived at by the calculation of method 1 at 250 and 400MHz for each polymer. Method 2 appears much less reliable. These figures show that despite the vigorous reagent used, methacryloyl chloride, conversions were far from quantitative, the highest being in the region of 45-48%, (MP15, method 1).

polymer	250 MHz method 1	250 MHz method 2	400 MHz method 1	400 MHz method 2
MP19	19	22	22	21
MP20	4	8	3	10
MP21	4	-6	4	-3
MP22	6	4	10	9
MP23	10	21	17	30
MP24	23	14	36	55
MP25	-	-	18	38
MP26	20	7	20	27
MP27	4	4	5	11
MP28	10	-8	7	28
MP29	16	22	17	26
MP30	7	18	10	7
MP31	9	9	10	10
MP32	9	12	10	6
MP33	22	29	24	26
MP34	-	-	38	65
MP35	-	-	44	63

Table 2.7 Estimates (by nmr) of the Percentage of -OH Groups Esterified, Dilution Studies of MP14.

These data (Table 2.7) again show that method 1 gives fairly good agreement between spectra run at 250 and 400 MHz (with the odd exception). Method 2 again proves to be unreliable, giving negative figures in some instances when conversions were low and large overestimates when conversions were high.

A comparison of the (400MHz, method 1) figures with the apparent solubility of samples of these polymers in 5% aqueous sodium carbonate solution shows that soluble polymers were produced at low conversions only, (Table 2.8). The cut-off point appears to be between 10 and 20 percent conversion, (17% may be the critical figure but there are no data between 10 and 17% to put this to the test). Determination of solubility was difficult with samples near this cut-off point, dissolution being slow, or perhaps incomplete with some swollen particles remaining.

polymer	soluble in 5% aq. sodium carbonate?	% esterification (400MHz, method 1)
MP20	yes	3
MP21	yes	4
MP27	yes	5
MP28	yes	7
MP22	yes	10
MP30	yes	10
MP31	yes	10
MP32	yes	10

Table 2.8 continued overleaf...

continued from previous page.

polymer	soluble in 5% aq. sodium carbonate?	% esterification (400MHz, method 1)
MP29	yes? (slow)	17
MP23	no	17
MP25	no	18
MP26	no	20
MP19	no	22
MP33	no	24
MP24	no	36
MP34	no	38
MP35	no	44

Table 2.8 A Comparison of the Solubility in 5% Aqueous Sodium Carbonate with the Degree of Esterification (as Determined by nmr).

The last set of data, (Table 2.9), shows the efficiency of the methacrylic anhydride reaction to be quite high, achieving conversions of 58 and 64 percent in the case of MP61 and MP62 respectively. These figures are higher than any seen using methacryloyl chloride as the acylating agent, reaction times of 8 and 12 hours were employed however.

Esterification (with methacrylic anhydride) of MP10 (giving MP59), MP14 (giving MP63) and MP37 (giving MP54 and MP60) were each carried out under the same conditions of concentration, time (4 hours) and temperature (ice-bath), although on varying scales. Degrees of conversion were similar for MP59 (35%) and

MP63 (34%) but slightly higher for the MP37 based samples MP54 (40%) and MP60 (42%). This higher conversion of MP37 based polymers may be due to the higher molar proportion of hydroxyethyl methacrylate residues in MP37 compared to MP10 and MP14 (Table 2.4, Section 2.4.1) giving a greater concentration of -OH groups in the mixture and hence a greater rate of reaction. Another factor which may be important is the conformation of the solvated polymer molecules, a tightly coiled molecule will be less accessible to bulky reagents. Viscosity is sensitive to the size of solvated polymer molecules and indeed polymers with higher acid contents have greater intrinsic viscosities, (Section 2.4.5), one possible explanation of this observation is that a less tightly coiled conformation of the solvated molecules is being adopted.

	250 MHz		400 MHz	
polymer	method 1	method 2	method 1	method 2
MP59*	45	16	35	32
MP48	7	19	16	3
MP49†	46	52	31	62
MP50	6	17	7	13
MP51	19	23	17	26
MP54	48	50	40	57
MP55	41	62	42	72
MP56	15	35	12	32

* Based on MP10. †Esterified using methacryloyl chloride.

Table 2.9 continued overleaf...

continued from previous page.

polymer	250 MHz		400 MHz	
	method 1	method 2	method 1	method 2
MP58	12	27	11	34
MP60	40	35	42	40
MP61	-	-	58	75
MP62	-	-	64	83
MP63[‡]	-	-	34	31

[‡] Based on MP14.

Table 2.9 Estimate (by nmr) of the Percentage of -OH Groups Esterified, MP37 and Methacrylic Anhydride.

With the exception of MP48, the conversion figure for which must be in doubt, a steady increase in conversion with increased reaction time can be seen, with an apparent levelling-off after the 8 hour conversion, (Table 2.10).

polymer	reaction time/h	% esterification (400MHz, method 1)	
MP48	0.5	16	
MP50	1	7	
MP51	2	17	mean 13
MP56	2	12	
MP58	2	11	

Table 2.10 continued overleaf...

continued from previous page.

polymer	reaction time/h	% esterification (400MHz, method 1)	
MP54	4	40	mean 41
MP60	4	42	
MP61	8	58	
MP62	12	64	

Table 2.10 A Comparison of the Degree of Esterification with Reaction Time for Esterifications of MP37 at 0°C Using Methacrylic Anhydride.

Such a set of data (Table 2.10) can, in principle, be used to derive kinetic information. If the kinetics of the process was the aim however, greater care would have had to have been taken in order to eliminate inconsistencies between experiments. The major variable was the reagent itself which was prepared in batches from time to time and generally contained some free methacrylic acid. Another possible influencing factor was the length of time between the initial, and second precipitation, when the last traces of reagent were removed from the product.

The spectra of the acetylated polymers, MP43, MP45 and MP47 are not amenable to quantitative analysis in the same way as the methacrylate esters. This is because the acetyl group resonance appears in the same region of the spectrum as the protons on the polymer backbone. A qualitative estimate may be arrived at by inspection, as has already been mentioned, (Section 2.3.4).

2.4.3 Determination of Free Acid Groups by Titration

The carboxylate groups of methacrylic acid residues are of prime importance to the solubility characteristics of the copolymers, particularly when considering 5% aqueous sodium carbonate as the developing agent. The determination of the molar percentage of methacrylic acid incorporated in copolymers will be subject to large errors when estimated from the nmr data as it is not measured directly but calculated by difference after determining the methyl methacrylate and hydroxyethyl methacrylate figures. A complementary analysis is therefore afforded by the direct titration of available acid groups.

Titrations were performed on samples of polymer which had been dried *in vacuo* over P_2O_5 for 24 hours before analysis. A solution in methanol was titrated with a 0.1N sodium hydroxide solution previously standardized by titration against analytical grade benzoic acid. A comparison of poly(methacrylic acid), (MP12), titrated as solutions in both water and methanol gave identical results, showing that methanol is a valid solvent for the titration of polymers. The results, tabulated below, (Tables 2.11 and 2.12) were the mean of four titrations in each case, corrected for a blank titre, and expressed as moles of $-CO_2H$ per gram of polymer.

polymer	moles of $-CO_2H$ per gram
MP1	1.570×10^{-3}
MP10	1.650×10^{-3}
MP14	2.075×10^{-3}
MP37	2.964×10^{-3}

Table 2.11 Results for the Titration of Copolymers

polymer	moles of $-CO_2H$ per gram
MPX20	1.835×10^{-3}
MPX25	2.327×10^{-3}
MPX30*	2.872×10^{-3}
MPX40*	3.793×10^{-3}

*Samples not re-dried before titration.

Table 2.12 Results for the Titration of the MPX Copolymers

The result for poly(methacrylic acid) was 1.101×10^{-2} mol g^{-1}. MPX10 was insoluble in methanol therefore titration analysis was not attempted on this product.

2.4.4 Comparison of Results

The estimate of the acid content of polymers determined by the analysis of nmr data may be compared with the figure obtained by titration by converting it to the same units. Good quantitative agreement is not expected for the reasons already given, but the figures should be in step with each other, (Table 2.13). It would also be possible to convert the titration figure to the molar percentage of methacrylic acid present in the polymer. This has been done for the MPX series of copolymers but not for the terpolymers as assumptions have to be made about the molar percentages of the other two monomers to do this. Figures are based on the analysis of 400MHz nmr spectra.

polymer	moles $-CO_2H$ g^{-1}		molar percentage of methacrylic acid	
	titration	calc.(nmr)	nmr	titration
MP1	1.570×10^{-3}	1.781×10^{-3}	20	
MP10	1.650×10^{-3}	2.252×10^{-3}	25	
MP14	2.075×10^{-3}	2.044×10^{-3}	23	
MP37	2.964×10^{-3}	2.846×10^{-3}	32	
MPX20	1.835×10^{-3}	1.323×10^{-3}	13	18
MPX25	2.327×10^{-3}	1.950×10^{-3}	19	23
MPX30	2.872×10^{-3}	2.055×10^{-3}	20	28
MPX40	3.793×19^{-3}	3.566×10^{-3}	34	36

Table 2.13 A Comparison of the Methacrylic Acid Content of Copolymers as Determined by Titration and nmr.

Inspection of this table (Table 2.13) shows a tendency to underestimate the methacrylic acid content in the nmr analysis of the MPX series of copolymers, as determined by titration. The situation is not so clear with the terpolymers, giving underestimates in some cases and overestimates in others, but the general agreement is fairly good except in the case of MP10.

As well as chemical and spectroscopic analysis, samples were subjected to (combustion) micro-analysis. The results for the copolymer series are compared with the figures predicted by the nmr derived compositions in the following table (Table 2.14).

polymer	experimental/% (micro-analysis)		calculated (nmr)	
	C	H	C	H
MP1	54.62	7.65	56.67	7.72
MP10	54.02	7.91	56.58	7.68
MP14	53.97	7.80	56.48	7.69
MP37	52.68	7.31	55.97	7.60
MPX10	58.59	7.92	59.62	7.96
MPX20	57.99	7.87	59.51	7.94
MPX25	57.17	7.72	59.28	7.88
MPX30	57.06	7.59	59.25	7.87
MPX40	56.14	7.57	58.70	7.74

Table 2.14 A Comparison of Experimentally Determined and Calculated Atomic Percentages of Copolymers.

The table above (Table 2.14) shows that the micro-analysis data tend to be on the low side but generally keep in step with the calculated figures. This may be due in part to the difficulty of getting polymer samples completely dry.

2.4.5 Viscosity Measurements[170]

The viscosity of a polymer solution is dependent on a number of factors: temperature, the nature of the solvent, concentration, the nature of the solute and its molecular weight. For any given polymer, all other conditions being constant, a relationship exists between the polymer molecular weight (M) and the intrinsic viscosity $[\eta]$ which may be expressed in the Mark-Houwink equation:

$$[\eta] = KM^{\alpha}$$

$$\text{or} \quad \log[\eta] = \log K + \alpha \log M$$

The constants K and α are determined experimentally from the slope and intercept of a plot of log (viscosity) against log M for a series of samples of known molecular weight. When such a relationship has been established the molecular weight of an unknown sample can be determined by a single viscosity measurement.

The viscosity is not a direct gauge of molecular weight, but is sensitive to the effective size of the solvated polymer molecules in solution. For this reason, only polymers with regular structures can be analysed in this way to give quantitative information. For copolymers, composition is an added variable making accurate calibration impossible. Qualitative results may still be obtained however.

The intrinsic viscosities of our polymers were determined as solutions in 2-methoxyethanol using a capillary viscometer. This was suspended in a water-bath at 25°C ± 0.2°C. Up to four solutions of differing concentrations were prepared by dilution of a single stock solution, additional dilutions being made in the viscometer. The highest concentration used was about 4% wt/v. The time taken for a constant volume of solution to pass through the capillary was measured, the mean of three runs being taken for each concentration. It must be mentioned that take-up of atmospheric moisture by polar solvents can be a source of error in viscometry measurements and in order to minimize this, freshly dried and redistilled solvent was used.

The results were treated as follows: the relative viscosity, η_r, at any particular concentration is given by:

$$\eta_r = \frac{t}{t_o} \cdot \frac{\rho}{\rho_o}$$

where t is the measured flow time, t_o is the flow time for pure solvent and ρ and ρ_o are the densities of solution and solvent. For dilute solutions $\rho/\rho_o \simeq 1$ and this term is ignored. A more convenient form is the specific viscosity, η_{sp}, given by:

$$\eta_{sp} = (\eta_r - 1) = \frac{(t - t_o)}{t_o}$$

The ratio η_{sp}/c, where c is the weight concentration of the polymer solution, is termed the viscosity number or reduced viscosity. The general form of the dependance of this quantity with concentration is a power series:

$$(\eta_{sp}/c) = [\eta] + \alpha c + \beta c^2 + \ldots\ldots$$

where $[\eta]$ is the limiting viscosity number or intrinsic viscosity of the Mark-Houwink eqation above. A semi-empirical equation, the Huggins equation, may be used to fit the experimental data, extrapolating to infinite dilution to find a value for $[\eta]$. The form of the Huggins equation is:

$$(\eta_{sp}/c) = [\eta] + k[\eta]^2c$$

It is general practice to plot a second set of data in accordance with the Kraemer equation:

$$(\ln \eta_r)/c = [\eta] + k'[\eta]^2c$$

Both plots should have a common intercept at $[\eta]$ and the figures quoted below are the mean of these two values. A computer best-fit method was used to treat the results, (see Appendix 2). The mean intrinsic viscosities of our copolymers are given below, (Table 2.15). MPX10 was not analysed by this method as it was not soluble in the solvent used.

polymer	$[\eta]$ / dl g^{-1}	No. of data points
MP1	0.178	6
MP10	0.180	6
MP14	0.214	6
MP37	0.220	7
MPX20	0.119	7
MPX25	0.133	6
MPX30	0.139	11
MPX40	0.152	12

Table 2.15 Mean Intrinsic Viscosities of Copolymers

The information that can be gleaned from these figures is limited. Results are, however, consistent within each of the copolymer series and are all of roughly the same order. In both series there is an increase in the viscosity as the percentage of methacrylic acid in the polymerization mixture is increased. This could be due to either a higher molecular weight product being formed in mixtures richer in methacrylic acid or polymer molecules of similar size with a higher proportion of acid groups having a larger effective radius in solution, the latter being due to solvation effects.

The molecular weights of these polymers are probably quite low, typically between 20,000 to 30,000 for an intrinsic viscosity of 0.1-0.2.[191] Low molecular weight polymers are required if the resolution of photopolymer images is not to suffer. Molecular weights of this magnitude were deemed to be acceptable for this application.

2.4.6 Gel-Permeation Chromatography[192]

Gel-permeation chromatography (g.p.c or non-aqueous size-exclusion chromatography) is another technique sensitive to the physical dimensions of polymer molecules in solution. The information it supplies complements that obtained by other means of molecular weight determination. The stationary phase used in g.p.c. consists of beads of an inert material, for example silica, the surfaces of which show features such as channels or pits of similar dimensions to solvated polymer molecules.

Polymer molecules dissolved in the mobile phase diffuse in and out of these surface pores and are therefore retarded in their passage through the column. Those molecules too large to fit in any of the pores are totally excluded and are eluted first. The distribution of pore sizes ensures that large molecules will fit into relatively few pores and will be eluted with short retention times. Smaller molecules will be retarded by the same pores as the large molecules and also by smaller pores into which it will fit, therefore their retention times will be greater. In this way a plot of molecular weight distribution can be obtained, although in the resulting chromatograph (Figure 2.3 for example) increasing molecular weight runs from right to left rather than left to right.

A uniform and narrow distribution of molecular weights is required of polymers for use in a photoimaging context for optimum development. Analyses of our polymers were carried out on solutions in THF and all show a single narrow distribution of molecular weight. A refractive index detector was used on a standard HPLC set-up to record the chromatographs. The trace recorded for MP14 is shown below, (Figure 2.3). Polymers analysed by this technique were MPX10, 20, 25, 30 and 40, MP1, 10, 14 and 37 and the derivatized polymers MP59, 60, 62 and 63.

The technique is, in principle, quantitative, calibrations being made with monodisperse polystyrene standards of known molecular weight. Similar problems of calibration arise when analysing copolymers as were discussed in the previous section on viscometry.

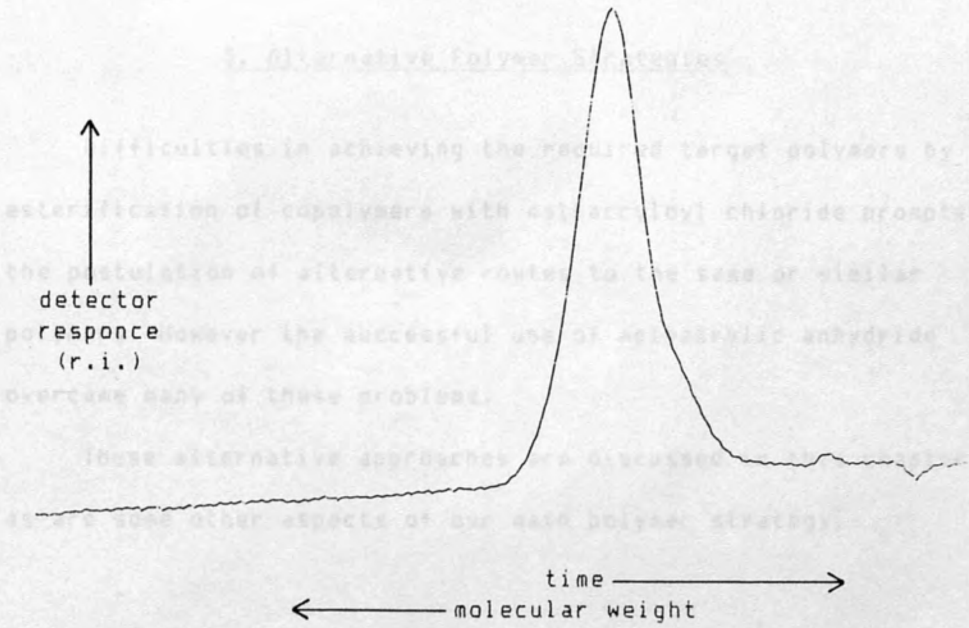


Figure 2.3 Gel-Permeation Chromatograph of MP14

3. Alternative Polymer Strategies

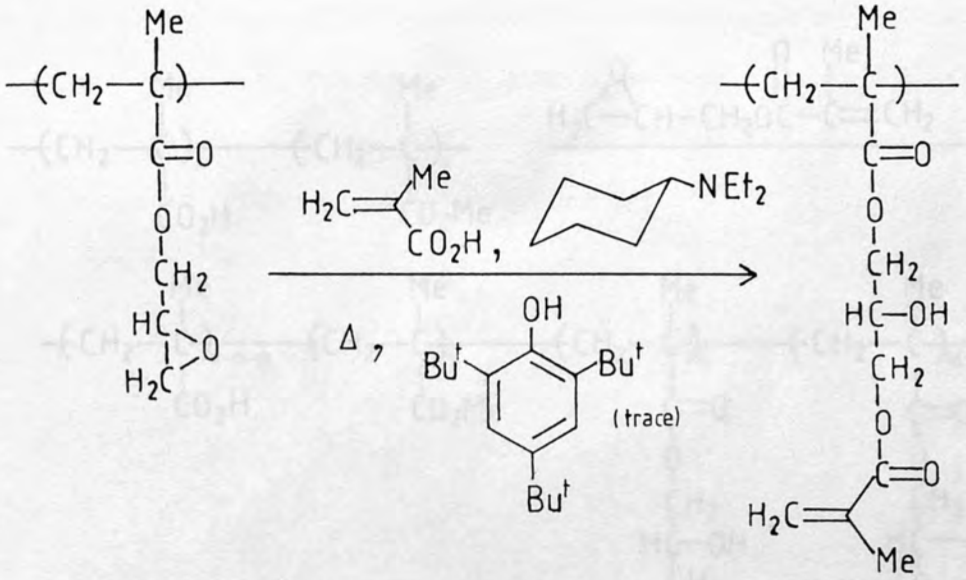
Difficulties in achieving the required target polymers by esterification of copolymers with methacryloyl chloride prompted the postulation of alternative routes to the same or similar polymers. However the successful use of methacrylic anhydride overcame many of these problems.

These alternative approaches are discussed in this chapter, as are some other aspects of our main polymer strategy.

3.1 Other Routes to the Target Polymers

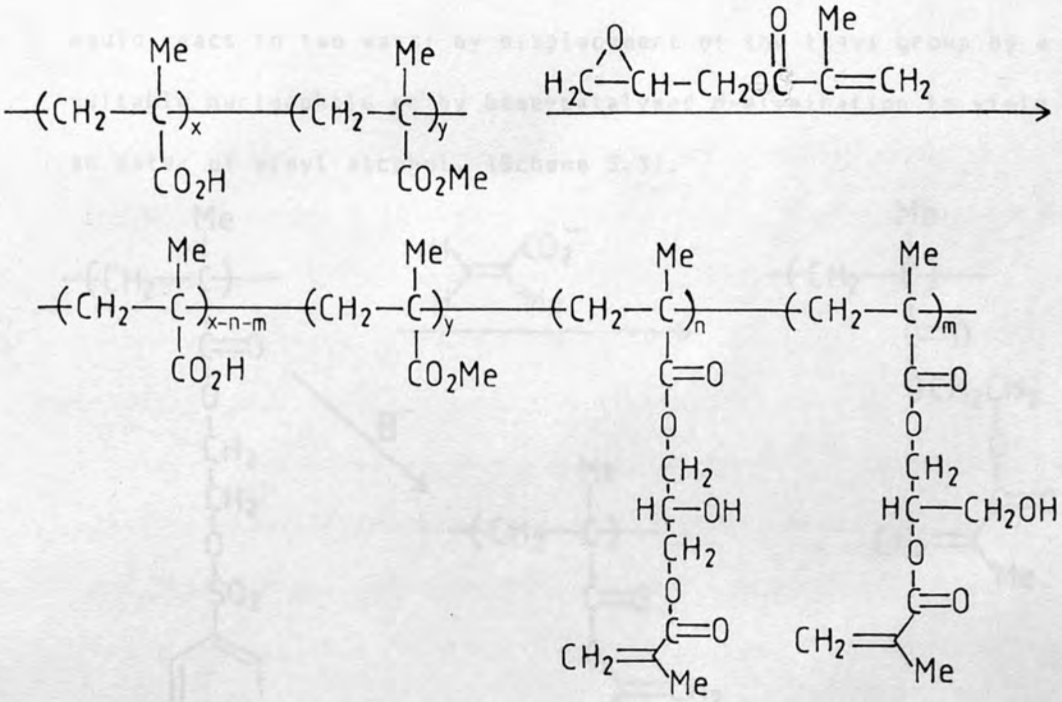
Polymers with similar cross-linkable functionality to our target structures have been prepared by workers at Kodak. In their studies copolymers of hydroxyethyl methacrylate were esterified with acryloyl or methacryloyl chloride in 1,2-dichloroethane using triethylamine as the acyl transfer agent.[118,193-195] It has not been possible to utilize this method with our polymers however as they are not completely soluble in suitable chlorinated solvents.

Methacrylate ester functionality may also be introduced by refluxing a glycidyl methacrylate copolymer with methacrylic acid in the presence of a base and a suitable inhibitor,[189] (Scheme 3.1). Under these conditions conversions were practically quantitative after 17 hours at 80°C. This method cannot be used with methacrylic acid copolymers however as this would lead to cross-linked products.



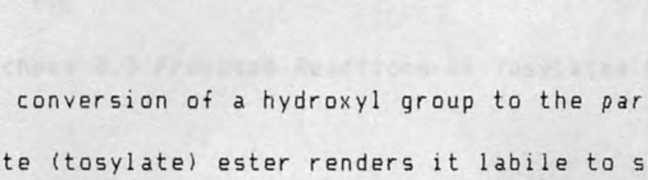
Scheme 3.1 Reaction of Glycidyl Methacrylate Copolymers with Methacrylic Acid.

This problem may be circumvented by reversing the reaction sequence; that is by the reaction of a methacrylic acid copolymer with glycidyl methacrylate monomer. Polymers of this type similar to fully esterified MP37 could be prepared, in principle, by reacting an 87:13, methacrylic acid-methyl methacrylate copolymer with one-half equivalent of glycidyl methacrylate, (Scheme 3.2). Such polymers would differ from fully esterified MP37 in the nature of the ester link to the polymer backbone. This would be a trihydroxypropyl ester rather than an ester derived from ethylene glycol. The epoxide ring of the glycidyl methacrylate would be subject to attack at two positions and two isomeric polymer-bound esters would be expected.



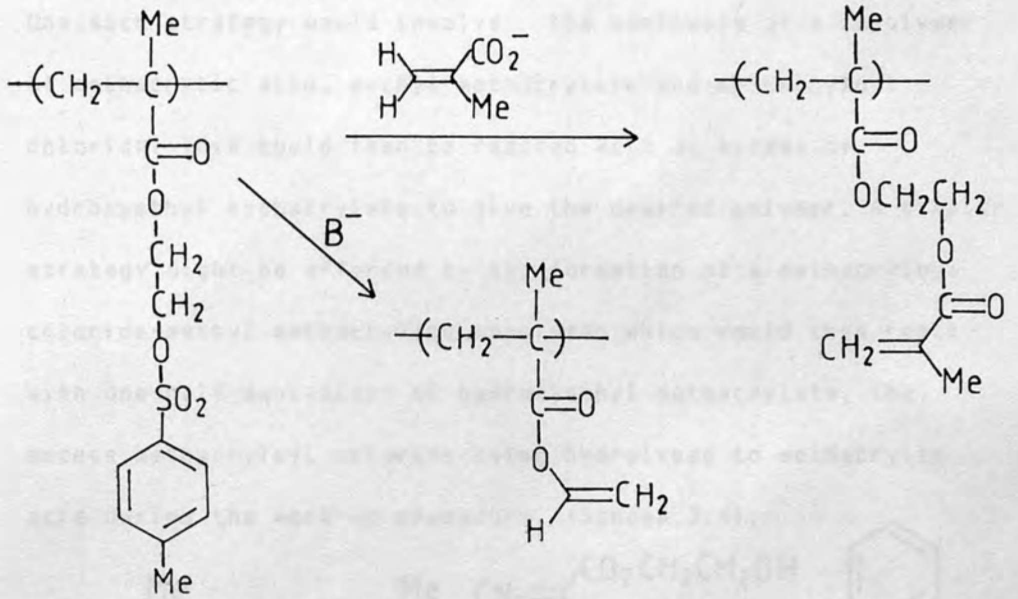
Scheme 3.2 The Reaction of a Methacrylic Acid-Methyl Methacrylate Copolymer with Glycidyl Methacrylate.

The conversion of a hydroxyl group to the *para*-toluenesulphonate (tosylate) ester renders it labile to substitution by nucleophiles. Such a reaction sequence offers an alternative method of attaching functionality to a copolymer. Tosylated polymers may be formed either by reacting hydroxyethyl methacrylate copolymers with *para*-toluenesulphonyl chloride or by polymerization of a tosylated monomer. This latter method was chosen for investigation and the tosylate ester of 2-hydroxyethyl methacrylate (55) was prepared.



(55)

This compound was polymerized under the same conditions as MP37, replacing the hydroxyethyl methacrylate in the polymerization mixture. It was hoped that this polymer, MP39, would react in two ways: by displacement of the tosyl group by a suitable nucleophile or by base-catalysed β-elimination to yield an ester of vinyl alcohol, (Scheme 3.3).

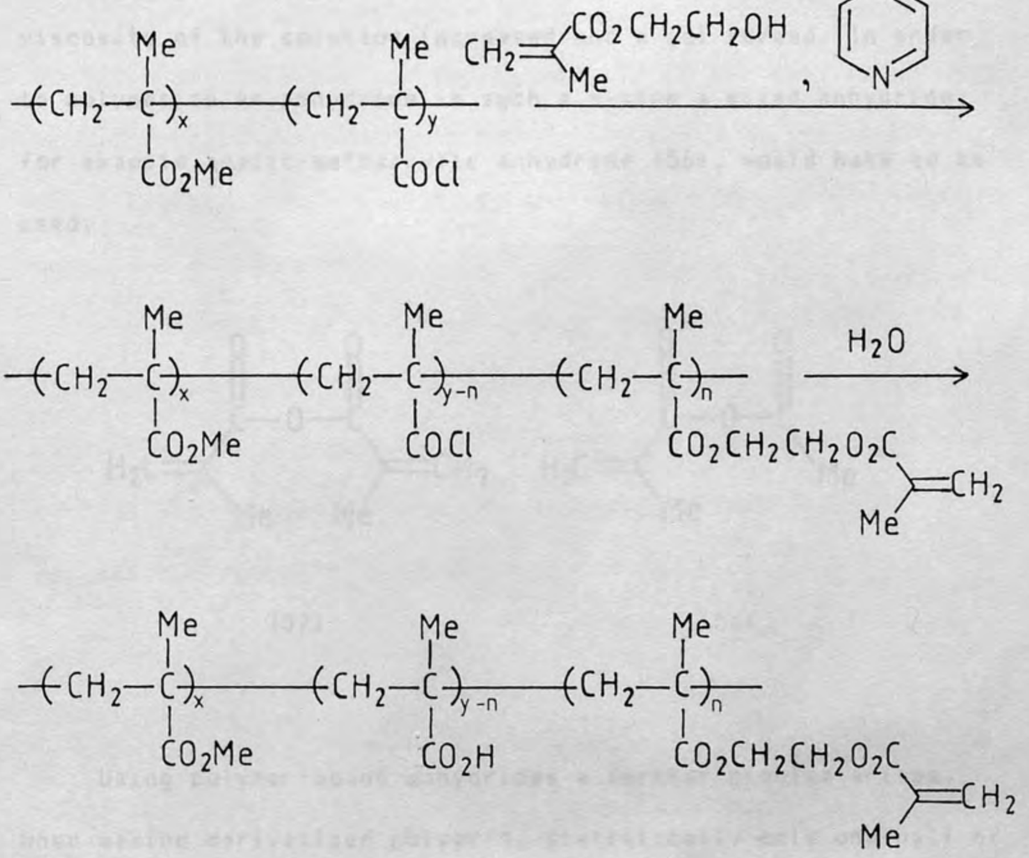


Scheme 3.3 Proposed Reactions of Tosylated Polymer.

Samples of this polymer were warmed with potassium carbonate in methanol and with sodium acetate in DMF in separate experiments. Very little change was detected in the product after heating with potassium carbonate for 5 hours. An insoluble product was obtained in the sodium acetate experiment. In both instances a competing pathway would have been displacement of tosyl by polymer-bound carboxyl groups. This may account for the cross-linked product found in the sodium acetate reaction.

The proton nmr spectrum of MP39 shows that some tosyl groups had been displaced by solvent residues during the polymerization reaction. The extra resonances in the spectrum prevented its analysis for the composition of this polymer in the same way as MP1 and copolymers of that sort. After long-term storage at room temperature MP39 was found to be insoluble in a range of organic solvents including DMF, THF and methanol indicating that it had cross-linked.

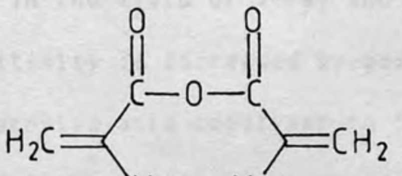
Other proposed routes to the target polymers involved polymerization of the reactive monomer methacryloyl chloride. One such strategy would involve the synthesis of a copolymer of methacrylic acid, methyl methacrylate and methacryloyl chloride. This could then be reacted with an excess of hydroxyethyl methacrylate to give the desired polymer. A simpler strategy might be afforded by the formation of a methacryloyl chloride-methyl methacrylate copolymer which would then react with one-half equivalent of hydroxyethyl methacrylate, the excess methacryloyl chloride being hydrolysed to methacrylic acid during the work-up procedure, (Scheme 3.4).



Scheme 3.4 The Formation of the Target Polymers via Methacryloyl Chloride Copolymers.

Polymerization of methacryloyl chloride would have to be carried out in a glove-box containing an inert atmosphere to exclude moisture. In addition inert solvents would have to be used. Storage of such a material would also be limited by its sensitivity to moisture. It might however be possible to carry out the derivatization step immediately following polymerization without isolation of the product.

Methacrylic anhydride (52) could not be used in place of the acyl chloride in polymerizations of this type as cross-linked polymers would be produced. Although the cross-links would be broken in the derivatization step, the formation of a cross-linked product in a solution polymerization would interfere with the progress of the reaction as the viscosity of the solution increased and a gel formed. In order to polymerize an anhydride in such a system a mixed anhydride, for example acetic-methacrylic anhydride (56), would have to be used.



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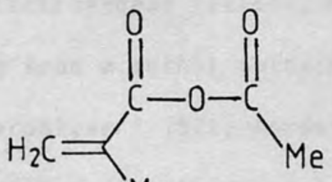
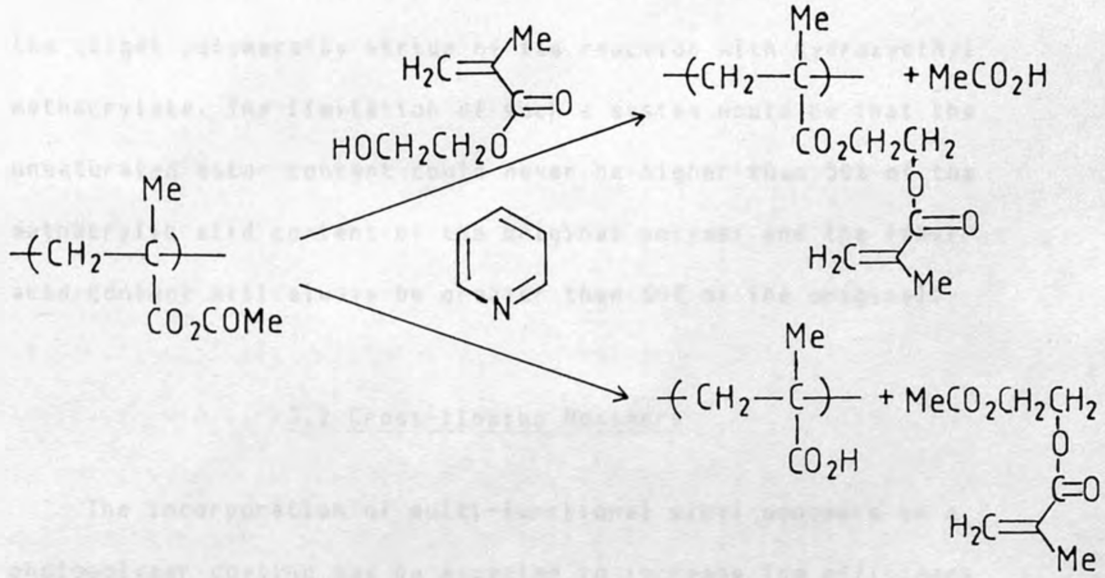


(56)

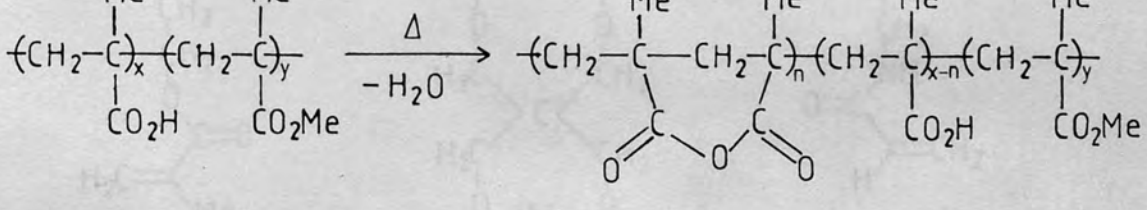
Using polymer-bound anhydrides a further problem arises. When making derivatized polymers, statistically only one-half of the anhydride groups will be converted to polymer-bound ester, the other half being converted to polymer-bound acid and free ester, (Scheme 3.5).



Scheme 3.5 Reactions of Polymer-Bound Anhydride with Hydroxyethyl Methacrylate.

An attempt to synthesize the mixed anhydride (56) from methacryloyl chloride and sodium acetate in the same manner as methacrylic anhydride gave a poorly fractionating product on distillation. This proved to be a mixture of anhydrides with some acid also present.

In the field of X-ray and electron-beam resists, radiation sensitivity is increased by going from a methyl methacrylate-methacrylic acid copolymer to "terpolymer" (57), formed by partial dehydration with the formation of intramolecular anhydride groups,[196] (Scheme 3.6).



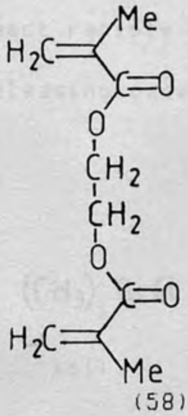
(57)

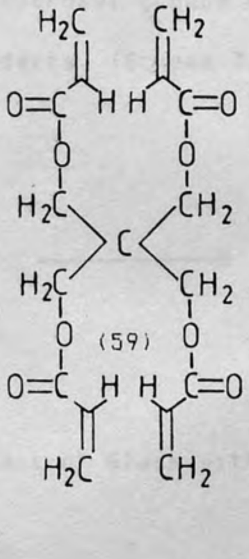
Scheme 3.6 The Formation of "Terpolymer"

Such a polymer could provide the basis of another route to the target polymers by virtue of its reaction with hydroxyethyl methacrylate. The limitation of such a system would be that the unsaturated ester content could never be higher than 50% of the methacrylic acid content of the original polymer and the final acid content will always be greater than 50% of the original.

3.2 Cross-linking Monomers

The incorporation of multi-functional vinyl monomers in a photopolymer coating may be expected to increase the efficiency of polymerization of vinyl substituted polymers. The increased efficiency will be due to the higher concentration of polymerizable groups within the coating, the greater mobility of the low molecular weight materials and the consequent increased probability of cross-link formation. This should result in greater sensitivity of coated layers under identical conditions of initiation. An enhancement of development may also result. Commonly used "cross-linkers" of this type include unsaturated esters of polyols such as ethylene glycol dimethacrylate[48,65] (58) and pentaerythritol tetraacrylate[115,118] (59) and amides such as *N,N'*-methylene-*bis*-acrylamide[44,47,50] (60).


(58)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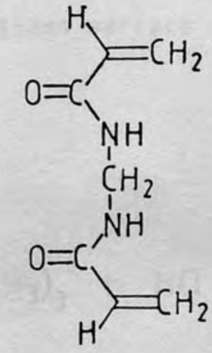
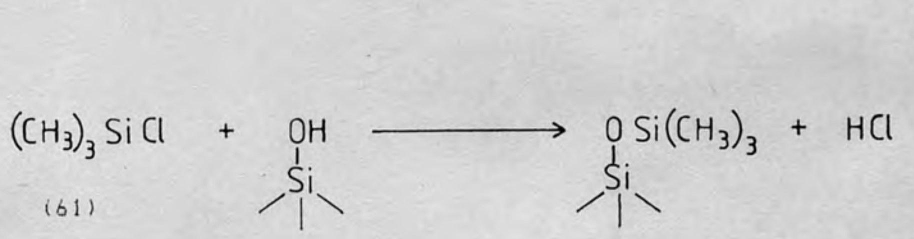

(60)

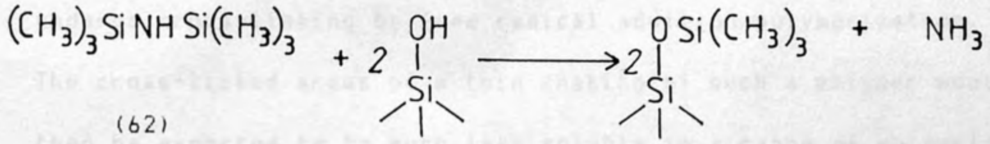
Ethylene glycol dimethacrylate was incorporated in a coating of MP51 sensitized with PATM. This resulted in a soft coating, the monomer being an oily liquid. An increase in photosensitivity of the coating was noted in this experiment although the tacky coating made this formulation impracticable. The use of very low concentrations of liquid cross-linkers may avoid this problem but for a photoresist application a tough layer is necessary and solid cross-linking agents, provided they do not crystallize in a coating, would be preferable. *N,N'*-methylene-*bis*-acrylamide is such a solid but incorporation of this monomer in a coating appeared to desensitize the same polymer using PATM as initiator.

3.3 Substrate Pre-treatment

It was considered at one point that the problems encountered with the aqueous development of polymer images might be due to a lifting-off of cross-linked polymer from the glass substrate because of inadequate adhesion. Adhesion promoters for glass substrates are generally trimethylsilylating agents. Both chlorotrimethylsilane (61) and 1,1,1,3,3,3-hexamethyldisilazane (62) can be used for this purpose. Both are volatile liquids and react rapidly with free hydroxyl groups on the glass surface releasing gaseous by-products, (Scheme 3.7).



Scheme 3.7a Pre-treatment of Glass with Chlorotrimethylsilane



$$(CH_3)_3SiNHSi(CH_3)_3 + 2\,\overset{OH}{\underset{|}{Si}} \longrightarrow 2\,\overset{OSi(CH_3)_3}{\underset{|}{Si}} + NH_3$$

(62)

Scheme 3.7b Pre-treatment of Glass with 1,1,1,3,3,3-Hexamethyldisilazane

Chlorotrimethylsilane was used to pre-treat glass substrates, previously cleaned with acetone and alcohol, in some experiments using aqueously developed polymers. No noticable increase in the quality of polymer images was seen in these experiments.

A second method of promoting adhesion to glass substrates is the use of a "subbing" layer cast from an aqueous latex. A sample of such a latex, FX 1/1, provided by Ilford Ltd., was spin-coated onto glass substrates before coating with polymer. The latex layer was patchy and had a milky appearance and was considered unsuitable for this application where layers with good optical qualities are required.

4 The Photocross-Linking of Polymers

The methacrylate copolymers described in Chapter 2 should undergo cross-linking by free radical addition polymerization. The cross-linked areas of a thin coating of such a polymer would then be expected to be much less soluble in a range of solvents than the uncross-linked regions. The addition of a suitable free radical photoinitiator to the solution of polymer prior to coating would therefore be expected to cause such a coating to behave as a negative photoresist.

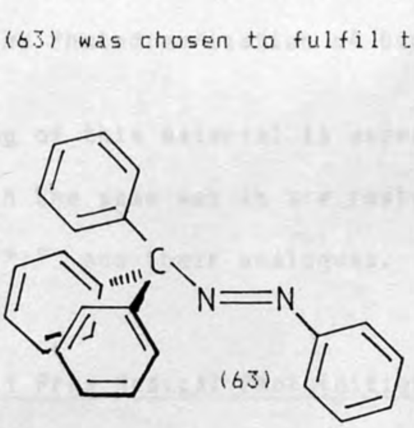
The intention of this work is to develop a photoresist capable of producing images using red (633nm, helium-neon) laser irradiation. Red-sensitivity presents problems when handling the materials; it may not be possible to use a form of safe-lighting and working in complete darkness may be necessary.

The methods by which free radicals may be generated using red light is limited by the photon energies available at these wavelengths, (Table 4.1) compared to the short wavelengths generally considered in organic photochemistry.

wavelength/nm	photon energy	
	eV	kJ mol^{-1}
400	3.10	299
500	2.48	239
600	2.07	199
633	1.96	189
700	1.77	171

Table 4.1 Photon Energies of Visible Light

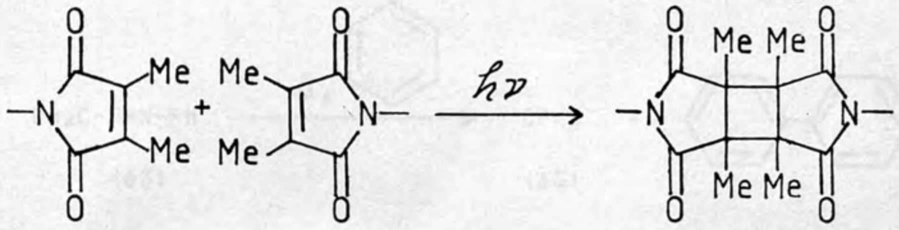
The initiator system for red-sensitive imaging was therefore the last step in the development of the photoresist system and would follow on from the production of a successful polymer system. This meant that testing of the imaging properties of new polymer batches, as they were produced, would require a model initiator of some kind. Phenylazotriphenylmethane (PATM), (63) was chosen to fulfil this role.



(63)

A range of compounds and combinations of compounds were tested for their ability to generate free radicals in a series of qualitative experiments. These involved exposure of solutions of a derivatized polymer, (MP59), containing the possible initiator, to white light. In other experiments tubes containing solutions of acrylamide in 2-methoxyethanol or acrylamide and *N,N'*-methylene-*bis*-acrylamide in water were used. Some promising initiator combinations were also tested with red laser radiation to establish their efficacy as photoinitiators at 633nm and at sensitizing polymer films.

In addition to tests with free radical initiators, a number of compounds were tested for their ability to sensitize the cross-linking of the Ciba-Geigy photopolymer Mü 1771/2316,[197] the photoactive group present in which is a dimethylmaleimide (64) which cross-links by a [2+2] photocycloaddition, (Scheme 4.1).



(64)

Scheme 4.1 The Photodimerization of Dimethylmaleimides

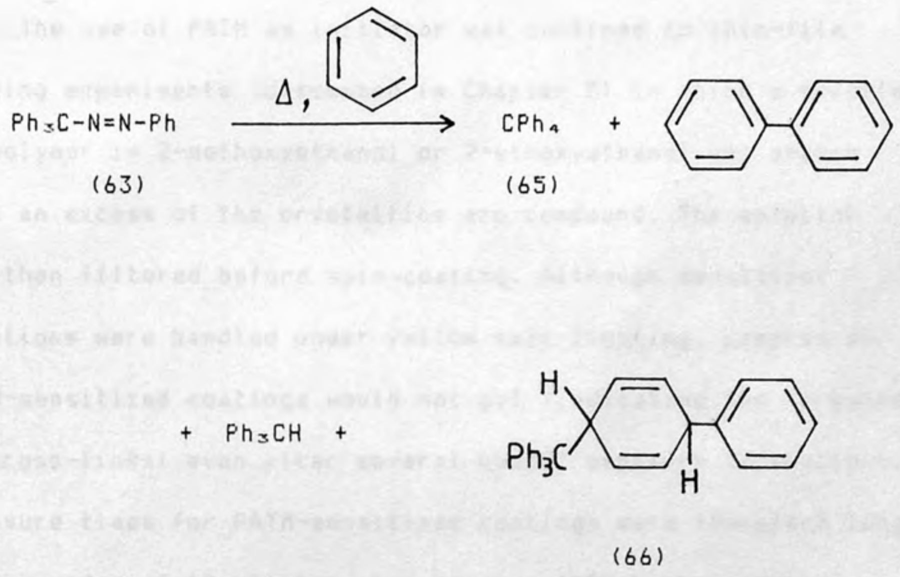
Cross-linking of this material is expected to be triplet-sensitized in much the same way as are resists based on cinnamate esters[98,99] and their analogues.

4.1 Free Radical Photoinitiators

Free radical photoinitiators which have been investigated include phenylazotriphenylmethane (PATM), some aryl diketones and a range of photo-redox initiators.

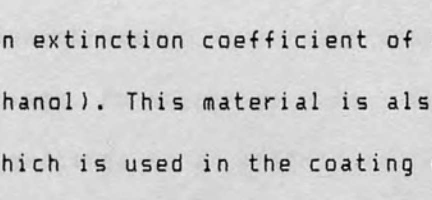
4.1.1 Phenylazotriphenylmethane (PATM) as Initiator

Phenylazotriphenylmethane (PATM), (63), decomposes thermally or photochemically to molecular nitrogen, phenyl radical and triphenylmethyl radical. The thermal fragmentation of PATM has been studied for many years and was originally reported by Gomberg[198-200] as a route to tetraphenylmethane (65). Tetraphenylmethane is also formed in very small amounts when PATM is decomposed in boiling benzene, other products being biphenyl, triphenylmethane and two isomeric 1,4-dihydro-4-tritylbiphenyls (66),[201,202] (Scheme 4.2).



Scheme 4.2 The Thermal Decomposition of PATM in Benzene

The photochemical decomposition of PATM may be accomplished by ultra-violet irradiation[182] or by exposure to light at the violet end of the visible spectrum,[185] the compound having a weak band in its absorption spectrum centred at 420nm (ε_{max} 204 M^{-1} cm^{-1}).[182] Among analogues of PATM described in the literature is the *para*-nitro compound,[203] (p-NAT), (67). The thermal decomposition of this compound has also been extensively studied.[203,204] The absorption spectrum of p-NAT shows a band at 436nm with an extinction coefficient of 339 M^{-1} cm^{-1} (in 2-methoxyethanol). This material is also more soluble in this solvent, which is used in the coating experiments, than the unsubstituted PATM.



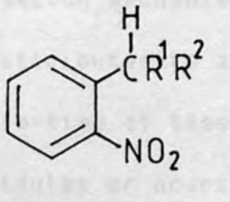
(67)

The use of PATM as initiator was confined to thin-film imaging experiments (discussed in Chapter 5) in which a solution of polymer in 2-methoxyethanol or 2-ethoxyethanol was shaken with an excess of the crystalline azo compound. The solution was then filtered before spin-coating. Although sensitized solutions were handled under yellow safe-lighting, samples of PATM-sensitized coatings would not gel (indicating the formation of cross-links) even after several hours' exposure to sunlight. Exposure times for PATM-sensitized coatings were therefore long, of the order of 60 minutes when using a 100W high-pressure mercury vapour lamp as the light source.

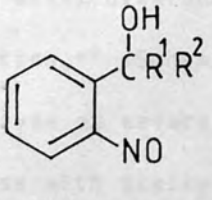
A solution of PATM in 2-methoxyethanol, prepared in the same way as the sensitized polymer solutions, by shaking with the azo compound, was determined by uv/visible spectroscopy to be 4.5 x 10^{-3} Molar.

Coatings sensitized with p-NAT, otherwise similar to PATM-sensitized coatings, including the polymer sample used, were much less effective at cross-linking the resist despite being present at a greater concentration and the higher molar extinction coefficient of the nitro compound. The same effect was seen when monochromatic (laser) irradiation was used to expose the coatings. An argon ion laser, operating at 458nm, was used to record gratings by an interferometric method (see Section 8.2.2). In these experiments, despite the absorption band of p-NAT at 436nm being closer to the irradiating wavelength than that of PATM at 420nm, PATM was still the better initiator.

The thermal decomposition of p-NAT[204,205] proceeds at a rate comparable to that of PATM so it is quite likely that the photochemical decomposition is also as facile. The explanation for the poor performance of p-NAT as an initiator maybe that it is also acting as an inhibitor of free radical polymerization, as is seen with aromatic nitro compounds.[206] An example of free radical polymerization proceeding in the presence of an aromatic nitro compound has, however been cited in the Introduction, (Section 1.5.3). In this instance polymerization proceeds in the presence of (68) but is inhibited by the nitroso compound (69) produced by the ultra-violet photolysis of (68).[21] Steric factors, or the rigorous exclusion of oxygen may be important in this case.



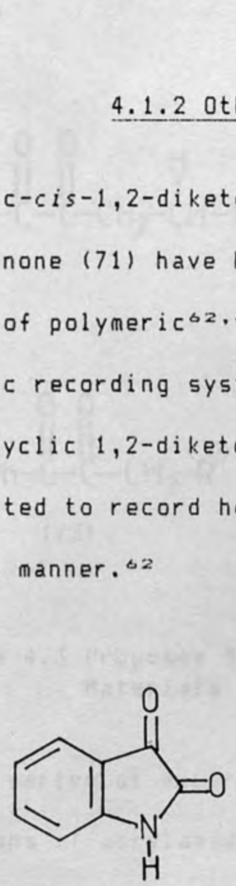
(68)



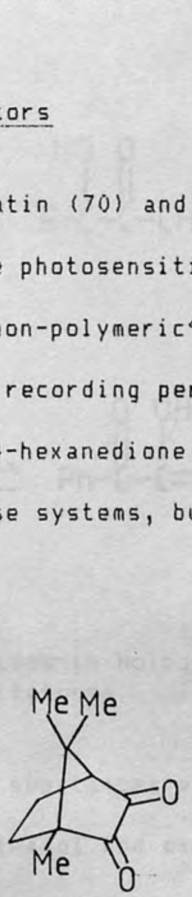
(69)

4.1.2 Other Photoinitiators

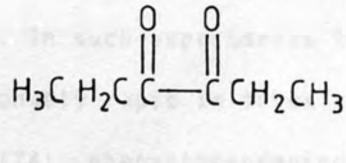
Cyclic-*cis*-1,2-diketones such as isatin (70) and camphorquinone (71) have been used as the photosensitive component of polymeric[62,63,207,208] and non-polymeric[64] holographic recording systems, generally recording permanent images. Acyclic 1,2-diketones such as 3,4-hexanedione (72) are also reported to record holograms in these systems, but in a reversible manner.[62]



(70)



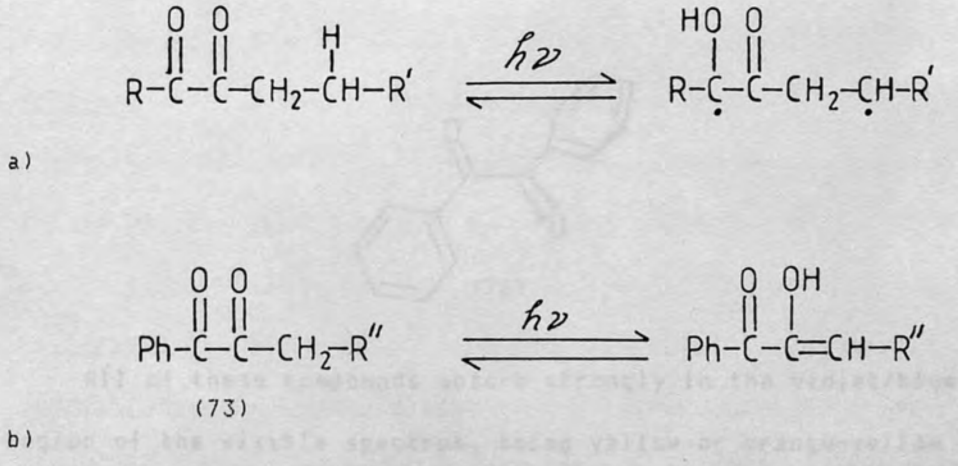
(71)



$H_3CH_2C\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_2CH_3$

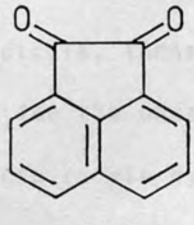
(72)

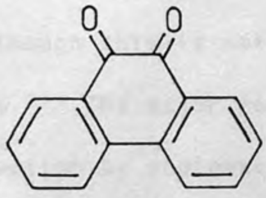
It was suggested that the mechanism of reversible hologram formation when dialkyl diketones such as (72) were used is an intramolecular hydrogen abstraction process,[62] (Scheme 4.3a). After the image had decayed a second hologram of the same diffraction efficiency could be recorded in the same material. The image formation mechanism when phenyl alkyl diketones (73) were used is attributed to a photoenolization,[62] (Scheme 4.3b). The life-time of these images is given as several days rather than minutes or hours as is the case with dialkyl diketones.

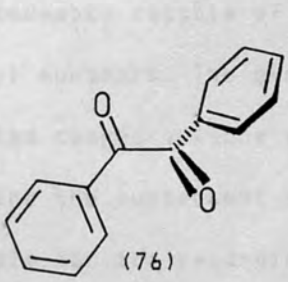


Scheme 4.3 Proposed Recording Mechanisms in Holographic Materials Employing 1,2-Diketones

In a series of experiments in which substances were added to solutions of acrylamide in 2-methoxyethanol and exposed to sunlight in clear glass tubes, the precipitation of polyacrylamide was taken as an indication of the production of active free radicals. In such experiments the formation of a precipitate was reasonably rapid in tubes containing acenaphthenequinone (74), phenanthrenequinone (75) and benzil (76). Similarly prepared tubes kept in darkness for a comparable time period all showed no polymer formation until subsequently exposed to light. A tube containing acrylamide solution alone also showed no polymer formation when exposed to light for the same length of time. Isatin (70) was found to be ineffective under these circumstances in a separate experiment. Lack of suitable material prevented the investigation of the cross-linking of polymers using these materials.


(74)

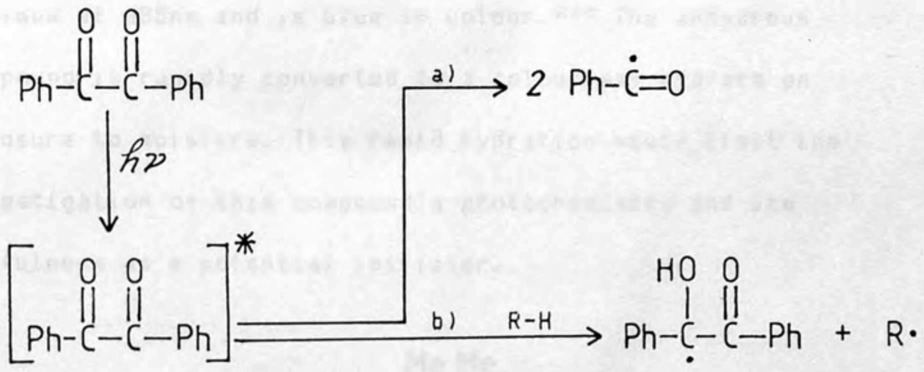

(75)


(76)

All of these compounds absorb strongly in the violet/blue region of the visible spectrum, being yellow or orange-yellow in colour, a characteristic of 1,2-diketones. Such initiators might be expected to cross-link polymer faster than PATM which shows no polymer formation under similar conditions. These three initiators, aceanthrenequinone (74), phenanthrenequinone (75) and benzil (76) were also shown to polymerize methyl methacrylate in a similar series of experiments, showing that this behaviour is not peculiar to the acrylamide monomer.

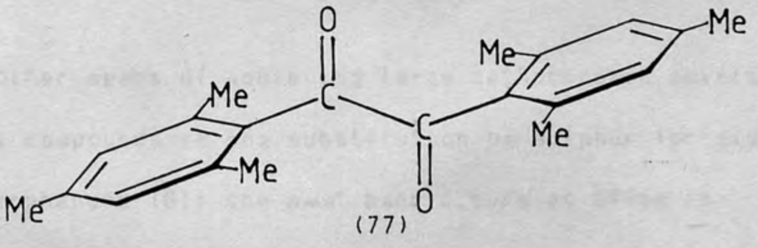
The question arises as to whether these compounds are functioning as free radical initiators (either by photofragmention or by hydrogen abstraction) or as triplet sensitizers transferring energy to monomers present in solution. Both mechanisms are possible; the same compounds have been shown to be sensitizers for the Ciba-Geigy photopolymer Mü 1771/2316 which cross-links by a [2+2] photocycloaddition, (Section 4.2).

Bunbury *et al* have studied the photolysis of solutions of benzil in cyclohexane,[209] propan-2-ol[210] and cumene.[210] Products detected include benzoin, benzoin benzoate, benzaldehyde and benzoic acid. These authors attribute the formation of benzaldehyde to the dissociation of benzil to two benzoyl radicals, (Scheme 4.4a), although this is not necessary to account for the observed products.[211] The major route to photoproducts is via hydrogen abstraction by photoexcited benzil, (Scheme 4.4b). Both of these pathways give rise to free radicals which are presumably capable of initiating the polymerization of vinyl monomers. The generation of free radicals by photoexcited camphorquinone abstracting hydrogen from a polymer host, and the subsequent reactions of these radicals, is responsible for the recording of permanent holograms. The diffraction efficiency of these images may be increased by the incorporation of additional monomer in the material, showing that polymerizations contribute to the imaging process.[63]



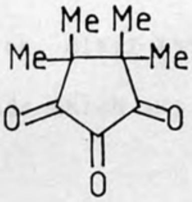
Scheme 4.4 Initial Steps in the Photolysis of Benzil

Benzil and related compounds appear to be capable of generating reactive free radicals on photolysis. This phenomenon has been used to record holograms at 488nm.[62] The effect of conformational factors on the absorption maxima of modified benzils has been investigated.[212,213] In particular steric hindrance at the position *ortho* to the carbonyl group, in for example mesitil, (2,2′,4,4′,6,6′-hexamethylbenzil), (77), induces a bathochromic shift in the dicarbonyl n→π* absorption. Maxima in the spectrum of this compound occur at 467 and 493nm, the corresponding absorption occuring in benzil at 370nm. Steric hindrance prevents the carbonyl groups from lying in the plane of the aromatic rings as they do in benzil. This causes the carbonyl-carbonyl angle to change from 90° to 180° with a corresponding increase in energy of the ground state giving rise to the bathochromic shift.



(77)

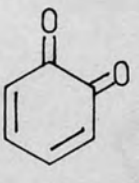
The non-enolizable cyclic triketone (78) has an absorption maximum at 685nm and is blue in colour.[214] The anhydrous compound is rapidly converted to a colourless hydrate on exposure to moisture. This rapid hydration would limit the investigation of this compound's photochemistry and its usefulness as a potential initiator.



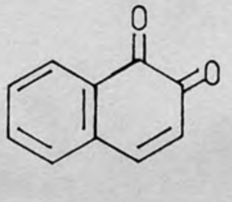
(78)

Among the quinones, *ortho*-benzoquinone (79) has an n→π* transition at 615nm. Extending the conjugation of this system, as in 1,2-naphthoquinone (80) has the effect of shifting the absorption maximum to shorter wavelength; 530nm in this example.[215]

While these carbonyl compounds absorb light at relatively long wavelengths, it is necessary for the photoexcited states to exhibit useful photochemistry, such as hydrogen abstractions, which will produce radical species, before they can be considered as photoinitiators.

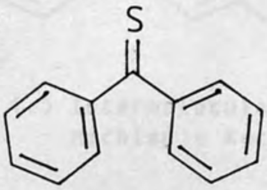


(79)

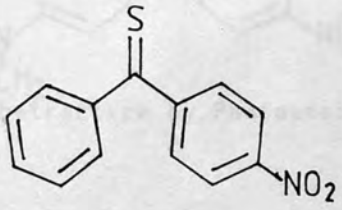


(80)

Another means of achieving large bathochromic shifts in carbonyl compounds is the substitution of sulphur for oxygen. In thiobenzophenone (81) the n→π* band occurs at 599nm in ethanol.[216] In the *para*-nitro derivative (82) this band is shifted to 625nm, (cyclohexane).[216] The reason for this large red-shift relative to the oxygen analogues is the relatively high energy of the sulphur non-bonding orbital as reflected in the low ionization potential of this element. The intensities of the bands are also rather high for $n \rightarrow \pi^*$ transitions, (ε_{max} = 181 in (81) and 168 in (82)), due to intensity borrowing from the allowed $\pi \rightarrow \pi^*$ transition. Alkyl thioketones are less stable than the aromatic compounds which are described as deep blue in colour.

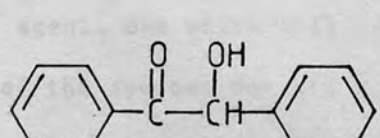


(81)



(82)

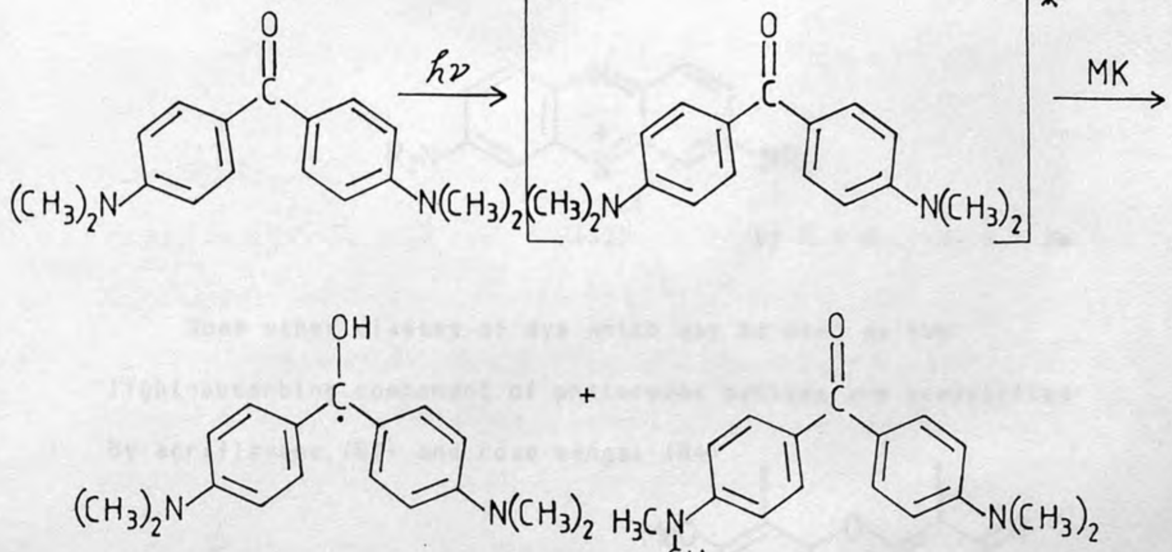
The most important group of ketone initiators is probably that based on benzoin (25) and its analogues. These deserve only passing mention here since their use is confined mainly to ultra-violet cured coatings on account of their high extinction coefficients at around 360nm. Benzoin and related initiators generally undergo fragmentation to free radicals on photolysis.



(25)

Other ketone initiators are used in conjunction with sources of abstractable hydrogen, generating free radicals by that means. Michler's ketone is one such initiator, the *para*-

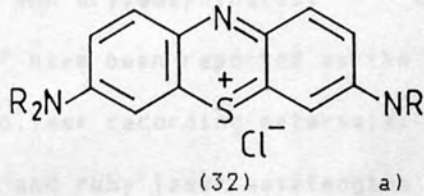
dimethylamino functionality providing the site for intermolecular hydrogen abstraction in the same molecule, (Scheme 4.5).



Scheme 4.5 Intermolecular Hydrogen Abstraction by Photoexcited Michler's Ketone, (MK).

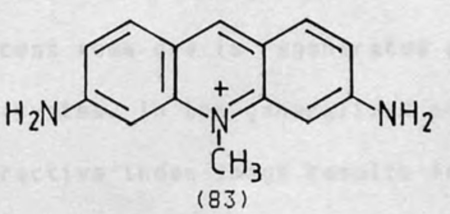
4.1.3 Photoredox Initiators

Photo-activated redox reactions provide a further means of initiating polymerization and cross-linking. Photoredox initiators are generally two component mixtures, the light-absorbing member of which can be a dye absorbing at relatively long wavelength. Dyes such as methylene blue (32b) and thionine (32a) have photoexcited states which are more strongly oxidizing than their ground states. In the presence of a suitable reducing agent, one which will reduce the photoexcited state of the dye but not its ground state, the redox process will only occur when light of the correct wavelength is falling on the mixture. Free radicals produced by the redox reaction may be utilized to initiate polymerizations. A number of photoinitiator systems employing phenothiazine dyes, exemplified by methylene blue, have been reported and are included in a recent review of dye-sensitized photopolymerization.[217]

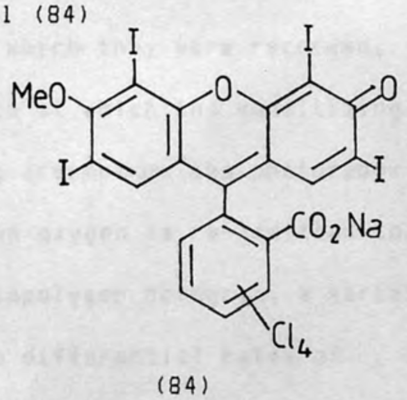


(32) a) R = H , b) R = Me

Some other classes of dye which may be used as the light-absorbing component of photoredox systems are exemplified by acriflavine (83) and rose bengal (84)

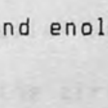


(83)



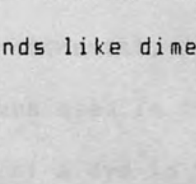
(84)

A number of groups of compounds have been recognised as reductants for photoreducible dyes. These include amines such as triethanolamine, triaryl phosphines and arsines (which are considered analogous in reactivity to amines), sulphur compounds such as metal sulphinates and sulphinate esters, heterocycles (85a-c) and enolates of carbonyl compounds like dimedone (86).



(85)

a) X = NH
b) X = O
c) X = S

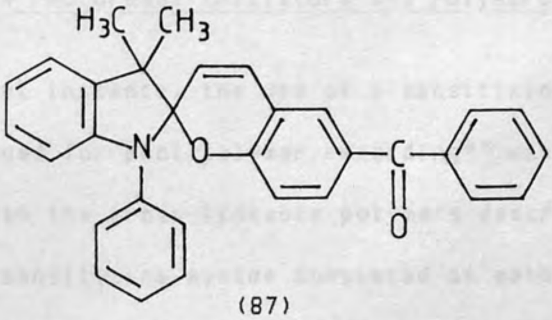


(86)

In practical applications of polymerizable systems employing visible light photoredox initiation, a number of advantages and disadvantages are evident. Systems employing phenothiazine dyes and arylsulphinates,[43,44] triethanolamine and acetylacetone[47] have been reported as the basis of new holographic photopolymer recording materials. High sensitivity at the helium-neon and ruby laser wavelengths are seen as are high diffraction efficiencies in the resultant holograms.

The presence of a dye in the resultant hologram is however to be avoided. This is because holograms perform best when replayed at the same wavelength at which they were recorded, which must be exactly the wavelength at which the sensitizing dye absorbs. Although dye bleaching accompanies the photoredox process some dye is regenerated when oxygen is re-admitted to the system. In the generalized photopolymer hologram, a variable refractive index image results from differential rates of photopolymerization and the resultant variations in the density or composition of the final polymer. The hologram so produced must be rendered transparent after processing. Methods of achieving this are not one-hundred percent satisfactory, but a temporary bleaching of the dye can be effected by ultra-violet initiated photoreduction by 4-nitrophenyl acetic acid.[123] Surface relief holograms, produced in photoresist, diffract light at the air-resist boundary and, when used in transmission, would still be affected by the presence of a dye in the resist layer. When surface relief holograms are used in reflection, after coating with a metallic mirror, the presence of a dye in the resist is irrelevant to the performance of the hologram or HOE.

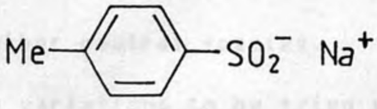
An attractive alternative to the use of dye sensitizers in photopolymer recording is the use of a photochromic material as part of the initiator system.[47] The spiropyran derivative (87), when excited by ultra-violet irradiation, develops an absorption band at 633nm. Exposure to a laser diffraction pattern at this wavelength then causes photopolymerization to be initiated. When the source of ultra-violet light is removed the photochrome returns to the ground state which is transparent at 633nm. This compound, (87), is used in conjunction with triethanolamine as the initiating system. A resolution in excess of 3000 l mm^{-1} is reported.



(87)

Another problem encountered when methylene blue is used as the sensitizing dye is due to the association of the dye cations in solution to form dimers. The dimer is inactive in the photoredox process and is reported by Chen to be a chain terminator.[134] The use of ethylene glycol as solvent , in which methylene blue does not aggregate, was found to overcome this problem.[137]

Aryl sulphinates, typically sodium *para*-toluenesulphinate (88) react with vinyl monomers, in the presence of water, to form sulphones which are inactive in the initiating system, (Scheme 1.20, Section 1.5.4). This reaction can cause complete desensitization of a polymerization mixture in a few hours and is accelerated at low pH.[142-144]



(88)

It was hoped that an initiating system of this type could be used to sensitize the polymers of Chapter 2 to helium-neon laser light to create a red-sensitive photoresist.

4.1.4 Photoredox Initiators and Polymers

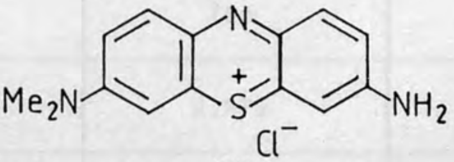
In the first instance, the use of a sensitizing system of the kind developed for photopolymer recording[43] was investigated with the cross-linkable polymers described in Chapter 2. The sensitizing system consisted of methylene blue (32b) and sodium *para*-toluenesulphinate (88). When a plate was coated with polymer mixed with a solution of this sensitizer and exposed to a grating pattern , development using an organic solvent mixture revealed no discernable image but a colourless deposit was seen across the whole of the plate. This inorganic deposit was sodium chloride derived from the counter-ions of the active parts of the initiating system.

This problem is a consequence of the requirement for an organic solvent development which was found to be necessary in order to achieve maximum resolution from these polymers. This also illustrates the different approach needed when considering the development of a photoresist holographic system rather than a photopolymer recording material.

An answer to this problem may be found in a number of ways: by replacing the sodium counter-ion of the sulphinate salt with one soluble in organic solvents; by using the sulphinic acid or a sulphinate ester; or by replacing either the cationic dye or the sulphinate with another neutral species.

The first of these variations to be tried was the replacement of the sodium salt with *para*-toluenesulphinic acid. This has also been used in photopolymer recording in conjunction with methylene blue.[44] Although cross-linking of a solution of polymer was rapid in sunlight using this sensitizing combination, an identical solution kept in the dark also cross-linked polymer, although not so rapidly. A solution containing polymer and sulphinic acid alone also cross-linked. Cross-linking in the absence of dye was found to have occurred after 30 minutes whereas the methylene blue sensitized solution was found to have cross-linked after 7 minutes exposure to sunlight. An investigation of the literature showed aryl sulphinic acids to have been reported as both accelerators[218] and initiators[219-21] for vinyl polymerizations.

The use of suitable quaternary ammonium salts as phase-transfer catalysts in various heterogeneous reactions is a common practice.[222,223] As counter-ions to the sulphinate, cations such as these would be expected to be soluble in organic solvents, even in the presence of chloride ion. Clean development of polymer coatings sensitized with mixtures containing tetra-alkylammonium arylsulphinates would be expected. In order to investigate this line of approach the tetra-n-butylammonium salt of *para*-toluenesulphinic acid was prepared. This substance appeared to be deliquescent and a crystalline material was not obtained. When a solution containing this salt and Azure A (89) was used to sensitize MP62 and an exposure was made using the expanded beam of a 5mW helium-neon laser, a 2 l mm^{-1} grating was recorded with the predicted clean development. This result could not be repeated 4 hours later. This deactivation of the the initiator was assumed to be due to addition of sulphinate anion to vinyl groups on the polymer, as has been reported to occur under similar circumstances.[142-144] This deactivation is likely to be fast as polymers similar to MP62 have quite high methacrylic acid contents, the reaction leading to desensitization proceeding at a greater rate at low pH.



(89)

A screening of combinations of organic substances was undertaken in order to find sensitizing systems capable of the photocross-linking of polymer. Initial studies of this type were carried out on solutions of polymer (MP59) in 2-methoxyethanol solution. When it became clear that there was insufficient polymer to continue these tests, the polymerization of acrylamide in 2-methoxyethanol or in an aqueous solution containing some *N,N'*-methylene-*bis*-acrylamide was used to show the presence of reactive free radicals. In 2-methoxyethanol polymerization is indicated by the precipitation of colourless polyacrylamide. In experiments using polymer or the aqueous mixtures of monomers, the formation of a network polymer is accompanied by the complete gelling of the solution.

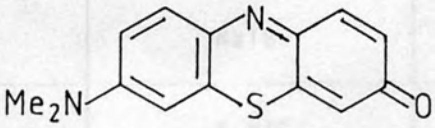
In the table below (Table 4.2) the cross-linking of MP59 in 2-methoxyethanol was used as the indicator, exposure was to sunlight through glass.

dye	co-initiator	cross-linked?
-	-	no
-	TSA	yes
-	NaTS	no
-	R_4NTS	no
M.B.	NaTS	yes
M.B.	R_4NTS	yes
M.B.	TEA	no
M.V.	R_4NTS	yes
M.V.	TEA	no
Azure II	R_4NTS	yes
T.B.	R_4NTS	yes (slow)

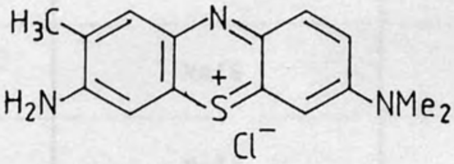
M.B.=methylene blue, M.V.=methylene violet, T.B.=toluidine blue, TSA=*para*-toluenesulphinic acid, NaTS=sodium *para*-toluenesulphinate, R_4NTS=tetra-n-butylammonium *para*-toluenesulphinate, TEA=triethanolamine.

Table 4.2 Phenothiazine Dyes and the Photocross-linking of MP59

In this group of experiments, (Table 4.2), it can be seen that the sulphinic acid cross-links polymer alone whereas its salts do not. Combinations of these salts and a phenothiazine dye are also shown to cross-link this polymer whereas combinations of triethanolamine and a phenothiazine dye do not. Methylene blue, methylene violet (90) and Azure II are good sensitizers but toluidine blue (91) sensitizes less well. Azure II is a mixture of dyes containing methylene blue.



(90)



(91)

Methylene violet (90) seems particularly attractive for use as a sensitizing dye in systems of this type: it is neutral and therefore does not introduce a counter-ion into the system and sensitizes well, even at 633nm, (see Section 4.1.5). Its use is however limited by its solubility which is too low to efficiently sensitize a thin film of polymer cast on glass. The failure of triethanolamine/phenothiazine dye mixtures to sensitize this polymer, when they are reported as photoinitiators for acrylamide,[49] may be due to interactions between the amine and acid groups on the polymer.

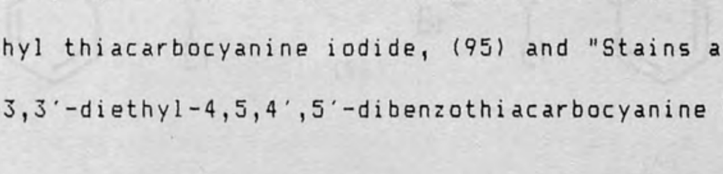
The following table, (Table 4.3) shows similar results for a series of cyanine dyes used to sensitize solutions of MP59 in 2-methoxyethanol.

dye	co-initiator	cross-linked?
(92)	-	no
(92)	NaTS	yes
(92)	R_4NTS	yes
(93)	NaTS	no
(94a)	NaTS	no
(95)	NaTS	some (slow)
(96)	NaTS	some (slow)

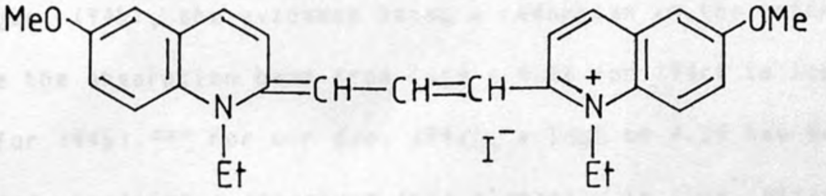
NaTS=sodium *para*-toluenesulphinate, R_4NTS=tetra-n-butylammonium *para*-toluenesulphinate,

Table 4.3 The Photocross-linking of MP59 with Cyanine Dyes and Sulphinates.

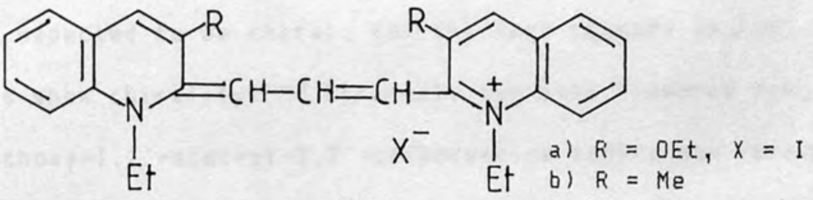
The dyes referred to in this table (Table 4.3) are 3,3′-diethyl-6,7,6′,7′-dibenzothiacarbocyanine iodide, (92), 6,6′-dimethoxy-1,1′-diethyl-2,2′-carbocyanine iodide, (93), 3,3′-diethoxy-1,1′-diethyl-2,2′-carbocyanine iodide, (94a), 3,3′-diethyl thiacarbocyanine iodide, (95) and "Stains all", 9-methyl-3,3′-diethyl-4,5,4′,5′-dibenzothiacarbocyanine bromide, (96).



(92)

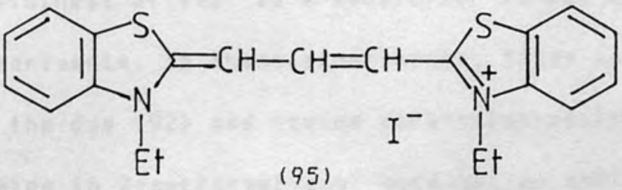


(93)

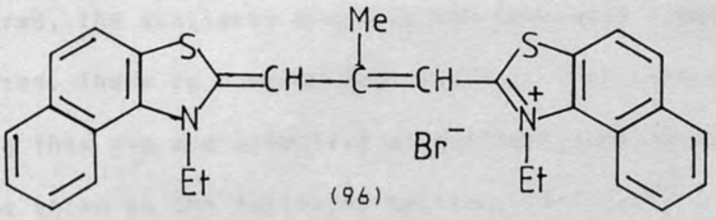


a) R = OEt, X = I
b) R = Me
c) R = H

(94)



(95)



(96)

Among these compounds the best sensitizer is the thiacyanine (92) and the worst are the dyes containing the quinoline nucleus, (93) and (94a).

The dye (94a) has an absorption maximum at 631nm in methanol, ideally suited to the helium-neon laser (633nm) if it were an efficient sensitizer. The presence of substituents at the 3-position would be expected to sterically hinder this molecule from adopting the planar cisoid structure expected of such dyes. Departure from planarity is seen in the 3,3'-dimethyl analogue, (94b), the evidence being a reduction in the intensity of the the absorption band from logε = 4.86 for (94c) to logε = 4.61 for (94b).[224] For our dye, (94a), a logε of 4.28 has been recorded, implying a departure from planarity in this instance also.

An extremely hindered, eclipsed structure of this type would be expected to be chiral, for the same reasons as the helicenes show chirality.[225] Strangely the less hindered dye, 4,4'-diethoxy-1,1'-diethyl-2,2'-carbocyanine iodide was formed less readily than (94a) under the same conditions and was not isolated.

The usefulness of (92) as a sensitizer is put in question by later experiments. In these experiments, tubes containing acrylamide, the dye (92) and sodium *para*-toluenesulphinate or triethanolamine in 2-methoxyethanol were set-up and exposed to light or kept in the dark. When the irradiated tubes had polymerized, the similarly prepared and unexposed tubes had also polymerized. There is however some evidence that combinations involving this dye are effective at photopolymerization at 633nm, as shown in the following section, (Section 4.2.5).

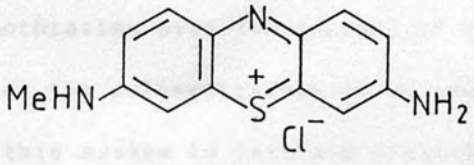
The use of aqueous solutions of acrylamides as a method of screening initiators is limited to dyes and co-initiators which are soluble in water. The following table, (Table 4.4) compares a series of phenothiazine dyes and phenoxazine dyes as sensitizers for the triethanolamine-initiated photopolymerization of aqueous acrylamide.

dye	co-initiator	polymer formed?
-	TEA	no
M.V.	-	no
M.V.	TEA	yes
M.B.	TEA	yes
M.G.	TEA	yes
Azure A	TEA	yes
Azure C	TEA	yes
Thionine	TEA	yes
Gallocyanine	TEA	no
Brilliant cresyl blue	TEA	no
Basic blue 3	TEA	no
Cresyl violet acetate	TEA	no

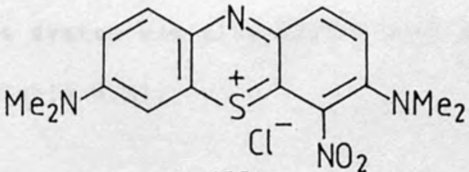
M.B.=methylene blue, M.V.=methylene violet, M.G.=methylene green
TEA=triethanolamine.

Table 4.4 The Photopolymerization of Aqueous Acrylamide by Phenothiazine Dye/Triethanolamine or Phenoxazine Dye/Triethanolamine Mixtures.

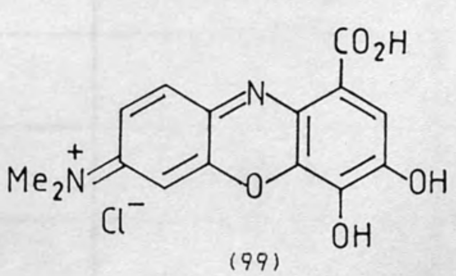
This table (Table 4.4) shows that all of the phenothiazine dyes tested sensitize the photopolymerization of aqueous acrylamide in the presence of triethanolamine and that none of the phenoxazine dyes listed do. The structures of Azure C (97), methylene green (98) and the phenoxazine dyes; gallocyanine (99), brilliant cresyl blue (100), basic blue 3 (101) and cresyl violet acetate (102) are shown below.



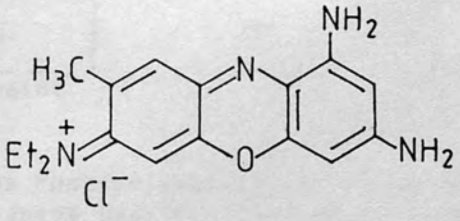
(97)



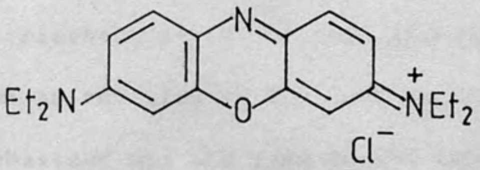
(98)



(99)



(100)



(101)

(102)

The above results, (Table 4.4) also show that triethanolamine functions as a component in initiator systems containing phenothiazine dyes (in support of claims in the literature[19]) for the polymerization of aqueous acrylamide. The failure of this system to initiate cross-linking of the polymer MP59 is therefore likely to be due to an interaction between the amine and the polymer.

This aqueous system was also tested with the cyanine dyes (92) and (95), (Table 4.5).

dye	co-initiator	polymer formed?
(92)	-	some
(92)	TEA	yes
(95)	-	no
(95)	TEA	yes

TEA=triethanolamine

Table 4.5 The Photopolymerization of Aqueous Acrylamide by Cyanine Dye/Triethanolamine Mixtures.

The benzothiacyanine, (92) shows some polymer formation in the absence of triethanolamine. In this instance a build-up of polymer was seen on the side of the tube facing the light source. This behaviour was not seen in the tube containing the simpler dye (95) when irradiated for a similar period of time. In the tubes containing triethanolamine, polymerization proceeded at a greater rate, (92) still being faster than (95) however.

In a further series of experiments methylene blue was combined with a range of possible co-initiators in tubes containing solutions of acrylamide in 2-methoxyethanol. Organic solutions were used in these experiments in order to extend the range of compounds tested. Commercially obtained materials were not subjected to further purification before testing. The results of these experiments are tabulated below, (Table 4.6).

co-initiator	polymer formed?
ethyl acetoacetate	yes
acetyl acetone	yes
malonic acid	no
diethyl malonate	no
ethyl cyanoacetate	no
1,3-indandione	yes
perinaphth-1,3-indandione	yes
methoxyphenalenone	no
2,2-dimethyl perinaphth-1,3-indandione	no
thiourea	yes
ascorbic acid	yes
thiodiglycolic acid	yes
monomethyl thiodiglycolate	yes
dimethyl thiodiglycolate	yes

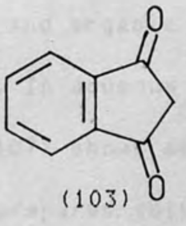
Table 4.6 continued overleaf...

continued from previous page.

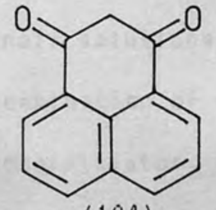
co-initiator	polymer formed?
thiodipropionic acid	yes
1,3-dithiane	yes

Table 4.6 Co-initiators in the Methylene Blue-Sensitized Photopolymerization of Acrylamide in 2-Methoxyethanol

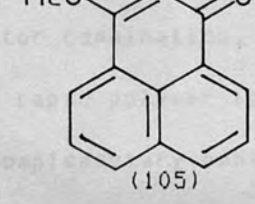
The results with acetyl acetone and ethyl acetoacetate confirm those given in the literature[138-140] and are examples of the use of enolizable diketones in phenothiazine dye-sensitized initiator systems. In contrast the compounds malonic acid, diethyl malonate and ethyl cyanoacetate, which also might be expected to enolize readily, did not appear to initiate polymerization under these circumstances. The enolate theory is supported by the results for 1,3-indandione, (103), perinaphth-1,3-indandione, (104), methoxyphenalenone, (105) and 2,2-dimethyl perinaphth-1,3-indandione, (106). The enol ether (105) and the compound with no enolizable proton (106) are inactive as co-initiators whereas the enolizable diketones (103) and (104) are.



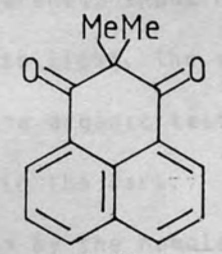
(103)



(104)

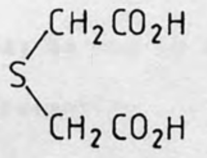


(105)

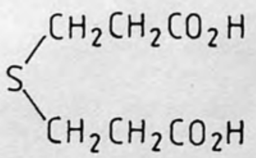


(106)

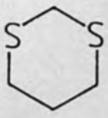
Thiourea and ascorbic acid are again examples from the literature confirmed by these results. The remaining compounds in this list (Table 4.6) are all substituted dialkyl sulphides: thiodiglycolic acid, (107), its mono- and dimethyl esters, its homologue thiodipropionic acid, (108) and 1,3-dithiane, (109). The results should be treated with caution since the compounds may not be pure and the activity shown may be due to the impurities, in particular good elemental analyses could not be obtained for the methyl esters of (107), (see the Experimental Section).



(107)



(108)



(109)

A more careful re-examination of some of these results shows variable behavior when using thiodiglycolic acid, (107) in aqueous and organic (2-methoxyethanol) solutions of acrylamide. In aqueous solution the combination of methylene blue and (107) shows activity as a photoinitiator, whereas a similarly prepared solution kept in darkness shows no polymer formation until subsequently exposed to light. The same initiator combination, when used in the organic test solution, showed rapid polymer formation, even in the dark.

Complementary behaviour was shown by the homologue, (108) and methylene blue. In aqueous solutions no polymer was formed, even after several hours exposure, but in the organic test solution this combination initiated polymerization when exposed to light but not when kept in the dark. The dark stored solution could be subsequently photopolymerized when exposed to light after 24 hours, showing at least some dark stability.

In these experiments, and generally in those described above, the concentration of methylene blue must not be too high or photopolymerization will not occur. A solution that is coloured but still transparent gives the best results. The failure of high concentrations of this dye to initiate solution polymerizations may be due to the extremely high optical density of the solution preventing the light penetrating far into the bulk or to chain termination by methylene blue dimers.[134]

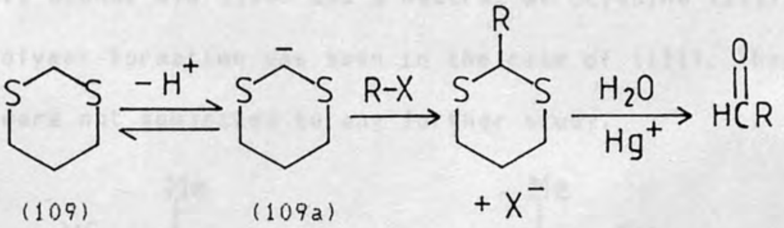
The interpretation of the results with the homologous acids (107) and (108), summarized below, (Table 4.7), is not clear and requires further investigation.

		polymer formation?	
solvent	acid	on exposure	in darkness
H_2O	(107)	yes	no*
$MeOCH_2CH_2OH$	(107)	yes	yes
H_2O	(108)	no	no
$MeOCH_2CH_2OH$	(108)	yes	no*

* Polymer formation seen on exposure to light after 24 hours in darkness.

Table 4.7 The Photopolymerization of Acrylamide by Methylene Blue and Thiodiglycolic Acid (107) or Thiodipropionic Acid (108) in Aqueous and Organic Media.

1,3-Dithiane (109) and substituted dithianes are used in synthesis as synthons for acyl carbanions, a negative charge at the 2-position being stabilized by the adjacent sulphur atoms, (Scheme 4.6). While the intermediate carbanion (109a) could be thought of as an analogue of an enolate, strong bases, such as organolithiums, are required to form this intermediate and the presence of this species in the sensitizing solution is unlikely.



Scheme 4.6 Dithianes in Organic Synthesis

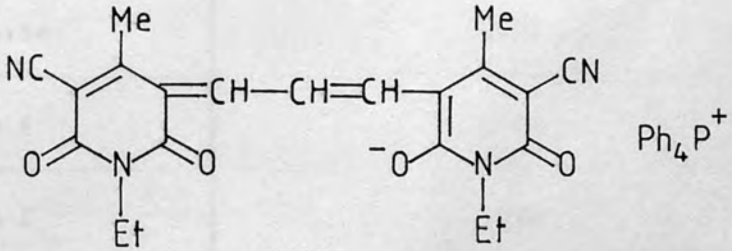
A few miscellaneous results are presented in the following table, (Table 4.8), for the photopolymerization of acrylamide.

solvent	dye	co-initiator	polymer formed?
H_2O	M.B.	Na_2S	yes
H_2O	-	Na_2S	no
H_2O	M.B.	$SnCl_2$	yes
H_2O	-	$SnCL_2$	yes
$MeOCH_2CH_2OH$	M.V.	EAA	yes
$MeOCH_2CH_2OH$	HPT 298, (110)	TEA	no
$MeOCH_2CH_2OH$	(111)	TEA	some

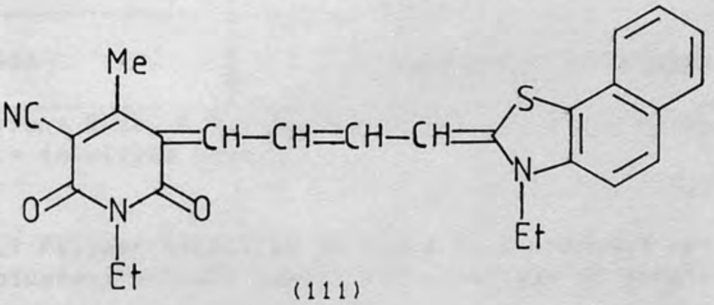
M.B.=methylene blue, M.V.=methylene violet, TEA=triethanolamine, EAA=ethyl acetoacetate.

Table 4.8 Miscellaneous Sensitization Experiments

Dye bleaching is extensive when sodium sulphide is used and dye must either be regenerated by aeration of the solution or more dye must be added before extensive polymerization is seen. Tin (II) chloride, which is reported to be a component of photoredox initiator systems,[111] gave polymer formation when it alone was added to aqueous acrylamide. The methylene violet result is not surprising and needs no further comment. The dyes (110) and (111)[226] represent two further classes of compounds, an anionic oxonol dye (110) and a neutral merocyanine (111). Slight polymer formation was seen in the case of (111). These results were not subjected to any further study.



(110)



(111)

4.1.5 Photoredox Initiation with Red Laser Irradiation

Some combinations of dye and sodium *para*-toluene sulphinate were tested in the unexpanded beam of a 2.5mW helium-neon laser for polymer formation on exposure to 633nm light. A solution of acrylamide containing some *N,N'*-methylene-*bis*-acrylamide was used, photopolymerization being shown to occur by the formation and build-up of polymer on the inside surface of the glass tube at the point illuminated by the laser beam. The dyes tested in this manner are listed below, (Table 4.9).

Dye	Polymer Formation?
M.B.	good
M.V.	excellent
(92)	good
M.G.	some
thionine	some
Azure A	some
Azure C	some
T.B.	some
(95)	some after 10 minutes

M.B.= methylene blue, M.V.= methylene violet, M.G.= methylene green, T.B.= toluidine blue.

Table 4.9 Polymer formation at 633nm by Dye-Sodium *para*-Toluenesulphinate Sensitized Solutions of Acrylamide

The most spectacular of these experiments was that in which methylene violet was used as the sensitizing dye: as polymerization proceeded at the point of irradiation a finger of solid polymer was built-up projecting from the side of the tube. Inversion of the tube, allowing the unpolymerized solution to flow to the opposite end of the tube revealed this structure. If the exposure time was long enough the "polymer finger" would bridge the walls of the tube. This behaviour was unusual among this series of experiments and is probably due to the dye-bleaching which is seen when methylene violet is used, this would tend to clear a path for the laser beam in the irradiated, polymerized zone. It may be that the colourless leuco form of this dye is formed irreversibly (whereas that of methylene blue is not) or that the reduced form of the dye could be active as an initiating species and that this initiation prevents the dye reforming. Whatever the mechanism this dye appears not to have been studied by workers investigating the recording of holograms using solution polymerization, to which this dye seems well suited. An investigation of methylene violet in this role might prove fruitful.

Among the other phenothiazine dyes examined methylene blue is the best, even performing better than Azure A which has its maximum absorbance at 633nm.

The cyanine dyes, (92) and (95), both show polymer formation under these conditions. (92) Performs well in this respect despite a fairly sharp cut-off in its absorption spectrum above about 600nm. Even more surprising is that any spot of polymer is produced by irradiating solutions containing (95) which has its maximum absorbance at 561nm.

4.1.6 Polymer-Bound Co-Initiators

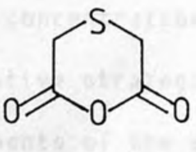
A characteristic of the photoredox initiator systems described above is that electron transfer processes occuring between a photoexcited dye and a photoreductant generate a free radical, derived from the photoreductant, which then initiates polymerization. There appears to be no reason why the photoreducing species need not be attached to the polymer as well as the polymerizable vinyl groups. Such a polymer would only require the addition of a suitable dye to sensitize it to photocross-linking. Similarly internally sensitized polymers have been prepared by Kodak workers by attaching trihaloacetate esters to polymers containing acrylate or methacrylate functionality.[119] These halogenated compounds exchange halogen with organometallic sensitizers generating polymer-bound radicals, (Scheme 4.6).

$$R\text{-}CX_3 + Ar\text{-}Cr(C{=}O)_3 \xrightarrow{h\nu} R\text{-}\dot{C}X_2 + Ar + CrX + 3C{=}O$$

Ar= benzene, X= Cl or Br, R= polymer.

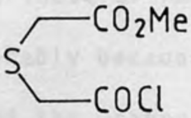
Scheme 4.6 The Generation of Polymer-Bound Free Radicals in Kodak Photopolymers Sensitized with Benzene Chromium Tricarbonyl

While the radical site and extent of fragmentation is not known, and the effect of the nature of solvent on the system is unclear, co-initiators based on thiodiglycolic acid, (107) will serve as an example of possible polymer-bound co-initiators for our polymers. A simple method of attaching this dicarboxylic acid is by reaction of an alcohol function of the polymer with the cyclic anhydride (112). This would probably prove unsatisfactory as the reaction of (112) with methanol leads to a mixture of mono- and dimethyl esters, the likely consequence of this reaction being applied to a polymeric alcohol would therefore be the production of a cross-linked material.

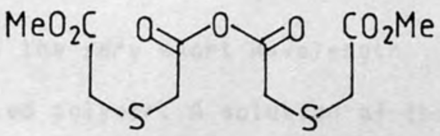


(112)

The method of attachment therefore requires a reactive form of a monoalkyl ester such as the acid chloride (113) or the anhydride (114). Experiments appear to show that the dimethyl ester of thiodiglycollic acid, the nearest model for the postulated polymer-bound ester, is an initiator when used in combination with methylene blue.



(113)



(114)

In the polymer-bound co-initiators considered so far the photoreductant is assumed to be joined to the same polymer chains as the cross-linkable vinyl groups, but this need not be the case. A polymer which is substituted only with the co-initiator residues, when used to sensitize a polymer of the type described in Chapter 2 would be expected to contribute to the cross-linking in much the same way as multi-functional monomers do, except that the additional cross-linking would be at the start of each polymerization chain. Such nonpolymerizable initiating polymers could also supply sites for the initiation of polymerization in monomer mixtures while providing a supporting matrix for them. Polymer-bound initiators may also provide a means of introducing higher concentrations of the co-initiator species when it has a tendency to crystallize in polymer coatings at high concentrations.

All of these alternative strategies may be worthy of consideration as developments of the system described in this thesis.

4.2 The Sensitization of Mü 1771/2316

Imaging experiments using the Ciba-Geigy photopolymer Mü 1771/2316 were all carried out on unsensitized coatings. The polymer in solution shows absorption bands at 243nm and 280nm with a shoulder at about 300nm. Exposure times with a 100W mercury vapour lamp and unsensitized coating were long, roughly comparable to those of PATM-sensitized coatings of our own polymers, probably because of the very short wavelength sensitivity of the unsensitized polymer. A solution of this polymer in 2-methoxyethanol could be left in a clear glass tube in sunlight for several weeks before gelling due to cross-link formation. It is therefore an easy matter to screen potential sensitizers by exposing tubes containing solutions of the polymer and possible sensitizers and monitoring the time taken for the formation of a gel relative to a sample of the unsensitized polymer.

Substances tested in these experiments were chosen from the classes of compound reported in the literature to sensitize cross-linking of polyvinyl cinnamate and related materials.[98] As well as typical triplet sensitizers, the methylene blue/sodium *para*-toluenesulphinate system was also mixed with the polymer as an efficient source of free radicals. No cross-linking was seen in this experiment, supporting the assumption that triplet-sensitized photocycloaddition, (Scheme

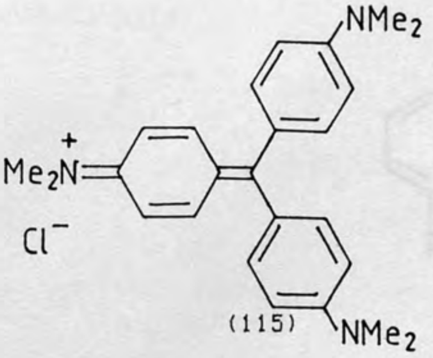
4.1) , is the mechanism of cross-linking in this material. The substances employed as sensitizers in this study are listed below, (Table 4.10).

sensitizer	cross-link formation?
aceanthrene	no
guaiazulene	no
fluorescein	no
5-nitroacenaphthene	yes
5,6-dinitroacenaphthene	yes
acenaphthenequinone	yes
phenanthrenequinone	yes
benzil	yes
crystal violet	yes, after several days

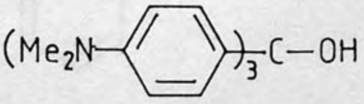
Table 4.10 Sensitizers for the Cross-Linking of Mü 1771/2316

Of the sensitizers listed in this table (Table 4.10) the most efficient appeared to be 5,6-dinitroacenaphthene (117a), phenanthrenequinone (75) and benzil (76) are also good sensitizers. Acenaphthenquinone (74) and 5-nitroacenaphthene (117b) are less good although all cross-link the polymer much faster than in the unsensitized case.

The remaining sensitizer, crystal violet (115) is a curiosity. This dye, along with other triphenyl methane dyes, is reported to be a sensitizer for polyvinyl cinnamate in a patent by workers at Kodak.[88] The moderate speed increase seen is further increased by "ageing" the solution at elevated temperature or in the presence of "stable peroxides". The colourless carbinol form of the dye (116) is also reported as a sensitizer. Whatever the mechanism of sensitization, or the identity of the sensitizing species, it appears to work for the Ciba-Geigy polymer also. From the description of the method of sensitization it appears likely that the long wavelength absorbing dye structure (115) is not involved in the photoprocess however.

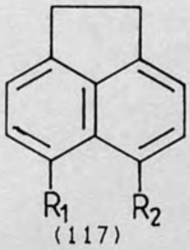


(115)



(116)

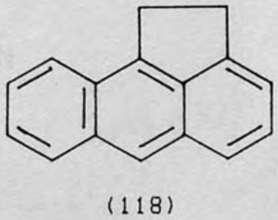
Aceanthrene (118) and the blue substance guaiazulene (119), both aromatic hydrocarbons, did not sensitize cross-linking in this polymer, nor did the dye fluorescein (120).



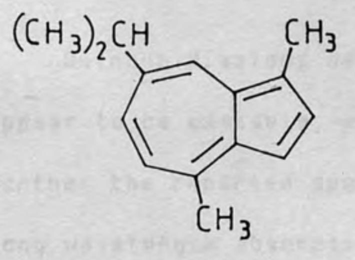
a) $R_1=R_2=NO_2$

b) $R_1=NO_2$, $R_2=H$

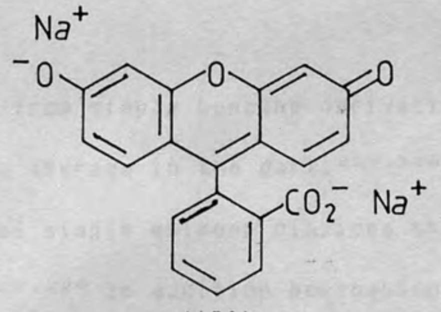
(117)



(118)



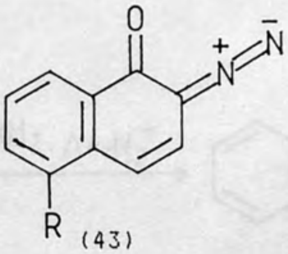
(119)



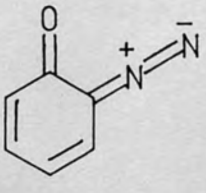
(120)

4.3 Diazoketone Sensitizers

The photoactive compound in positive photoresists is a quinone diazide, typically a derivative of (43). The photodecomposition of this compound to carboxylic acid-derived, alkali-soluble products is suppressed when typical triplet sensitizers are employed.[153] An extension of the sensitivity of these compounds to longer wavelengths must therefore rely on structural modifications to the quinone nucleus to shift the visible absorption maximum.

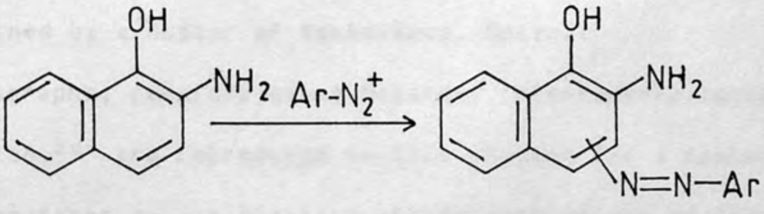

(43)

Taking the aromatic quinones as models for quinone diazides, the *ortho*-quinone diazide (121) might be expected to have a long wavelength absorption, as the corresponding quinone has an n → π* band at 615nm.[215]


(121)

Quinone diazides derived from simple benzene derivatives appear to be unstable, even to storage in the dark.[227,228,162] Further the reported spectra of simple quinone diazides show no long wavelength absorptions.[227,228] In addition benzoquinone diazides are more prone to form azo dyes on photolysis than are naphthoquinone diazides and therefore produce less of the products of ring-contraction.[162]

An alternative method of introducing long wavelength absorption bands in quinone diazides is to incorporate the photolysible functionality into a dye molecule. Probably the simplest method of achieving this is to couple the reactive amino phenol precursors of quinone diazides, for example (122), with diazonium salts to form azo dyes, (123), (Scheme 4.7), which may be converted to the quinone diazide by treatment with nitrous acid.



(122) (123)

Scheme 4.7 Azo Dyes from Quinone Diazide Precursors

This approach has been followed up no further than the preparation of some dyes based on amino naphthols.

5 Imaging Experiments

In order to test new batches of polymer as they were produced, sensitized coatings were subjected to exposure conditions intended to record diffraction gratings in the photopolymer layer, either by contact printing using a mask or by intercepting a laser-generated diffraction pattern. The production of cross-linked images in the resist layer in this manner also allowed the investigation of a range of solvents to find those suitable for use as developing agents for high-resolution polymer images.

The surface relief grating patterns produced by this method were examined by a number of techniques. Optical photomicrographs, recorded using Nomarski interference contrast illumination,[227] are reproduced in this chapter for a number of these gratings as are electron micrographs of two of the high resolution images. As well as recording the appearance of gratings by microscopy the surface profiles of some grating were recorded in cross-section by the use of a Talystep recorder (manufactured by Rank Taylor Hobson). In this technique a chisel shaped stylus is moved across the surface of the resist pattern and the vertical movement of the stylus is recorded on a moving chart. The Talystep traces for a number of the experiments described in this chapter are reproduced. In the case of one particular experiment, where three exposure steps were recorded in the same coating, a tentative exposure characteristic is plotted as depth of resist against exposure time.

Not all of the sixty or so exposure experiments will be discussed here but only those that illustrate a particular point and for which illustrative material is available. The gratings featured in this chapter will be referred to by number, the exposure and development conditions for which can be found by reference to the appropriate table.

5.1 Aqueously Developed Polymer Images

The requirement for an aqueous development procedure with our polymer system could not be fulfilled with the initial formulations, (see Chapter 2). Despite this some coating experiments were carried out which established 2-methoxyethanol and 2-ethoxyethanol as suitable solvents from which to deposit smooth layers of useful thickness and quality by the spin-coating method. Although acceptable solubility of the unfunctionalized base polymers in 5% sodium carbonate solution was seen, little success was gained in imaging experiments on functionalized polymers, (before polymers based on MP37, derivatized using methacrylic anhydride were produced, that is).

The Ciba-Geigy photopolymer, Mü 1771/2316,[197] is also intended to be developed using 5% aqueous sodium carbonate solution[230] and as such can be used as a comparative standard for the studies on our own materials.

5.1.1 Aqueous Development of Methacrylate Polymer Images

The standard developer, a 5% solution of sodium carbonate, gave disappointing results when used in imaging experiments with early batches of our polymers. An image was produced in a coating of MP5, albeit a poor one, and this result was encouraging but could not be repeated with later batches of similarly prepared materials. Much work subsequently went into developing the polymer system, both on the methacrylic acid content of the base polymers and on the conditions of the derivatization step, (see Chapter 2), until polymers of reproducible quality and consistent imaging properties could be produced. These polymers were the result of derivatizing MP37 with methacrylic anhydride. Of these MP51, with 17-19% conversion to the methacrylate ester, was used successfully in PATM-sensitized coatings in a series of imaging experiments, with aqueous development.

Gratings 1 and 2, of 2 and 10 lmm^{-1} resectively, were recorded in MP51 + PATM (Table 5.1) and Talystep profiles were recorded for them, (Figure 5.1 and 5.2). Smooth resist profiles were not obtained. In fact distortion of the resist due to swelling is apparent to the naked eye and accounts for the surface roughness. In the case of grating 2, removal of resist between the surface features is not complete.

The transfer typical of the positive photoresist, Shipley AZ 1350 (described in Section 1.6.2) for the same type of exposure set-up (grating 3, Table 5.1) is shown (Figure 5.3) and contrasts sharply with the crude images obtained from our material.

grating no.	resist	exposure time	lmm^{-1}	developer
1	MP51 + PATM	80m	2	5% Na_2CO_3
2	MP51 + PATM	80m	10	5% Na_2CO_3
3	AZ 1350	80s	2	AZ developer

Table 5.1 Exposure and Development Conditions of Aqueously Developed Gratings

The aqueously developed images of gratings 1 and 2 were

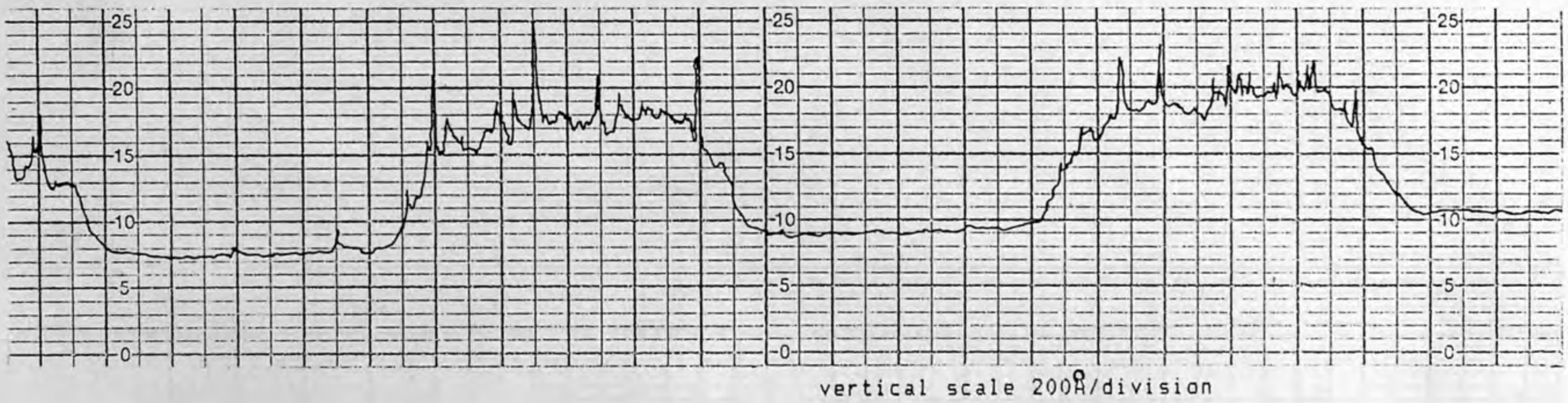


Figure 5.1 Talystep of Grating 1 (MP51 + PATM, 2 lmm^{-1})

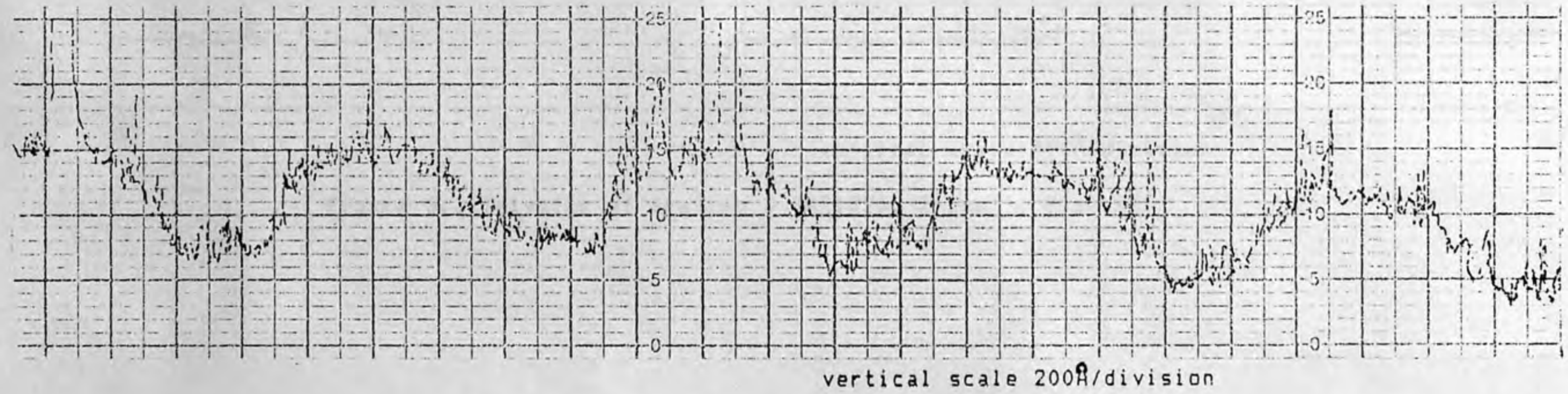
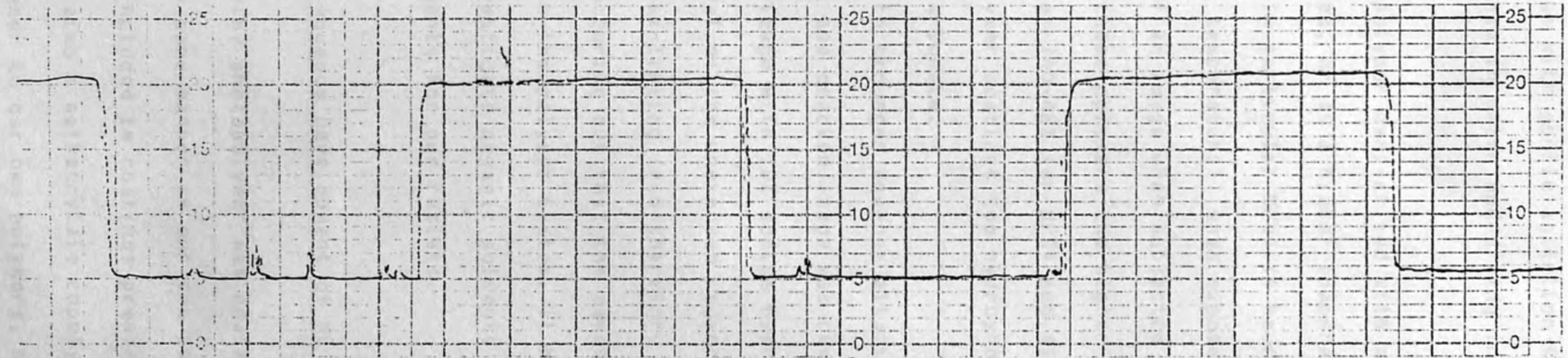


Figure 5.2 Talystep of Grating 2 (MP51 + PATM, 10 lmm^{-1})



vertical scale 400Å/division

Figure 5.3 Talystep of Grating 3 (AZ1350, 2 lmm^{-1}, 80s exp) very fragile when wet. Development consisted of immersion in the carbonate solution with gentle agitation for 10 to 20 seconds followed by a rinse in water and drying in a stream of filtered air.

Batches of polymer derivatized with methacrylic anhydride for longer periods, or at a higher temperature than the 2 hours at 0°C of MP51, in particular MP54 (4 hours at 0°C) and MP55 (2 hours at room temperature), when exposed in the same way, showed no sign of an image when subjected to the normal aqueous development. In these polymers the higher conversion to the methacrylate ester (40-48% for MP54 and 41-42% for MP55) had rendered the polymer coatings too hydrophobic to be affected by aqueous sodium carbonate.

In tests with stronger aqueous alkaline developers a severely swollen and cracked image was revealed on treatment of an MP55 polymer image with 10% sodium hydroxide, but with incomplete removal of the unexposed region. It was evident that the intended cross-linking (and therefore latent image formation) was occuring but that the aqueous developers were incompatible with the polymer system. It had therefore become necessary to investigate organic solvents and solvent mixtures as developing agents for our resists.

5.1.2 Aqueous Development of Mü 1771/2316

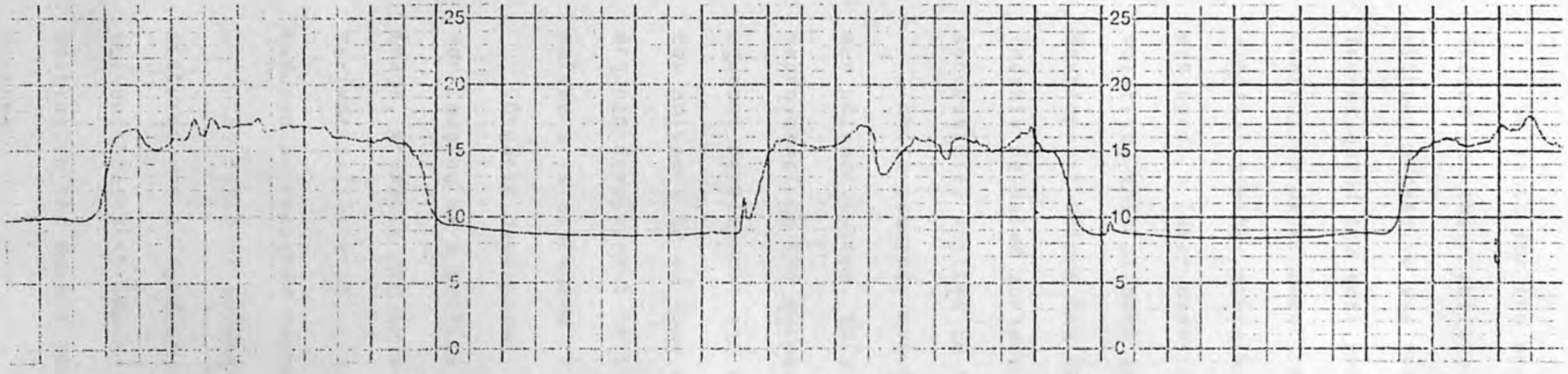
The Ciba-Geigy photopolymer was coated, exposed and developed in the same manner as our own polymers except that no sensitizer was included in coatings prepared for this purpose. This polymer is also a methacrylate copolymer and behaved in a very similar manner to our own polymers, being coated from the same solvents. The viscosities of solutions of this polymer were slightly higher than the viscosities of solutions of our own polymers of the same concentration (normally 10% w/v) and, in order to prepare coatings of similar thicknesses, were either used at higher dilution or coated at higher spin rates.

The exposure conditions for gratings 4 and 5, the Talystep profiles for which are shown, (Figures 5.4 and 5.5), are given in the following table, (Table 5.2). The plate used to record grating 5 was pre-baked for 20 minutes at 60°C before exposure. Pre-baking is recommended for commercial resists[231] as part of the processing sequence[232] both to eliminate residual solvent in the polymer coating and to relieve stresses introduced in the spin-coating. It was thought inadvisable to pre-bake our own polymers as the sensitizer, (PATM), is readily thermally decomposed.

grating no.	resist	exposure time	$l\,mm^{-1}$	developer
4	Mü 1771/2316	35m	2	5% Na_2CO_3
5	Mü 1771/2316	35m	10	5% Na_2CO_3

Table 5.2 Exposure and Development Conditions of Aqueously Developed Gratings

The Talystep traces, (Figures 5.4 and 5.5) show slightly better resolved images than those from our polymer, though still rough to the eye. The jagged structure superimposed on the resist lines in grating 5 (figure 5.5) may be a result of the exposure conditions, (see Section 5.2.1).



vertical scale 400Å/division

Figure 5.4 Talystep of Grating 4 (Mü1771/2316, 2 lmm^{-1}, 35m exp.)

vertical scale 200Å/division

Figure 5.5 Talystep of Grating 5 (Mü1771/2316, 10 lmm^{-1}, 35m exp., 20m pre-bake at 60°C)

5.2 Organic Development of Polymer Images

Solvents for the organic development of polymer images were tested for their ability to dissolve the uncross-linked polymer without excessive swelling. Of the range of solvents investigated the most promising was acetone. To give a more controlled development, mixtures of acetone and an acetate (initially ethyl acetate) nonsolvent were used. n-Pentyl acetate was used in later experiments to make the solvent mixture less volatile, this allowed an ethyl acetate rinse to follow development before the developer had a chance to dry onto the freshly revealed surface. The same developing sequence was also successfully applied to the Ciba-Geigy photopolymer.

While possibly not the optimum development conditions for our polymer system, this new processing method was a vast improvement on the excessively swollen images produced by aqueous development and enabled the resolution capabilities of the polymers to be more fully investigated. The consequences of organic development on the choice of sensitizers for these polymers is discussed in Chapter 4.

Organic development also highlighted the purity of polymers for imaging as a critical factor. Noise in the photopolymer image, probably due to some ionic material from the derivatization step, (insoluble in the developer) could be reduced by repeated reprecipitation of the polymer.

The ratio of solvent to nonsolvent used in the developer mixtures was arrived at by determining the minimum amount of solvent needed in the mixture to cleanly remove an unexposed coating in the normal processing sequence, normally 50-60% acetone.

5.2.1 Organic Development of Low Resolution Methacrylate Polymer Images

MP54 was the first polymer used successfully to produce grating images by contact printing with organic solvent development. Images of 40 and 100 lmm^{-1} were produced, grating 6 and 7 respectively. The exposure conditions for these experiments and for the others discussed in this section are given in the following table, (Table 5.3).

grating no.	resist	exposure time	lmm^{-1}	developer
6	MP54 + PATM	30m	40	50% A/EA
7	MP54 + PATM	20/40m	100	50% A/EA
8	MP60 + PATM	30/45/60m	10	60% A/PA
9	MP60 + p-NAT	75/90/105m	10	60% A/PA
10	MP59 + PATM	85/136m	10	MEK

A = acetone, EA = ethyl acetate, PA = n-pentyl acetate, MEK = methyl ethyl ketone (butanone).

Table 5.3 Exposure and Development Conditions for Organically Developed, Low Resolution Polymer Images

The appearance of grating 6 under the optical microscope is shown, both as the intact grating (Figure 5.7a), and with a scratch (Figure 5.7b). Scratching the polymer image helps to distinguish the raised resist pattern from the base layer which might not otherwise be clear. The Talystep trace for this grating, (Figure 5.8), shows additional structure due to artifacts introduced by the method of exposing the resist. Some of this stucture can just be seen in the photomicrographs as

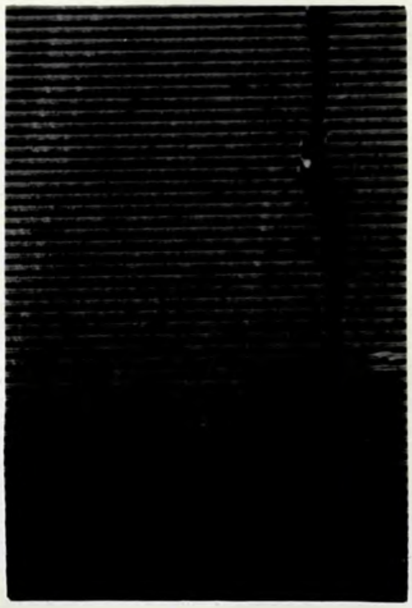
(Facing Page)

TOP LEFT: Figure 5.6a Photomicrograph of Grating 7 (MP54 + PATM, 100 lmm^{-1}).

TOP RIGHT: Figure 5.6b Photomicrograph of Grating 7 (with scratch).

BOTTOM LEFT: Figure 5.7a Photomicrograph of Grating 6 (MP54 + PATM, 40 lmm^{-1}).

BOTTOM RIGHT: Figure 5.7b Photomicrograph of Grating 6 (with scratch).



vertical scale 100Å/division

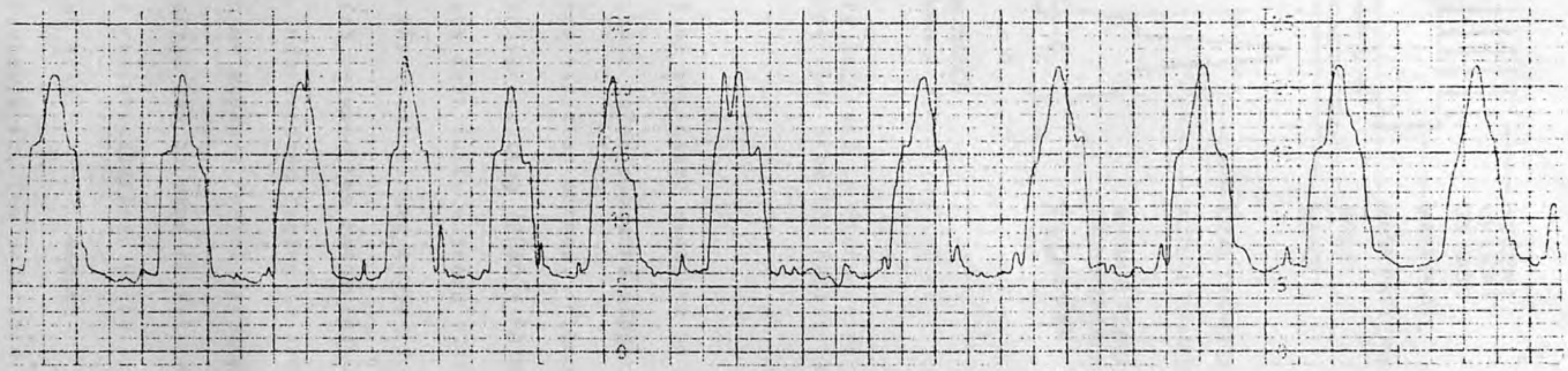
Figure 5.8 Talystep of Grating 6 (MP54 + PATM, 40 lmm^{-1}, 30m exp.)

narrow fringes on the raised resist lines running parallel to their sides. In this particular image a perfectly clean development is not seen; bumps of particulate matter or resist residues are distributed over the whole of this section of the grating.

Grating 7, while prepared at the same time as grating 6 and developed in the same manner, shows a much cleaner resist image, (Figures 5.6a and 5.6b). Scratching again helps to identify the resist lines. The Talystep traces for two exposure steps are shown, (Figures 5.9a and 5.9b), and show a remarkable resemblance to the resist transfer reported for contact printing using a 1:1 mask held slightly above the resist surface,[233] (Figure 5.10). The implication of this experiment is that this resist is capable of recording significantly higher resolution images than 100 lmm^{-1} as the features recorded here (due to interference effects) are narrower than the ideal 100 lmm^{-1} line width.

vertical scale 100Å/division

a) (20m exp.)



vertical scale 100Å/division

b) (40m exp.)

Figure 5.9 Talystep of Grating 7 (MP54 + PATM, 100 lmm^{-1})

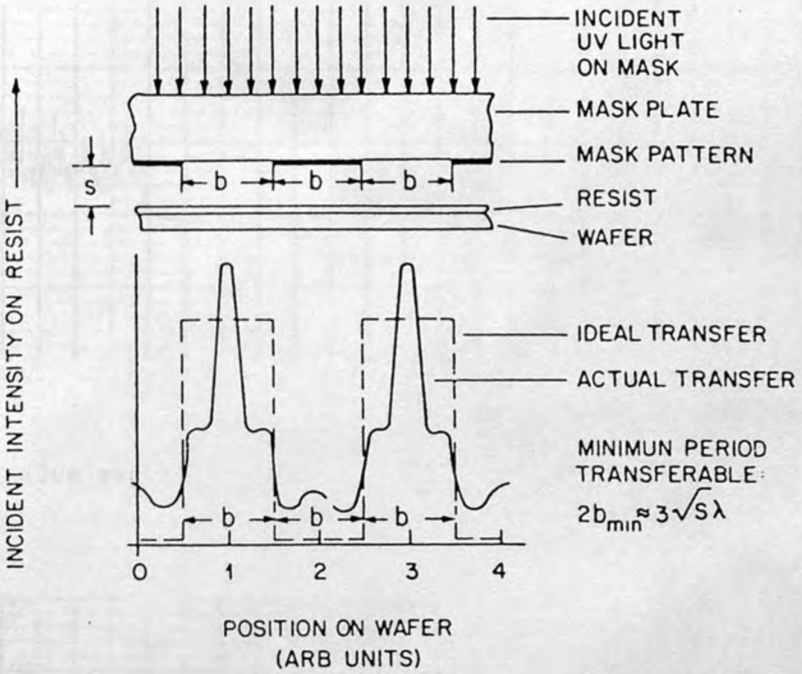
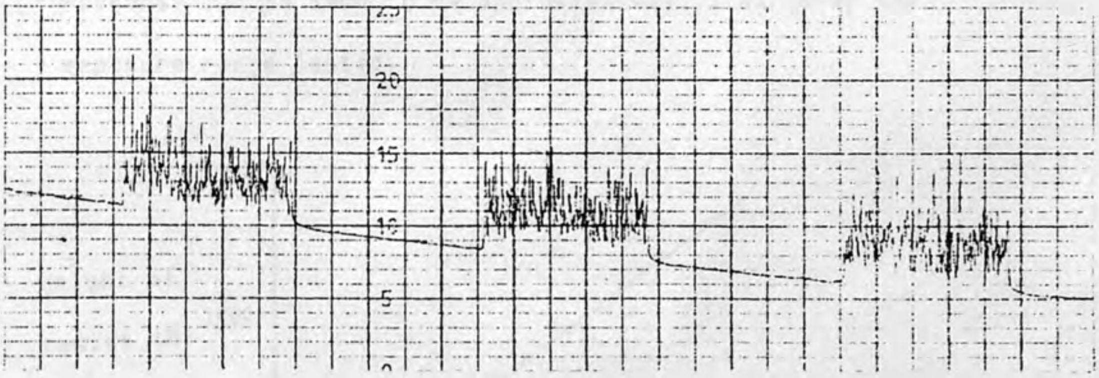


Figure 5.10 The Surface Profile Recorded in Photoresist for an Equispaced Mask Separated from the Resist Layer by a Distance s.

Grating 8 shows the effect of increased exposure on the grating profile. In this experiment three exposure steps have been recorded and examined by the Talystep method, (Figures 5.11a, b and c). For this particular coating (MP60 + PATM) all of the exposure steps appear less than fully exposed (30, 45 and 60 minutes) as a smooth top to the cross-linked image is not seen. Removal of unexposed resist between the image features is very good however. The grossly underexposed region is very noisy (Figure 5.11a) making the depth of exposed resist difficult to measure. A series of exposure steps can be used to determine an exposure characteristic for the resist material. While a sequence of three steps does not give enough information for a complete characteristic, the available data is plotted below, (Figure 5.12). The height of resist for each of

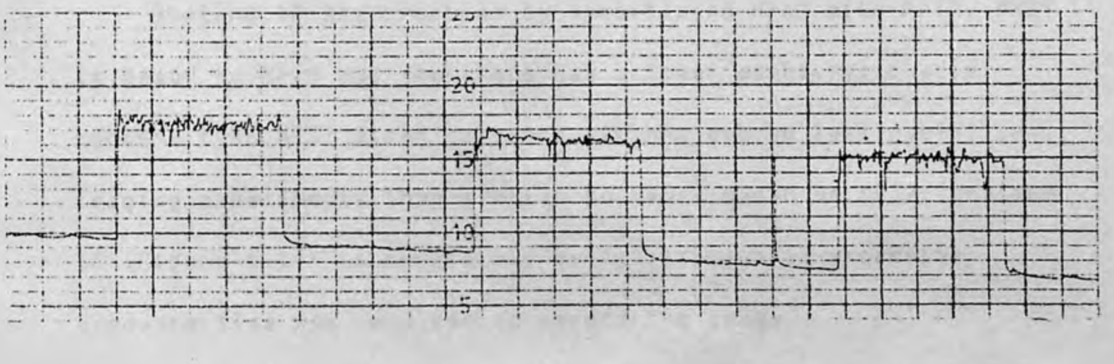


vertical scale 200Å/division

a) (30m exp.)

vertical scale 200Å/division

b) (45m exp.)



vertical scale 200Å/division

c) (60m exp.)

Figure 5.11 Talystep of Grating 8 (MP60 + PATM, 10 lmm^{-1})

these steps is the mean of ten separate measurements. The response can be seen to be approximately linear over the exposure range tested.

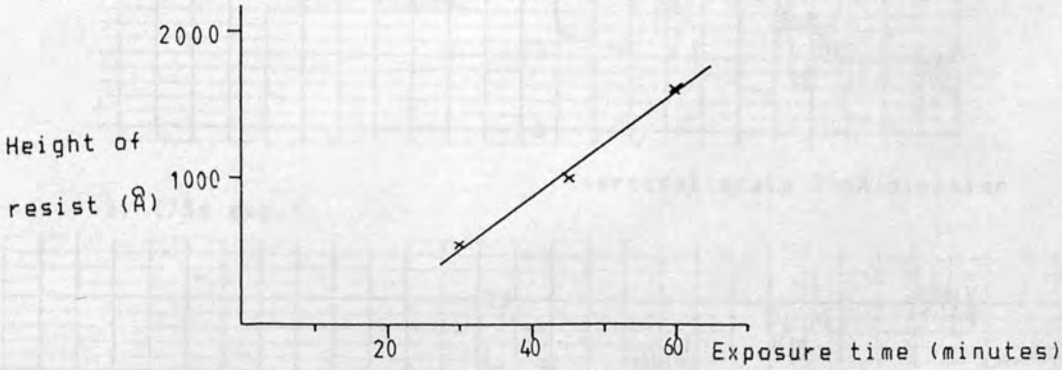
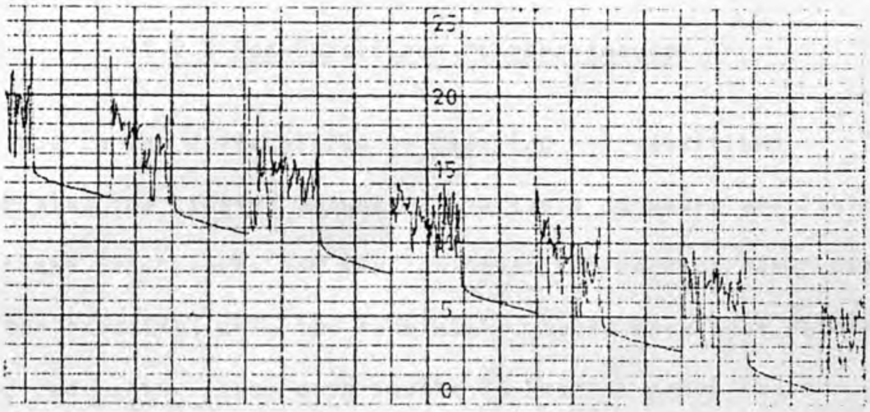


Figure 5.12 Exposure Characteristic of Grating 8 (MP60 + PATM)

Grating 9 was prepared in the same manner as grating 8 except that *para*-nitrophenylazotriphenylmethane (p-NAT) was used as the sensitizer. Talystep traces for this grating at three different exposures are shown, (Figure 5.13a, b and c). Exposure times are all greater than for the same polymer sensitized with PATM (grating 8) and in all cases the resist lines possess the ragged tops seen only in the lowest exposure step of grating 8. Removal of unexposed resist is good in all three traces however.

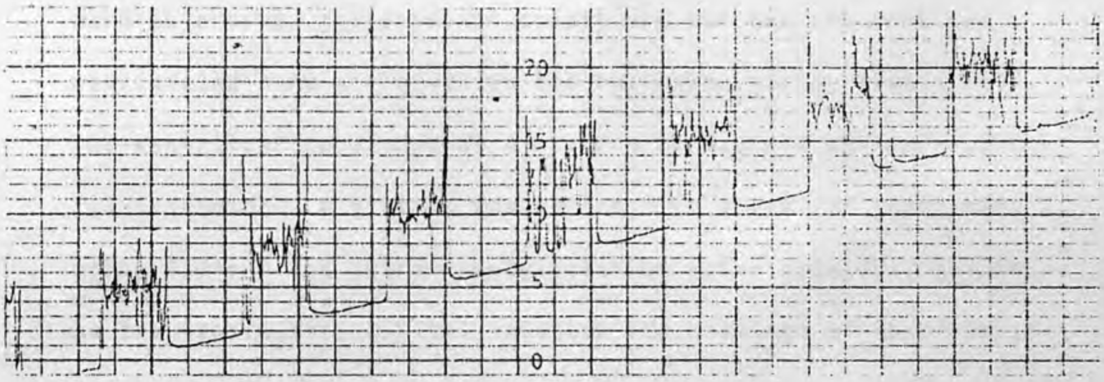
Grating 10 was prepared by sensitizing MP59 with PATM. MP59 is based on MP10 and therefore has a lower methacrylic acid content than MP37 based polymers. It has proved less useful in imaging experiments than similar polymers based on MP37. Grating 10 (Figure 5.14) is moderately good, although an excessive exposure time was required to record the image.

These last two examples show the generally observed trends: that PATM is a better sensitizer than p-NAT and that MP37-based polymers are superior to otherwise similar polymers with lower acid contents



vertical scale 200Å/division

a) (75m exp.)



vertical scale 200Å/division

b) (90m exp.)

vertical scale 200Å/division

c) (105m exp.)

Figure 5.13 Talystep of Grating 9 (MP60 + pNAT, 10 lmm^{-1})

vertical scale 200Å/division

Figure 5.14 Talystep of Grating 10 (MP59 + PATM, 10 lmm^{-1})

5.2.2 Red-Sensitized Polymer Images

Due to the difficulties of handling red-sensitized materials, the limited amounts of suitable polymers available for these experiments and the low power helium-neon laser used for the exposure, only low resolution images have been recorded using red light. These experiments do however prove that red-sensitization of our materials is possible, which was the main objective. The exposure conditions for the two gratings represented here are given in the following table, (Table 5.4). The sensitizer consisted of a mixture of Azure A and perinaphth-1,3-indandione. A grating was recorded in a similar experiment using Azure A and tetra-n-butylammonium *para*-toluenesulphinate as the sensitizer, but the solution and coatings of this resist fomulation deactivated rapidly in the dark.

grating no.	resist	exposure time	lmm^{-1}	developer
11	MP62	30m	2	60% A/PA
12	MP62	10m	10	60% A/PA

A = acetone, PA = n-pentyl acetate.

Table 5.4 Exposure Conditions for Red-Sensitized Images

Optical micrographs reveal the structure of grating 11 (Figure 5.15) and grating 12 (figure 5.16). Residual dye is evident over the surface of these plates, possibly indicating that Azure A is not ideal for polymer imaging applications using this developer. In sensitization experiments using red laser light, methylene blue has been shown to be superior to Azure A in initiating dye-sensitized photopolymerization, (Section

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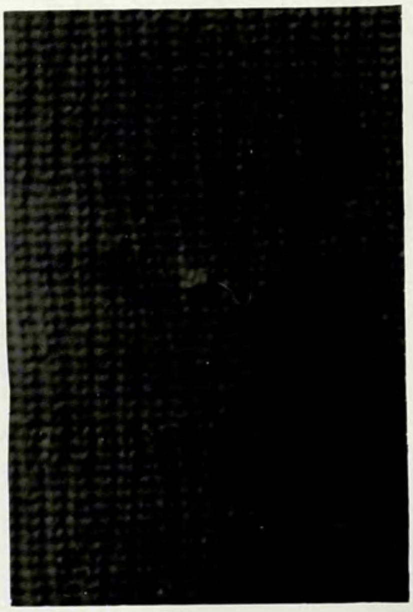
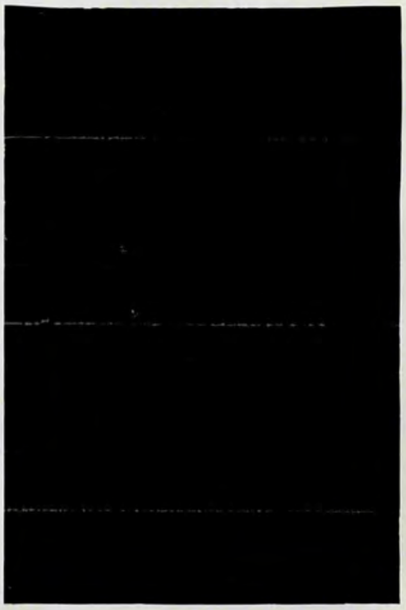
TOP LEFT: Figure 5.15 Photomicrograph of Grating 11 (MP62 + Azure A/perinaphth-1,3-indandione, 2 lmm^{-1}).

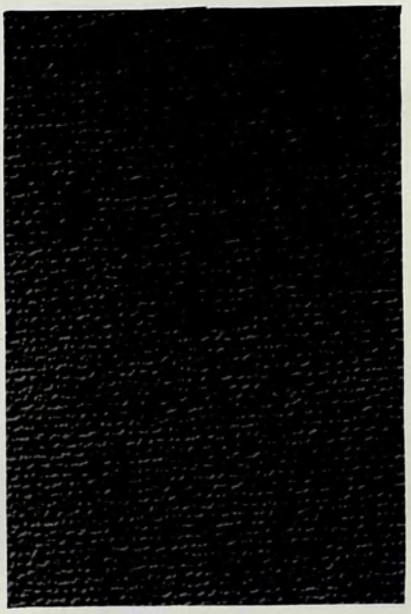
TOP RIGHT: Figure 5.16 Photomicrograph of Grating 12 (MP62 + Azure A/perinaphth-1,3-indandione, 10 lmm^{-1}).

BOTTOM LEFT: Figure 5.17 Photomicrograph of Grating 13 (MP60 + PATM, 600 lmm^{-1}).

BOTTOM RIGHT: Figure 5.18 Photomicrograph of Grating 14 (MP62 + PATM, 1200 lmm^{-1}).







4.1.5), despite the latter dye's absorption maximum being centred on 633nm. Image quality possibly, and sensitivity certainly may therefore be improved by using methylene blue. Methylene violet, while performing well in solution polymerization experiments, failed to produce an image when used to sensitize a polymer coating, probably because not enough dye would dissolve in the polymer solution.

5.2.3 High Resolution Polymer Images

The switch to organic solvent development greatly increased the image quality and resolution capability of our polymers. In order to investigate the resolution obtainable some high resolution images were recorded. A laser generated diffraction pattern was used to expose PATM-sensitized polymer coatings. The exposure conditions used were those for the recording of blazed gratings, (Section 1.4.3) as this set-up is the most stable for long exposure times. The light source was an argon laser operating at 458nm with an output power of around 400mW. Two polymer samples were used in these experiments (MP60 and MP62) and gratings of 600 and 1200 lmm^{-1} were recorded. The conditions for these experiments are given in the table below, (Table 5.5).

grating no.	resist	exposure time	lmm^{-1}	developer
13	MP60 + PATM	40m	600	60% A/PA
14	MP62 + PATM	40m	1200	15% A/PA

A = acetone, PA = n-pentyl acetate.

Table 5.5 Exposure Conditions for High Resolution Polymer Images

Grating 13 was recorded in MP60. The grating surface has a matt appearance (probably due to some inorganic deposit) and the grating structure is uneven and broken, as seen under the optical microscope, (Figure 5.17). The Talystep trace for this grating (not shown) shows no recognizable structure and is extremely noisy. The scanning electron microscope reveals the structure of this grating in more detail, (Figure 5.19). Distortion of the grating structure is evident in the form of links between the polymer features and a poor transfer of the blazed profile. Distortions of this type are seen when the solvent used for the development is one which causes the image to swell excessively[180] or when "shock-rinsing" is used.[180] The exposure conditions of grating 13 were used in an attempt to record a 1200 lmm^{-1} grating but the result was of very poor quality with the image only covering part of the plate.

MP62, which has a higher conversion to the methacrylate ester than MP60, and which was reprecipitated twice, was used successfully to record 1200 lmm^{-1} gratings at various exposure times. One of these gratings is represented here as grating 14. The image recorded using this polymer is much cleaner in appearance than that produced using MP60 and the Talystep for this grating (Figure 5.21) shows a regularly repeating structure, albeit with a rather low depth modulation. The photomicrograph (Figure 5.18) and electron micrograph (Figure 5.20) both show similar structures, the low depth modulation making photographic contrast rather low however. An interesting feature of these photographs is a ripple-like pattern which can be seen across the whole of the surface of the resist image, the direction of which is at right-angles to the linear grating. This effect is seen in all of the gratings of this type examined

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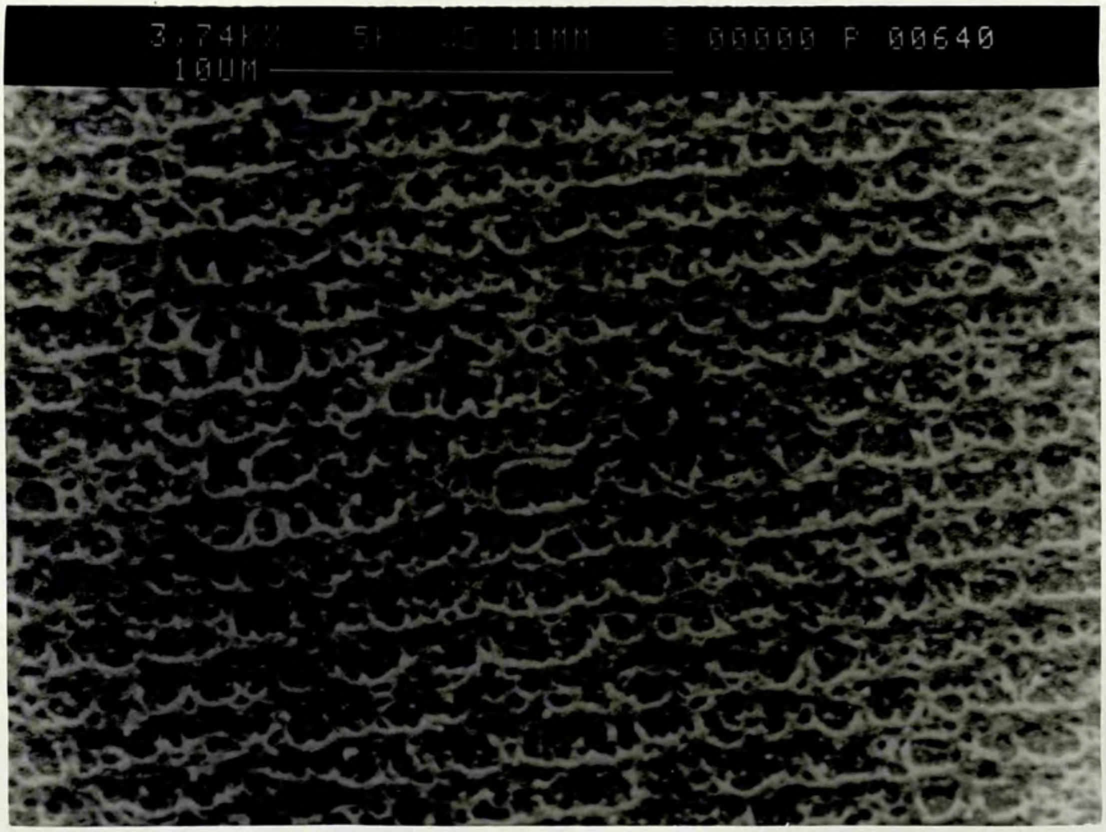
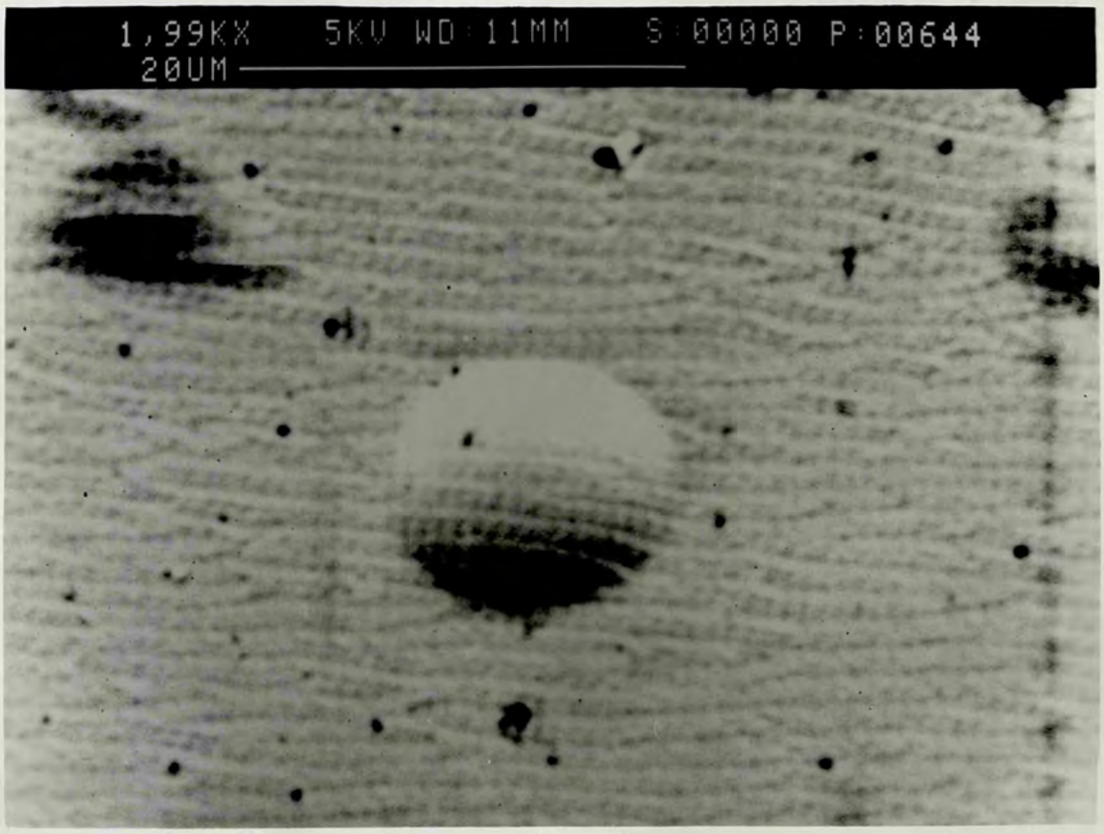
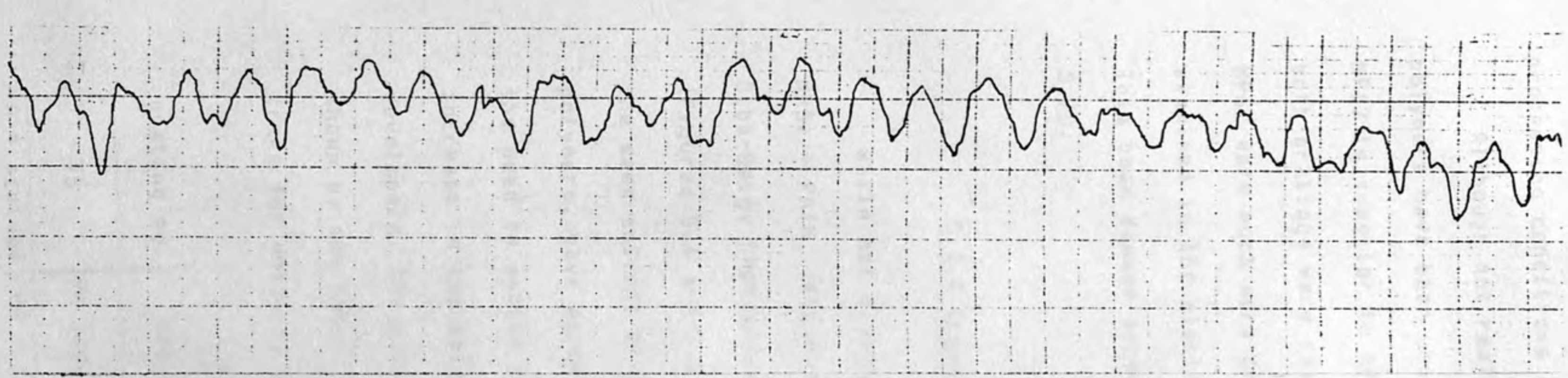
TOP: Figure 5.19 Scanning Electronmicrograph of Grating 13 (MP60 + PATM, 600 lmm^{-1}).

BOTTOM: Figure 5.20 Scanning Electronmicrograph of Grating 14 (MP62 + PATM, 1200 lmm^{-1}).

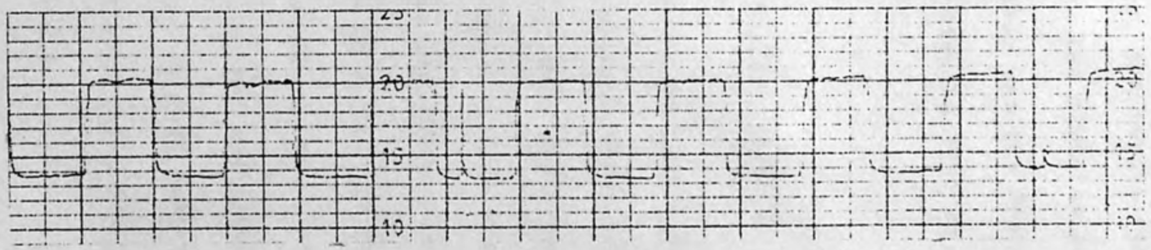

3,74KX 5KV WD 11MM S 00000 P 00640
10UM


1,99KX 5KV WD:11MM S:00000 P:00644
20UM



vertical scale 40Å/division

Figure 5.21 Talystep of Grating 14 (MP62 + PATM, 1200 lmm^{-1})



vertical scale 200Å/division

Figure 5.22 Talystep of Grating 15 (Mü1771/2316, 10 lmm^{-1})

by microscopy and is presumably an artifact introduced by the processing conditions or during the exposure.

Although not really comparing like with like, since the polymers have been used to record gratings of different pitches, MP62 is superior to MP60 as might reasonably be expected. While both gratings were coated in aluminium, the images recorded in MP62 were much more prone to damage by the electron beam when examined in the electron microscope than was the MP60 image. This beam damage accounts for the blistering seen in Figure 5.20.

5.2.4 Organic Development of Mü 1771/2316

While not giving images as rough as aqueously developed MP51 + PATM, (Figures 5.1 and 5.2), aqueous development of the Ciba-Geigy photopolymer, Mü 1771/2316, gave distorted images, (Figures 5.4 and 5.5). Switching to organic development, using the same solvent mixtures found to be effective with our own polymers, gave extremely good images with this polymer without the need to modify the processing sequence. No noticeable increase in the speed of this material was seen when changing developers. The clean images produced by this combination is shown by the result of grating 15 (Table 5.6), the Talystep trace for which is shown, (Figure 5.22).

grating no.	resist	exposure time	lmm^{-1}	developer
15	Mü 1771/2316	41/45/50/55m	10	60% A/PA

A = acetone, PA = n-pentyl acetate.

Table 5.6 Exposure Conditions for Grating 15

In all of the experiments employing this polymer, unsensitized coatings were used, although the results of solution experiments (Section 4.2) suggest that great increases in the photographic speed of coatings of this polymer may be achieved by sensitization with any of a range of compounds.

CONCLUSION

6 Conclusions

6.1 The Polymer System

In fulfilling the specifications for a red-sensitive photoresist, a compromise has had to be made between the resolution capability and spectral sensitivity and the other initially specified requirements. In particular the aqueous developer was not retained, the switch to organic solvent development having a profound effect on the resolution seen in photopolymer images.

There is no doubt that the polymer system described in this thesis "works", i.e. that is it is capable of producing relief images on exposure to light when coated with a suitable sensitizer and given an appropriate development. The present polymers, however, cannot be seen as the optimum state of this material. A number of important factors remain to be investigated such as the effect of polymer molecular weight, and higher conversions than those already obtained, on the imaging results.

When considered as a possible commercial material a number of disadvantages are evident: the synthesis is long and moderately complex and consequently would prove expensive in manufacture. Some of the modifications described in Chapter 3 might be worthy of consideration as simplifications to the synthesis of cross-linkable polymers. The polymer has so far only been prepared in small batches and a significant loss of material has occured at each precipitation step. This loss of material could be due to the requirement for a low molecular weight polymer, soluble to some extent in the nonsolvents used. A number of precipitation steps are required to produce a polymer capable of giving cleanly developed images. The loss of material might improve when larger scale preparations are carried out, alternatively preparative gel-permeation chromatography might be considered as a method of purification.

The development and imaging properties of the polymers have not been fully investigated due to a lack of suitable materials. The organic organic solvent developers based on acetone were found after a few experiments and very probably do not represent the ideal development conditions for these materials. The search for developers for photoresist is an empirical problem, the choice of solvent having a marked effect on the image resolution and appearance. Factors such as temperature and humidity can also have drastic effects on polymer images.[234]

The polymer has performed reasonably well in resolution tests up to 1200 lmm^{-1}, although the depth modulation of the final images was low, the resolution limit has not yet been reached. This resolution is approaching that required for holographic recording. The resolution requirements for a holographic recording material are less stringent at long wavelengths than for blue or violet light, however features smaller than the wavelength of the recording light may still need to be resolved. For helium-neon laser light, 633nm, this represents a line spacing of 1680 lmm^{-1}. The actual carrier frequency of a hologram depends on the geometry of the system as well as the wavelength of the recording light, as explained in the Introduction, (Section 1.4.1). If an efficient infra-red sensitizer could be found for this polymer, the resolution achieved so far would be sufficient to use this material to produce holographic optical elements for infra-red imaging.

The advantage of a polymer imaging system of the type described in this thesis is that the polymer structure is not dependant on the wavelength of the light used for the exposure, the wavelength specific part being the sensitizer included in the coatings. The same polymer is therefore capable of being cross-linked by light from both extremes of the visible spectrum, as has been shown in this work, merely by the judicial selection of the sensitizer used. The limiting wavelengths at which imaging is possible may therefore be defined by the regions of the spectrum at which the polymer itself shows strong absorptions.

6.2 The Sensitizing System

Red-sensitized imaging of these polymers has been demonstrated using two photoredox initiators and a number of other photoredox initiator combinations have been found. Further investigation is clearly needed, both to clarify somewhat ambiguous results and to put the results using these initiators onto a quantitative basis. In any further work the role of oxygen should also be considered. No attempts have been made to work in oxygen free atmospheres since the ideal resist material should be capable of imaging on an optical bench where the provision of special atmospheres is not a requirement of normal working. The presence of oxygen is found either to be necessary for,[130,131] or to inhibit photopolymerization,[128,129] depending on the nature of the photoredox initiator used.

The experiments in which polymer coatings were sensitized to red laser light were necessarily limited by the quantity of polymer available for these experiments and the low power red laser available at the National Physical Laboratory for the exposures. Difficulties in the handling of red-sensitized materials, calling for working in complete darkness, also accounted for loss of material in the filtration and coating operations.

In the light of these difficulties, the recording of, albeit low resolution, red-exposed images is a significant result and should be seen as extremely encouraging. Other red-sensitive intitators could have been investigated with these polymers if sufficient was available. Some of these initiators, when used with acrylamide, appear to have good dark stability, in the short term at least.

6.3 Applications

The materials described in this thesis have been developed to fulfill the need for a high resolution resist material capable of forming images on exposure to long wavelength light. In this application the commercial materials have little value, as sensitivity to short wavelength light is both a requirement of, and an advantage to, their major consumers, the microelectronics industry. As well as resists sensitive to ultra-violet light, much research effort is also centred on the development of materials sensitive to high energy radiation for X-ray and electron beam lithography. These materials are also for use by the microelectronics industry where the finer lithographic masks made possible by these techniques are their main attraction.

X-ray resists have also found a use for which the ideal specification is at odds with the precise requirements for a material for lithographic mask replication. In soft X-ray contact microscopy,[235-237] like holographic work, the resist material used for imaging must posess a good contrast range, rather than the high contrast exposure characteristic ideal for making masks for etching.

Positive-working X-ray resists are generally simple polymers and copolymers which are degraded by the exposing radiation. Polymers which have been reported as X-ray resists (which are generally also electron resists) include[238] poly methyl methacrylate, (PMMA), copolymers of methyl methacrylate and methacrylic acid, (P(MMA-MA)), or of glycidyl methacryate and ethyl acrylate, (P(GMA-EA) or COP), and "terpolymer".[196] Since all of these materials are polymers of fairly simple acrylate and methacrylate monomers, our own polymers may well prove useful in this role, even in unfunctionalized form. Such an investigation is envisaged for the future.[239] It may be that higher molecular weight polymers are required than those currently available to us to take fullest advantage of a degradative imaging mechanism. A new development system would also need to be found to take advantage of imaging by this means as our current developers are intended to completely remove uncross-linked resist. A developer for a positive-working resist must leave the original, unmodified coating untouched and only etch those areas where radiation-promoted degradation has occured.

Soft X-ray contact microscopy[235-237] is currently arousing interest as a method of examining biological samples without extensive (and possibly destructive) pre-treatment required of other forms of microscopy. In this technique a live sample is mounted in intimate contact with a resist coating. A high powered, pulsed laser is fired at a target which vapourizes with the formation of a plasma. Ions and electrons recombine in the plasma, the result of which being a pulse of X-rays of very short duration. Passing through the sample, this pulse of X-rays then leaves a latent image in the resist in the form of a 1:1 shadow print, modulated by internal structures which absorb the radiation during its passage through the sample. Development of the resist, (carefully, by inspection), gives a polymer relief image which may then be examined by conventional microscopy techniques. Apart from the absence of destructive sample preparation, and the possible introduction of misleading artifacts which this might entail, there is evidence that detail is revealed by this technique that may otherwise be missed by optical microscopy or by transmission electron microscopy.

EXPERIMENTAL

7 Experimental I: Synthesis

7.1 General Details and Instrumentation

Melting points were determined using an Electrothermal Melting Point Apparatus and are uncorrected.

Elemental analyses were performed by Miss M. Easton or Mrs. E. Whitaker at R.H.B.N.C., Egham.

Infra-red spectra were recorded on nujol mulls or liquid films using a Perkin Elmer 1710 Infra-red Fourier Transform Spectrometer or a Perkin Elmer 197 Infra-red Spectrometer.

UV/visible spectra were recorded using a Perkin Elmer 55S UV-VIS Spectrophotometer and 1cm quartz cells.

Nuclear magnetic resonance spectra were referenced to TMS and were recorded on the following instruments:

Perkin Elmer R-24B High Resolution NMR Spectrometer: 60MHz ^{1}H spectra.

Jeol FX-90Q Fourier Transform NMR Spectrometer: 90MHz ^{1}H and 22.5MHz ^{13}C spectra.

Nicolet 293A NMR Spectrometer with 1180 Data System: 200.1MHz ^{1}H and 50.3MHz ^{13}C spectra.

Bruker WM-250 Fourier Transform NMR Spectrometer, (King's College): 250MHz ^{1}H polymer spectra.

Bruker WH-400 Fourier Transform NMR Spectrometer, (Queen Mary College): 400MHz ^{1}H polymer spectra.

7.2 Polymer Preparations

The polymers, for which details of their syntheses follow, were numbered for reference in chronological sequence, the first being designated MP1, the second MP2 and so on. The reference number therefore does not bear any relation to polymer structure, except by reference to the preparations and tables that follow. A further series of polymers, all copolymers of methyl methacrylate and methacrylic acid, have reference numbers preceeded by MPX. The number following these letters is the mole percentage of methacrylic acid present in the mixture of monomers polymerized.

7.2.1 Polymerization Reactions

7.2.1.1 The Synthesis of Copolymers of Methacrylic Acid, Methyl Methacrylate and 2-Hydroxyethyl Methacrylate

Purification of Starting Materials and Reagents

Solvents and monomers were redistilled before use:-

2-Methoxyethanol was distilled from anhydrous potassium carbonate at atmospheric pressure.

Butanone was distilled from anhydrous calcium chloride at atmospheric pressure.

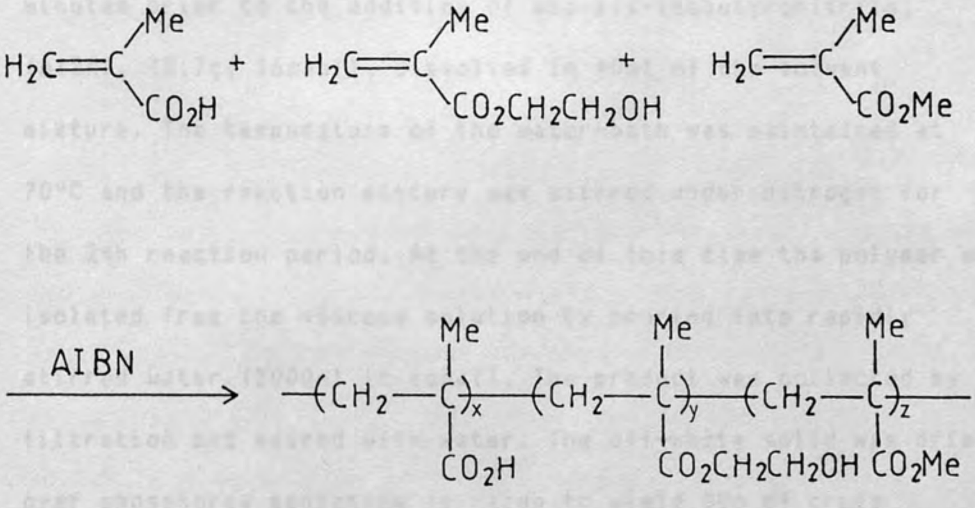
Monomers were redistilled at reduced pressure, the temperature being kept low enough to prevent thermal polymerization:-

Methyl methacrylate (MMA) was collected boiling at 24-26°C at approximately 35mm Hg.

Methacrylic acid (MAA) was collected boiling at 32°C at 2mm Hg.

2-Hydroxyethyl methacrylate (HEMA) was collected boiling at 53°C at 0.5mm Hg. Some thermal polymerization always occured in the distillation flask when this was distilled.

The general reaction being followed in these preparations is shown below, (Scheme 7.1). Percentage yields are quoted relative to the complete polymerization of all the monomers present in the polymerization mixture and ignore contributions from the initiator. The theoretical analysis figures have also been calculated based on monomer alone and ignore contributions from the initiator.



Scheme 7.1 Polymerization of Methyl Methacrylate, Methacrylic Acid and 2-Hydroxyethyl Methacrylate

Spectroscopically the polymers are very similar and so comprehensive details are not given here for each preparation. A discussion of the proton nmr spectra of these polymers can be found in Chapter 2 along with spectra of typical derivatized and underivatized polymers. Infra-red spectra of these polymers are characterized by a broad carbonyl peak at around 1730 cm^{-1}.

MP1

A 700ml flanged flask was charged with a mixture of freshly distilled (less than 24h beforehand) monomers, methacrylic acid, (MAA), (14.0g, 13.8ml, 0.16mol), methyl methacrylate, (MMA), (24.0g, 25.6ml, 0.24mol) and 2-hydroxyethyl methacrylate, (HEMA), (52.1g, 50.3ml, 0.40mol) dissolved in 470ml of a 1:1 mixture of butanone and 2-methoxyethanol. The flask, fitted with a mechanical stirrer, thermometer, nitrogen inlet and reflux condenser with calcium chloride guard tube, was supported in a thermostatted water-bath held at 70°C. The polymerization mixture was stirred under a slow stream of nitrogen for 30 minutes prior to the addition of azo-*bis*-isobutyronitrile, (AIBN), (2.7g, 16mmol), dissolved in 40ml of the solvent mixture. The temperature of the water-bath was maintained at 70°C and the reaction mixture was stirred under nitrogen for the 24h reaction period. At the end of this time the polymer was isolated from the viscous solution by pouring into rapidly stirred water (5000ml in total). The product was collected by filtration and washed with water. The off-white solid was dried over phosphorus pentoxide *in vacuo* to yield 80g of crude material. Batches of this product, 20g at a time, were dissolved in methanol (200ml) and precipitated into water (2000ml) yielding between 14 and 17g of purified material after drying. The total yield was 61g (68%) of a white powder. Found: C, 54.62; H, 7.65. Calc: C, 56.65; H, 7.73%.

MP10

The conditions of the preparation given above for MP1 were repeated yielding 75g of crude product which gave 46g (51%) of a white powder after reprecipitation. Freeze-drying was used as a rapid method for the removal of water from the precipitated polymer. Found: C, 54.02; H, 7.91. Calc: C, 56.65; H, 7.73%.

MP14

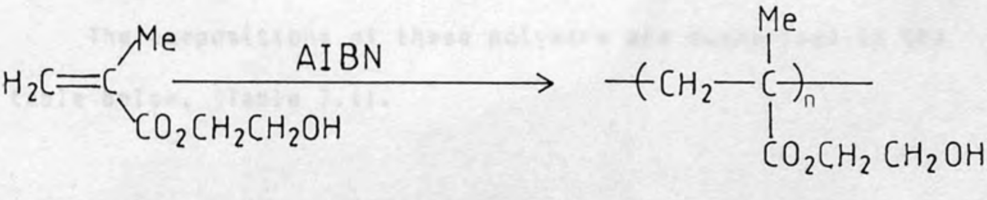
The conditions of the preparation given above for MP1 were repeated using the same total concentration of monomers and volume of solvent but the monomer mixture was modified. This was methacrylic acid, (17.5g, 17.3ml, 0.20mol), methyl methacrylate, (20.0g, 21.3ml, 0.20mol) and 2-hydroxyethyl methacrylate, (52.0g, 50.3ml, 0.40mol). The crude yield of polymer was 78g (87%). Reprecipitation of 50g of this material, in two batches, gave 43g of the final product as a white powder. Found: C, 53.97; H, 7.80. Calc: C, 56.48; H, 7.69%.

MP37

The basic preparation method of MP1 was again repeated with modified monomer ratios. The quantities used were: methacrylic acid, (25.5g, 25.1ml, 0.296mol), methyl methacrylate, (10.4g, 11.1ml, 0.104mol) and 2-hydroxyethyl methacrylate, (52.0g, 50.3ml, 0.40mol). Precipitation into water gave a swollen product which formed a glassy, brittle pinkish solid on drying, crude yield 90g. Reprecipitation from methanol into ethyl acetate, and later batches into ether, gave 71g (81%) of a colourless, powdery solid. Found: C, 52.68; H, 7.31. Calc: C, 56.03; H, 7.59%.

7.2.1.2 Homopolymer Preparations

A homopolymer of 2-hydroxyethyl methacrylate (MP11) was prepared under similar conditions to the preparation of MP1, (Scheme 7.2).

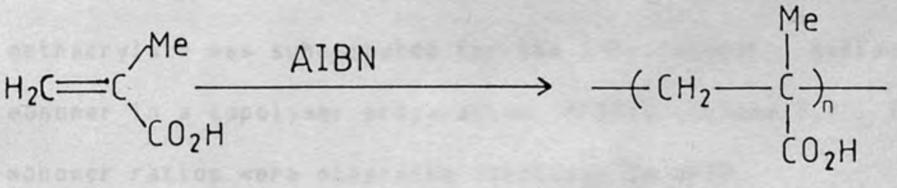


Scheme 7.2 Polymerization of 2-Hydroxyethyl Methacrylate

MP11

2-Hydroxyethyl methacrylate, (52.0g, 50.3ml, 0.40mol), was polymerized by the method of MP1, the volume of solvent and weight of initiator being reduced by half. The reaction time was 44h. Attempts at precipitating the polymer into aqueous media failed, giving a two phase system. A solid was obtained by pouring away the water and allowing the polymer to dry. This

A homopolymer of methacrylic acid (MP12) was also prepared under similar conditions to the preparation of MP1, (Scheme 7.3).



Scheme 7.3 Polymerization of Methacrylic Acid

MP12

Methacrylic acid, (35.0g, 34.5ml, 0.40mol) was polymerized in a half-scale reaction as described above. After a reaction time of 22h the polymer was precipitated into 4M aqueous hydrochloric acid. Reprecipitation from methanol gave 25g (71%) of an off-white solid after drying.

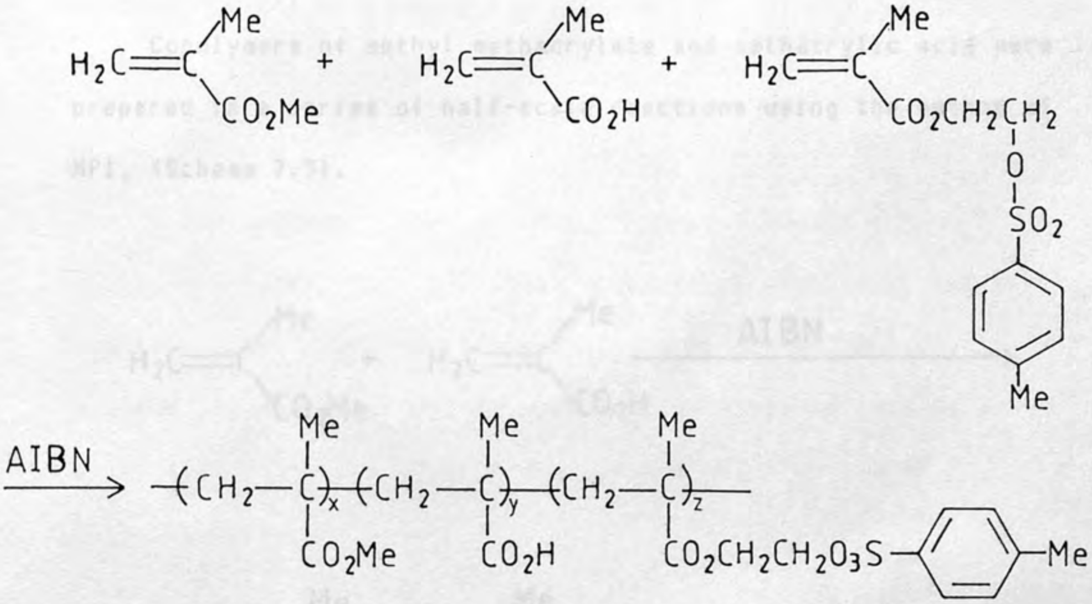
The compositions of these polymers are summarized in the table below, (Table 7.1).

	mole percentage		
polymer	MAA	MMA	HEMA
MP1	20	30	50
MP10	20	30	50
MP14	25	25	50
MP37	37	13	50
MP11			100
MP12	100		

Table 7.1 Compositions of Polymers

7.2.1.3 Tosylated Polymer

The *para*-toluenesulphonate ester of 2-hydroxyethyl methacrylate was substituted for the 2-hydroxyethyl methacrylate monomer in a copolymer preparation (MP39), (Scheme 7.4). The monomer ratios were otherwise identical to MP37.



Scheme 7.4 Polymerization of Methyl Methacrylate, Methacrylic Acid and 2-Hydroxyethyl Methacrylate *para*-Toluenesulphonate

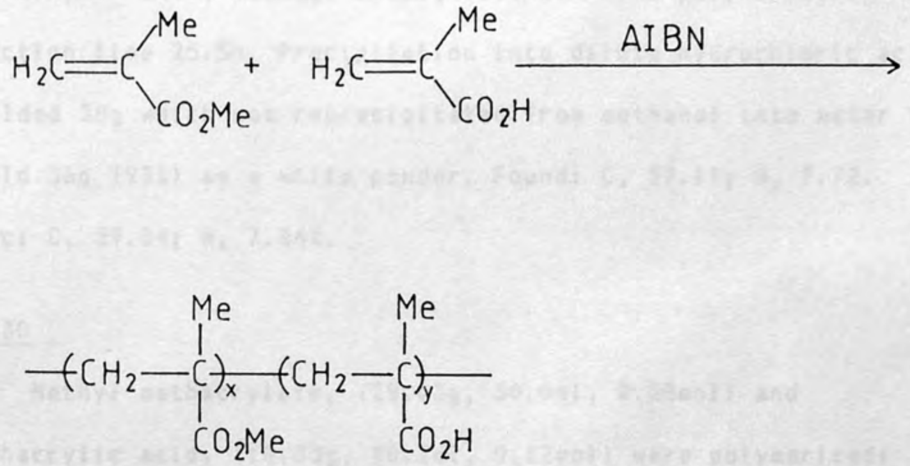
MP39

In a one-third scale preparation using the method of MP1, 2-(4-toluenesulphonyl)ethyl methacrylate, (37.9g, 0.133mol), methacrylic acid, (8.49g, 8.4ml, 0.099mol) and methyl methacrylate, (3.47g, 3.7ml, 0.035mol) were polymerized. Ether was used as the non-solvent in the precipitation step. The yield of reprecipitated polymer was 17g (34%) of a white solid.

The nmr spectrum of a sample of this product, in addition to the anticipated peaks, showed some due to solvent having displaced some of the tosylate groups. On long-term storage at room temperature the polymer had become insoluble in all solvents tried, indicating that cross-linking had occured.

7.2.1.4 Copolymers of Methyl Methacrylate and Methacrylic acid

Copolymers of methyl methacrylate and methacrylic acid were prepared in a series of half-scale reactions using the method of MP1, (Scheme 7.5).



Scheme 7.5 Polymerization of Methyl Methacrylate and Methacrylic Acid

MPX10

Methyl methacrylate, (36.04g, 38.5ml, 0.36mol) and methacrylic acid, (3.44g, 3.4ml, 0.04mol) were polymerized: reaction time 26h. Precipitation into dilute hydrochloric acid yielded 41g which was reprecipitated from dimethyl formamide (DMF) into water to yield 30g (76%) as a white solid. Found: C, 58.59; H, 7.92. Calc: C, 59.59; H, 7.98%.

MPX20

Methyl methacrylate, (32.04g, 34.2ml, 0.32mol) and methacrylic acid, (6.89g, 6.8ml, 0.08mol) were polymerized: reaction time 25h. Precipitation into dilute hydrochloric acid yielded 38g which was reprecipitated from DMF into water to yield 30g (77%) as a white powder. Found: C, 57.99; H, 7.87. Calc: C, 59.23; H, 7.89%.

MPX25

Methyl methacrylate, (30.04g, 32.1ml, 0.30mol) and methacrylic acid, (8.61g, 8.5ml, 0.10mol) were polymerized: reaction time 25.5h. Precipitation into dilute hydrochloric acid yielded 38g which was reprecipitated from methanol into water to yield 36g (93%) as a white powder. Found: C, 57.17; H, 7.72. Calc: C, 59.04; H, 7.84%.

MPX30

Methyl methacrylate, (28.03g, 30.0ml, 0.28mol) and methacrylic acid, (10.33g, 10.2ml, 0.12mol) were polymerized: reaction time 24h. Precipitation into dilute hydrochloric acid yielded 37g which was reprecipitated from DMF into water to yield 36g (94%) as a white solid. Found: C, 57.06; H, 7.59. Calc: C, 58.86; H, 7.79%.

MPX40

Methyl methacrylate, (24.03g, 25.7ml, 0.24mol) and methacrylic acid, (13.77g, 13.6ml, 0.16mol) were polymerized: reaction time 24h. Precipitation into dilute hydrochloric acid yielded 35g which was reprecipitated from DMF into water to yield 34g (90%) as a white powder. Found: C, 56.14; H, 7.57. Calc: C, 58.46; H, 7.70%.

The composition of these copolymers is summarized in the table below, (Table 7.2).

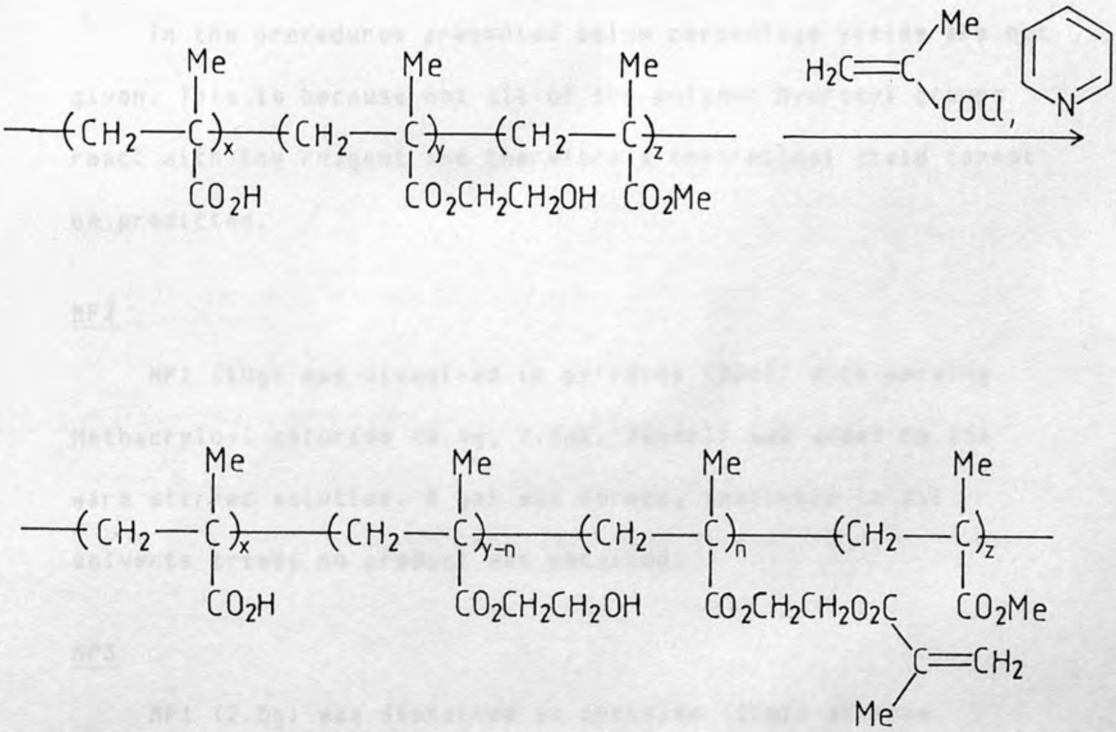
polymer	mole percentage MAA	MMA
MPX10	10	90
MPX20	20	80
MPX25	25	75
MPX30	30	70
MPX40	40	60

Table 7.2 Compositions of Copolymers

7.2.2 Derivatization of Polymers

The purpose of the derivatization step is to convert the hydroxyl group of the hydroxyethyl methacrylate residue of the copolymers, (MP1, 10, 14 and 37), to the methacrylate ester group. Initial studies used a variety of conditions. Later preparations varied the quantities of the solvent and reagent used, (methacryloyl chloride). A number of further preparations using methacryloyl chloride and methacrylic anhydride followed. Model reactions using acetyl chloride and acetic anhydride were also carried out.

The reaction with methacryloyl chloride is shown below, (Scheme 7.5).



Scheme 7.5 Derivatization of Copolymers with Methacryloyl Chloride

7.2.2.1 Esterifications Using Methacryloyl Chloride

Purification of Starting Materials and Solvents

Pyridine, 2-picoline (2-methyl pyridine) and 2,6-lutidine (2,6-dimethyl pyridine) were all distilled from KOH pellets at atmospheric pressure and stored over KOH.

Dimethyl formamide (DMF) was stirred over calcium hydride before distillation at reduced pressure. Redistilled DMF was stored over 4A molecular seive.

Methacryloyl chloride (Aldrich) was distilled at reduced pressure, (20-22°C at 37mm Hg). Redistilled reagent was stored in a refrigerator for no more than two weeks and preferably less than 24h before use.

In the procedures presented below percentage yields are not given. This is because not all of the polymer hydroxyl groups react with the reagent and therefore a theoretical yield cannot be predicted.

MP2

MP1 (10g) was dissolved in pyridine (50ml) with warming. Methacryloyl chloride (8.0g, 7.5ml, 76mmol) was added to the warm stirred solution. A gel was formed, insoluble in all solvents tried; no product was obtained.

MP3

MP1 (2.5g) was dissolved in pyridine (20ml) at room temperature. Methacryloyl chloride (1.1g, 1.0ml, 10mmol) was added and the solution was stirred at room temperature for 30 minutes. Methanol (50ml) was added and the polymer was obtained by precipitation into dilute hydrochloric acid. The yield of crude polymer was 2.13g of a white solid. The product was swollen by polar solvents such as methanol but would not dissolve.

MP4

MP1 (10g) was dissolved in pyridine (50ml) and cooled in an ice-bath before the addition of methacryloyl chloride (8.0g, 7.5ml, 76mmol), the addition taking place over about 2h. Further pyridine (20ml) was added after 1.5h to aid stirring. Stirring was continued for a further hour at room temperature before the addition of methanol (50ml) and precipitation into dilute hydrochloric acid. Precipitation of the polymer only occured on standing for several days, the crude yield being 11.61g. This material was reprecipitated to yield 9.06g of a white solid which was subsequently found to swell but not dissolve in polar solvents.

MP5

MP1 (2,5g) was dissolved in pyridine (40ml) with mechanical stirring. The flask was cooled in an ice-bath and wrapped in foil to exclude light. Methacryloyl chloride (2.1g, 2.0ml, 20mmol) was added over about 20 minutes and the flask was stirred overnight. The product again precipitated on standing after pouring into dilute hydrochloric acid. The crude yield was 2.43g and 1.81g of a white powder after reprecipitation.

MP6

The conditions of MP5 were repeated on MP1 (2.7g) using the same quantity of reagent: Crude yield 2.09g, 1.66g of a white solid after reprecipitation.

MP7

The conditions of MP5 were repeated using triethylamine (40ml) and pyridine (3ml) as the solvent. An insoluble gel resulted; no product was obtained.

MP8

The conditions of MP5 were repeated using 2,6-lutidine (15ml) as the solvent: Crude yield 1.97g, 1.24g of a white solid after reprecipitation.

MP9

The preparation above, MP8, was repeated on double the scale, using MP1 (5.0g) and methacryoyl chloride (4.28g, 4.0ml, 41mmol). The product did not redissolve in methanol.

MP13

The conditions of the preparation above, MP9, were repeated using pyridine (30ml) as the solvent. No product was obtained.

MP15

The conditions of MP5 were repeated on MP1 (2.5g) using 2-picoline (15ml) as the solvent. The crude yield was 2.99g; 1.71g of a white solid after reprecipitation.

MP16

The conditions of MP15 were repeated using MP10 (2.5g) in 2-picoline (15ml), the product being precipitated after 30 minutes reaction time. The product was found to be insoluble when reprecipitation was attempted.

MP17

MP1 (2.5g) in 2-picoline (15ml) was stirred in an ice-bath prior to the addition of methacryloyl chloride (2.1g, 2.0ml, 20mmol). The reaction mixture was stirred for 30 minutes, the flask being wrapped in foil to exclude light. Precipitation into water (200ml) and hydrochloric acid (100ml) gave 2.50g of crude product and 1.75g of a white solid after reprecipitation.

MP18

MP1 (2.5g) was dissolved in a mixture of dimethyl formamide (DMF) (13.5ml) and pyridine (1.6ml). Methacryloyl chloride (2.1g, 2.0ml, 20mmol) was added dropwise to the cooled solution. The reaction and precipitation were carried out as described above (MP17). The weight of crude product obtained was 3.22g which yielded 1.55g of a white solid after reprecipitation.

Some of the conditions for the preparations described above are tabulated below, (Table 7.3).

polymer	base polymer	wt/g	solvent	solvent volume/ml	reagent volume/ml
MP2	MP1	10	py	50	7.5
MP3	MP1	2.5	py	20	1
MP4	MP1	10	py	50	7.5
MP5	MP1	2.5	py	40	2
MP6	MP1	2.7	py	40	2
MP7	MP1	2.5	Et_3N:py	40:3	2
MP8	MP1	2.5	lut	15	2
MP9	MP1	5	lut	30	4
MP13	MP1	5	py	30	4
MP15	MP1	2.5	pic	15	2
MP16	MP10	2.5	pic	15	2
MP17	MP1	2.5	pic	15	2
MP18	MP1	2.5	DMF,py	15	2

py = pyridine, lut = 2,6-lutidine, pic = 2-picoline, DMF = dimethyl formamide.

Table 7.3 Esterification Conditions for Initial Studies

The conditions and yields for the following series of preparations, MP19-36 are tabulated below, (Table 7.4). All preparations were carried out on 2.5g of MP14.

MP19

MP14 (2.5g) was dissolved in a mixture of dimethyl formamide (13.5ml) and pyridine (1.6g, 1.6ml, 19mmol) and the reaction flask was cooled in ice. The flask was covered in foil to exclude light. Methacryloyl chloride (2.1g, 2.0ml, 20mmol) was added dropwise. The reaction mixture was stirred in ice for 30 minutes, at the end of which time methanol (15ml) was added and the polymer was precipitated by pouring into water (250ml) acidified with hydrochloric acid (50ml). The product was collected by filtration and washed with water. The crude product was reprecipitated from methanol to yield a white solid.

MP20-36

The preparation above, MP19, was repeated in a series of experiments varying the quantities of solvent and reagent used. The amount of pyridine in the solvent mixture was adjusted to take account of the quantity of reagent added. All other conditions were the same except that methanol was not added to the reaction mixture before precipitation in the cases of MP33-36.

	volumes used/ml			yield/g	
polymer	DMF	py	MACl	crude	reppt
MP19	13.5	1.6	2.0	2.24	1.12
MP20	28.5	1.6	2.0	2.01	1.67
MP21	14.0	0.8	1.0	2.00	1.54
MP22	29.0	0.8	1.0	2.33	1.65
MP23	14.0	1.2	1.5	2.25	1.90
MP24	21.0	1.6	2.0	2.30	1.66
MP25	21.3	1.2	1.5	2.48	2.14
MP26	28.8	1.2	1.5	2.44	2.23
MP27	21.7	0.8	1.0	2.26	2.03
MP28	25.5	1.0	1.25	2.43	2.13
MP29	25.0	1.2	1.5	2.54	2.22
MP30	21.3	1.0	1.25	2.44	2.22
MP31	21.3	1.2	1.5	2.37	2.10
MP32	21.3	1.2	1.5	2.34	1.56
MP33	13.4	1.6	2.0	5.23	2.23
MP34	11.8	3.2	4.0	2.53	1.48
MP35	26.8	3.2	4.0	3.32	2.66
MP36	23.6	6.4	8.0	3.49	-

py=pyridine, MACl=methacryloyl chloride, reppt=reprecipitated.

Table 7.4 Volumes of Solvents and Reagent Used and the Yields Obtained for MP19-36

MP38

The conditions of MP34 were repeated using MP37 (2.5g). Precipitation into dilute hydrochloric acid gave no product, the polymer being too water-soluble.

MP40

A second preparation using MP37 (2.5g) and the conditions of MP35 also produced no sample when precipitation was attempted.

MP44

The preparation above, MP40, was repeated, this time *para*-benzoquinone (0.1g) was included in the reaction mixture as a polymerization inhibitor. Again no product was obtained because of the extreme solubility of the polymer.

MP46

The conditions of MP44 were repeated, a mixture of saturated brine (300ml), water (200ml) and hydrochloric acid (25ml) being used in the precipitation step. Solid polymer was obtained but this redissolved when left in contact with water on the filter after washing.

MP49

The conditions of MP44 were again repeated using the aqueous brine work-up described above, (MP46). The soft crude material, containing water and inorganics, was washed with brine and dried over P_2O_5 to yield 5.22g. The crude product was dissolved in methanol, the solution filtered, and reprecipitated into ether. The yield was 1.68g of a white powder.

MP57

The conditions of MP49 were repeated, except that *para*-benzoquinone was not included in the reaction mixture. The crude product, 4.60g, was insoluble in organic solvents.

The conditions of the preparations described above are summarized below, (Table 7.5). All preparations were carried out on 2.5g of MP37.

polymer	volumes used/ml DMF	py	MAC	pBZ	brine work-up
MP38	11.8	3.2	4.0	-	No
MP40	26.8	3.2	4.0	-	No
MP44	26.8	3.2	4.0	0.1g	No
MP46	26.8	3.2	4.0	0.1g	Yes
MP49	26.8	3.2	4.0	0.1g	Yes
MP57	26.8	3.2	4.0	-	Yes

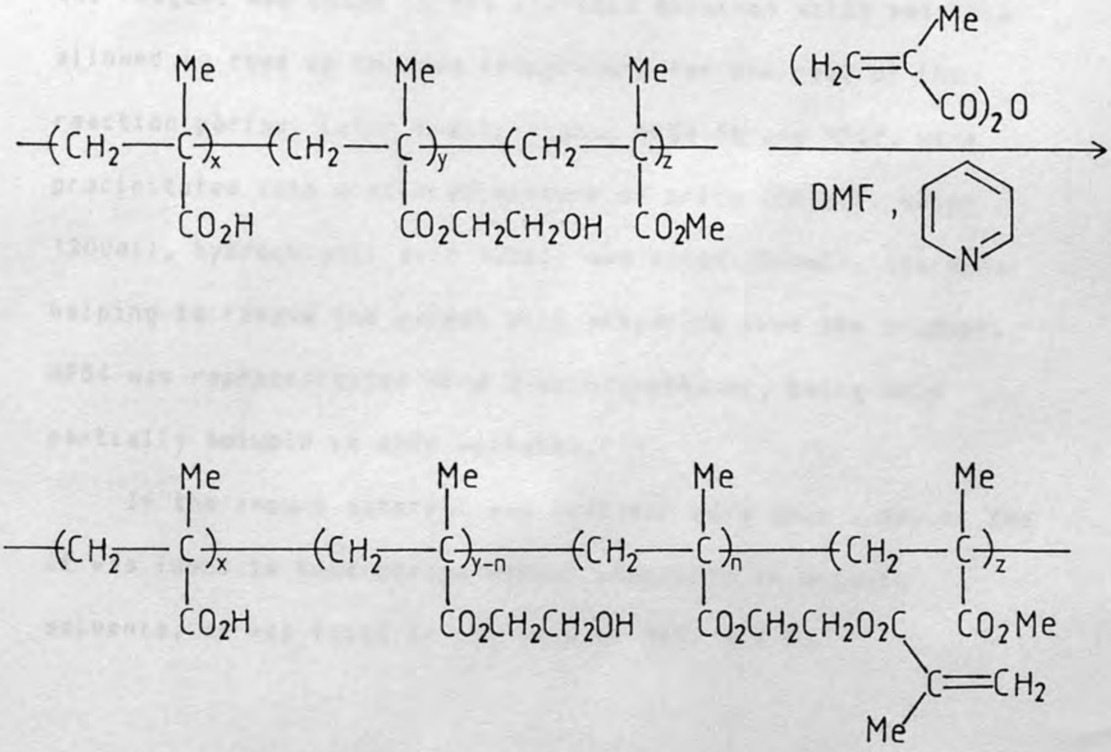
DMF = dimethyl formamide, py = pyridine, MAC = methacryloyl chloride, pBZ = *para*-benzoquinone.

Table 7.5 Conditions of Esterifications of MP37 Using Methacryloyl Chloride.

7.2.2.2 Esterifications Using Methacrylic Anhydride

Methacrylic anhydride was prepared as described in a subsequent section (Section 7.4) and redistilled before use. Solvents were treated in the same manner as described above for preparations using methacryloyl chloride.

The reaction of methacrylic anhydride with a copolymer is shown below, (Scheme 7.6).



Scheme 7.6 Derivatization of Copolymers with Methacrylic Anhydride

MP48

MP37 (2.5g) and *p*-benzoquinone (0.1g) were dissolved in dimethyl formamide (26.8ml) and pyridine (3.2ml). The flask, wrapped in foil, was cooled in ice before the addition of methacrylic anhydride (12.6g, 12.5ml, 82mmol) to the stirred solution. After 30 minutes reaction time the polymer was precipitated into brine (300ml), water (200ml) and hydrochloric acid (25ml). The polymer was washed with brine and dried over

P_2O_5 to give 7.73g. This product was dissolved in methanol, filtered and precipitated into ether to yield 1.44g of a white solid.

MP50-53, 54-56 and 58

The conditions of MP48 were repeated, keeping the quantity of polymer and volumes of solvents and reagent fixed but varying reaction time and temperature. In room temperature preparations the reagent was added to the ice-cold solution which was then allowed to come up to room temperature for the rest of the reaction period. Later preparations, MP54-56 and MP58, were precipitated into a stirred mixture of brine (300ml), water (200ml), hydrochloric acid (25ml) and ether (200ml), the ether helping to remove the excess oily anhydride from the product. MP54 was reprecipitated from 2-methoxyethanol, being only partially soluble in cold methanol.

If the impure material was left for more than a day or two it was found to have become mostly insoluble in organic solvents, as was found in the case of MP52 and 53.

The conditions are summarized below (Table 7.6) for this series of reactions along with the yields obtained.

			yields/g	
polymer	reaction time/h	Temperature	crude	reppt
MP48	0.5	ice	7.73	1.44
MP50	1	ice	3.26	2.20
MP51	2	ice	3.38	2.30
MP52	2	R.T.	-	-
MP53	4	ice	-	-
MP54	4	ice	-	2.01
MP55	2	R.T.	3.09	2.18
MP56	2	ice	4.21	0.90
MP58	2	ice	2.59	1.33

Table 7.6 Reaction Times and Temperatures and Yields Obtained in Reactions of MP37 with Methacrylic Anhydride

<u>MP59</u>

MP10 (20g) in dimethyl formamide (214.4ml) and pyridine (25.6ml) was reacted with methacrylic anhydride (100ml, 0.67mol) in the presence of *para*-benzoquinone (0.8g) for 4h in an ice-bath under nitrogen. Precipitation of the product was achieved by pouring into a rapidly stirred mixture of water (2000ml), hydrochloric acid (25ml) and ether (200ml). The product at this stage was a swollen lump which was immediately dissolved in methanol (100ml) and precipitated into ether to yield 18.71g. This product was redissolved in methanol. The solution was filtered through a Whatman No.1 filter paper and precipitated into water. The yield was 14.64g. A further sample of this material (5g) was dissolved in methanol (1000ml) and reprecipitated into ether (1700ml) to yield 4.11g of a white powder.

MP60

The conditions of MP54 were repeated on MP37 (4g) in dimethyl formamide (42.9ml) and pyridine (5.1ml), treated with methacrylic anhydride (20ml, 131mmol) in the presence of *para*-benzoquinone. Precipitation was carried out using water (1250ml), hydrochloric acid (50ml) and ether (500ml) which yielded 4.52g. This product, like MP54, was found not to be completely soluble in a small quantity of cold methanol but to dissolve on warming. 2-Methoxyethanol was added to the solution to form a stable solution before reprecipitation into ether (1500ml) to yield 3.08g of a white solid.

MP61-62

MP37 (5g) in dimethyl formamide (53.6ml) and pyridine (6.4ml) was treated with methacrylic anhydride (25ml, 164mmol) in the presence of *para*-benzoquinone (0.2g) under a nitrogen atmosphere in the manner of MP60. Reaction times were 8 and 12h in an ice-bath. The precipitation step was as MP60 giving crude yields of 8.31g and 7.89g for MP61 and MP62 respectively. Reprecipitation from 2-methoxyethanol gave 0.90g of MP61 as a white solid, an earlier attempt using insufficient ether leading to the loss of some material. MP62 was reprecipitated from 2-methoxyethanol (45ml) into ether (2 x 1000ml) to yield 4.55g. A further sample of this material (2.5g) was dissolved in acetone (20ml) and reprecipitated into ether (2000ml) to yield 1.77g of a white powder.

MP63

The conditions of MP60 were repeated using MP14 (5g) in dimethyl formamide (53.6ml) and pyridine (6.4ml) using methacrylic anhydride (25ml). The crude yield was 5.81g. Reprecipitation from acetone (40ml) into water (2000ml) gave 4.08g of material as a white powder.

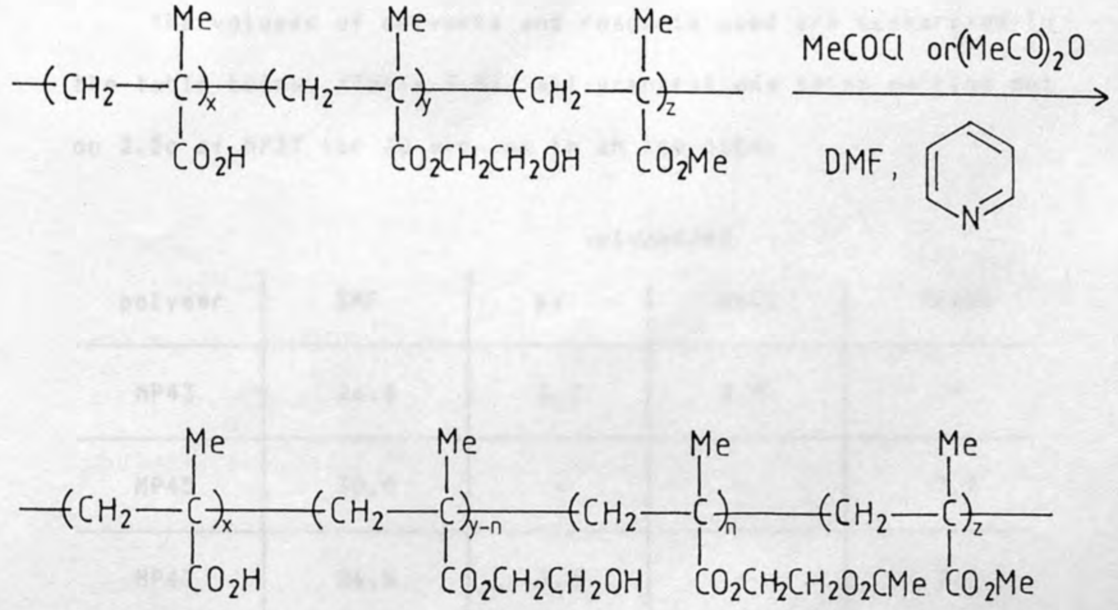
The conditions for this series of preparations are summarized in the table below, (Table 7.7).

polymer	base polymer	wt/g	time/h	temperature
MP59	MP10	20	4	ice
MP60	MP37	4	4	ice
MP61	MP37	5	8	ice
MP62	MP37	5	12	ice
MP63	MP14	5	4	ice

Table 7.7 Conditions of Preparations using Methacrylic Anhydride

7.2.2.3 Acetylated Polymers

In a series of preparations intended to model the conditions of the reaction with methacryloyl chloride and methacrylic anhydride, MP37 was reacted with acetyl chloride and acetic anhydride, (Scheme 7.7). The molar quantity of acetic anhydride used was double the quantity of acetyl chloride. The reaction with anhydride was investigated both in the presence and absence of pyridine.



Scheme 7.7 Acetylation of Copolymers

MP43

MP37 (2.5g) in dimethyl formamide (26.8ml) and pyridine (3.2ml) was treated with acetyl chloride (2.9ml, 41mmol) under the same conditions as MP40. The polymer was precipitated into water (400ml) and hydrochloric acid (50ml), yield 2.86g. Reprecipitation from dimethyl formamide (20ml) into water (600ml) gave 2.20g of white powder. The product was soluble in DMF, acetone, THF and 2-methoxyethanol and softened in methanol.

MP45 and 46

The preparation above was repeated using acetic anhydride (7.7ml, 82mmol) as the reagent. In the first instance, MP45, dimethyl formamide alone (30ml) was used as the solvent, in the second preparation, MP47, dimethyl formamide and pyridine were used in the proportions given above. The crude yields were 1.73g and 2.30g, reprecipitation yielding 1.04g and 1.77g for MP45 and MP47 respectively, both producs being in the form of white powders.

The volumes of solvents and reagents used are summarized in the table below, (Table 7.8), all preparations being carried out on 2.5g of MP37 for 30 minutes in an ice-bath.

polymer	volumes/ml DMF	py	AcCl	AcAnh
MP43	26.8	3.2	2.9	-
MP45	30.0	-	-	7.7
MP47	26.8	3.2	-	7.7

DMF = dimethyl formamide, py = pyridine, AcCl = acetyl chloride, AcAnh = acetic anhydride.

Table 7.8 Conditions for the Acetylation of MP37

7.3 Characterization of Polymers

The methods used for the characterization of polymer samples may be classified into those giving information on the chemical composition of the polymers and those giving molecular weight information. Nuclear magnetic resonance spectroscopy, micro-analysis and titration all give chemical data while gel-permeation chromatography and viscometry measurements may be used to make inferences about polymer molecular weights.

7.3.1 Nuclear Magnetic Resonance Spectroscopy

Proton nuclear magnetic resonance (nmr) spectra were run in (generally deuteromethanol) solution at high field (250 and 400MHz) using the University inter-collegiate service. The polymer spectra and the calculation of compositions based on them are dealt with elsewhere, (Sections 2.4.1 and 2.4.2). Where possible insoluble polymer samples were run as swollen gels.

7.3.2 Titration Method

The free carboxylic acid content was determined by a titration technique. A nominally 0.1N sodium hydroxide solution was standardized by titration against analytical grade benzoic acid, previously dried over P_2O_5 in vacuo, using phenolphthalein as indicator. Polymer samples were analysed by dissolving approximately 0.1g, accurately weighed, in 5ml of methanol, adding three drops of phenolphthalein solution and titrating to the first permanent pink colouration. The results, corrected by subtracting a blank titre, were calculated as the number of moles of acid groups per gram of polymer. The mean of four titrations was taken in each case. Analyses of poly(methacrylic acid) (MP12) in methanol and water gave identical values, confirming the validity of using the former solvent. Water used for diluting the stock sodium hydroxide solution and in the titrations was previously boiled to drive-off dissolved carbon dioxide and stored using a soda-lime guard tube.

7.3.3 Viscometry

The intrinsic viscosities of solutions of polymers in 2-methoxyethanol were determined using an Ubbelohde suspended level dilution capillary viscometer, (Figure 7.1). The viscometer and solutions were suspended in a water-bath thermostatted at 25°C. A filtered stock solution of approximately 4% w/v was diluted accurately to give four solutions of known strength, further dilutions were made in the viscometer. The time taken for a certain volume of solution to pass through the viscometer was measured, the mean of three runs being taken for each dilution. Time was allowed for thermal equilibration and mixing before each set of runs. From the results, Huggins and Kraemer plots[190] were performed using a computer line fitting procedure and a value of the intrinsic viscosity, [η], was determined as the mean of the intercepts of the two graphs.

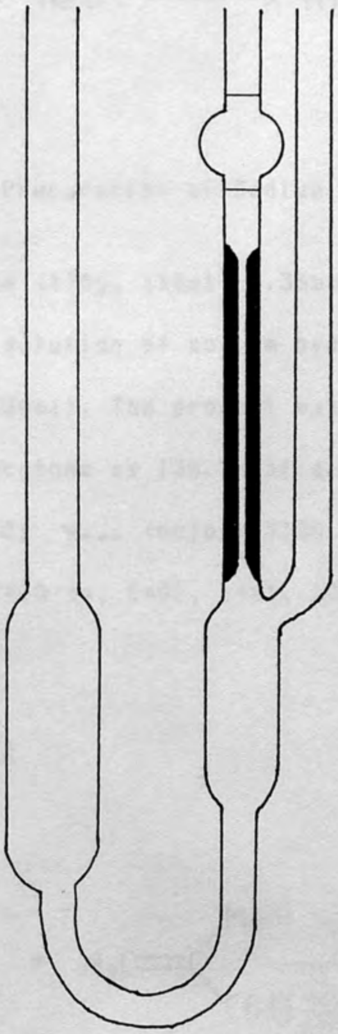


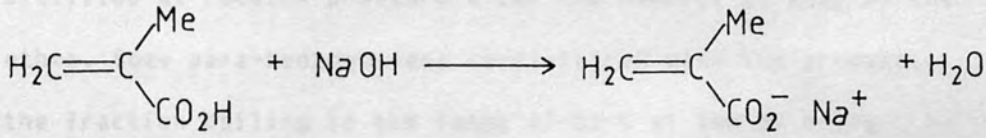
Figure 7.1 Ubbelohde Suspended Level Dilution Viscometer

7.3.4 Gel-Permeation Chromatography

Non-aqueous size-exclusion chromatography (gel-permeation chromatography) was performed on polymer samples dissolved in tetrahydrofuran.

7.4 Reagents and Monomers

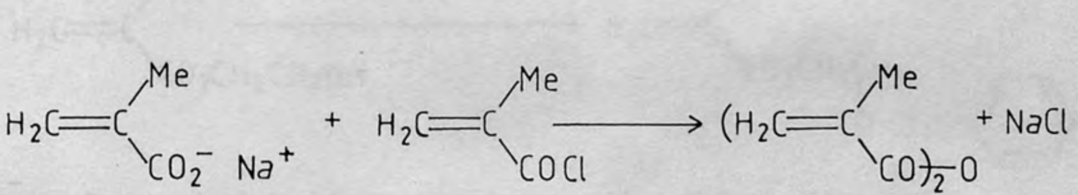
Sodium Methacrylate



Scheme 7.8 Preparation of Sodium Methacrylate

Methacrylic acid (120g, 118ml, 1.36mol) was added dropwise, with stirring, to a solution of sodium hydroxide (55.8g, 1.40mol) in water (150ml). The product was obtained by precipitation into acetone as 136.7g of a colourless crystalline material, m.p. >350°C; ν_{max} (nujol) 3100 (w, C-H), 1646 (m, C=C), 1556 and 1420 (s, C=O), 1461, 1391, 1243, 921, 856, 836, 602 cm^{-1}.

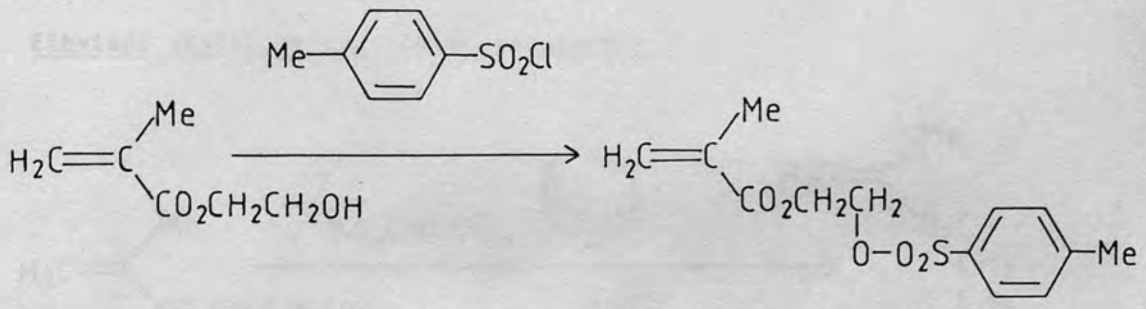
Methacrylic anhydride



Scheme 7.9 Preparation of Methacrylic Anhydride

Finely ground sodium methacrylate (100g, 0.906mol) was suspended in anhydrous ether (400ml). *para*-Benzoquinone (4g) and methacryloyl chloride (101.7g, 95ml, 0.972mol) were added. The stirred suspension was warmed on a water-bath, under a nitrogen atmosphere and maintained at reflux overnight. The cooled solution was filtered from the finely-divided precipitate using a closed filtration apparatus[240] and the precipitate washed with several portions of dry ether. The filtrate was distilled at reduced pressure after the removal of most of the ether. Some *para*-benzoquinone co-distilled with the product, the fraction boiling in the range 47-52°C at 1mm Hg being collected. Methacrylic anhydride is a mobile colourless liquid, coloured yellow by the benzoquinone and is a potent lachrymator. The yield was 82g (59%) (Found: C, 62.06; H, 6.66. $C_8H_{10}O_3$ requires C, 62.33; H, 6.54%) ν_{max} (liquid film) 2988, 2963, 2931 (w-m, C-H), 1785, 1724 (s, C=O), 1637 (m, C=C), 1050 (s, C-O-C), 1455, 1403, 1380, 1298, 1126, 1004, 950, 811, 642 cm^{-1}; δ_H ($CDCl_3$) 1.98 (d, 6H), 5.84 (m, 2H), 6.23 (s, 2H), δ_C 17.82, 127.33, 135.98, 163.23, n_D^{20} 1.4528.

Ethylene glycol methacrylate *para*-toluenesulphonate

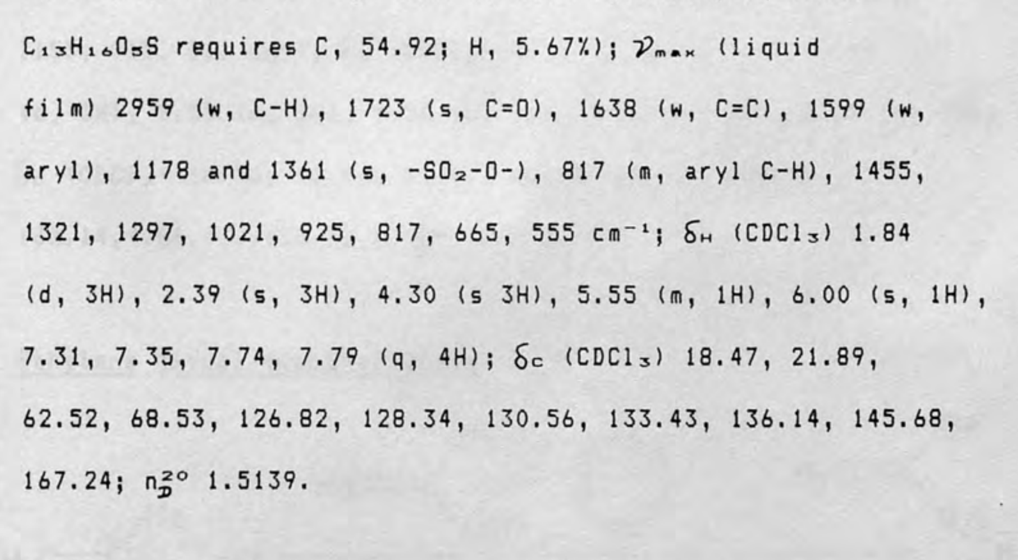


Scheme 7.10 Reaction of 2-Hydroxyethyl Methacrylate and *para*-Toluenesulphonyl Chloride

para-Toluenesulphonyl chloride (40.3g, 0.21mol) was dissolved in pyridine (60ml) and 2-hydroxyethyl methacrylate

(25g, 24.2ml, 0.19mol) was added to the stirred, ice-cold solution. The mixture was allowed to stir overnight. The reaction mixture was added to hydrochloric acid (80ml) diluted to 500ml with ice-water. The mixture was transferred to a separating funnel and extracted with dichloromethane (3x100ml). The organics were washed with water, then brine and dried ($MgSO_4$). Evaporation at room temperature yielded 55.84g (100%) of a colourless oil. The product was used at this stage, without further purification, in the preparation of MP39, the major contaminant being dichloromethane (nmr). A sample (7.8g) was distilled from a small quantity of hydroquinone to yield 4.15g of a viscous oil, bp 166-170°C (1.5mm Hg), which crystallized on storage in a refrigerator (Found: C, 54.81; H, 5.82. $C_{13}H_{16}O_5S$ requires C, 54.92; H, 5.67%); ν_{max} (liquid film) 2959 (w, C-H), 1723 (s, C=O), 1638 (w, C=C), 1599 (w, aryl), 1178 and 1361 (s, $-SO_2-O-$), 817 (m, aryl C-H), 1455, 1321, 1297, 1021, 925, 817, 665, 555 cm^{-1}; δ_H ($CDCl_3$) 1.84 (d, 3H), 2.39 (s, 3H), 4.30 (s 3H), 5.55 (m, 1H), 6.00 (s, 1H), 7.31, 7.35, 7.74, 7.79 (q, 4H); δ_C ($CDCl_3$) 18.47, 21.89, 62.52, 68.53, 126.82, 128.34, 130.56, 133.43, 136.14, 145.68, 167.24; n_D^{20} 1.5139.

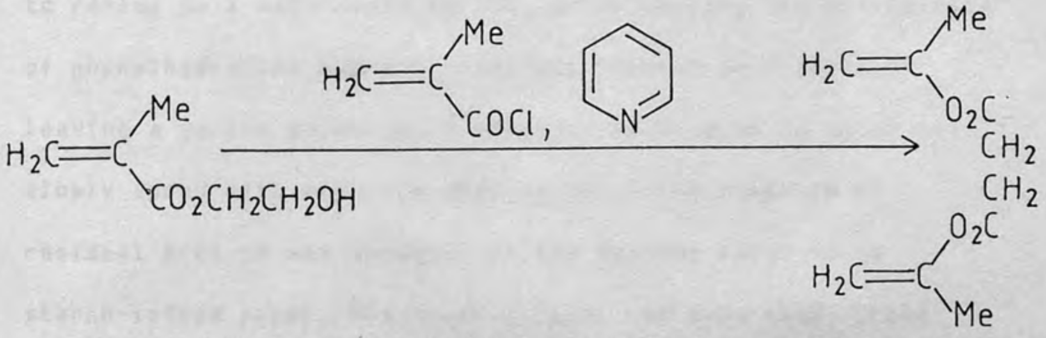
Ethylene glycol methacrylate isobutyrate



Scheme 7.11 Reaction of 2-Hydroxyethyl Methacrylate and Isobutyryl Chloride

2-Hydroxyethyl methacrylate (10g, 9.7ml, 76.8mmol) in pyridine (10ml) was stirred in an ice-bath during the addition of isobutyryl chloride (9.82g, 9.7ml, 92.2mmol). The reaction mixture was stirred for 4h, at the end of which time it was poured into dilute hydrochloric acid and extracted with dichloromethane (2 x 50ml). The extracts were washed, dried ($MgSO_4$) and evaporated to yield a fragrant colourless oil, 24.34g. This was distilled at reduced pressure after the addition of a few crystals of hydroquinone, bp 60-61°C (2mm Hg), yield 7.72g, (50%) the remainder polymerizing in the distillation flask (Found: C, 60.43; H, 8.13. $C_{10}H_{16}O_4$ requires C, 59.97; H, 8.07%); ν_{max} (liquid film) 2977 (m, C-H), 1724 (s, C=O), 1639 (w, C=C), 1472, 1455, 1321, 1298, 1153, 945, 816 cm^{-1}; δ_H ($CDCl_3$) 1.13, 1.20 (d, 6H), 1.94 (d, 3H), 2.57 (m, 1H), 4.35 (s, 4H), 5.58 (m, 1H), 6.11 (s, 1H); δ_C ($CDCl_3$) 18.26, 18.96, 33.97, 61.98, 62.52, 125.79, 136.14, 166.97, 176.66 ; n_D^{20} 1.4350.

Ethylene glycol dimethacrylate



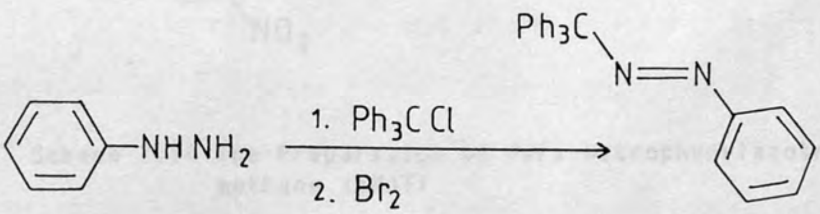
Scheme 7.12 Reaction of 2-Hydroxyethyl Methacrylate with Methacryloyl Chloride

The procedure above was repeated using 2-hydroxyethyl methacrylate (10g, 9.7ml, 76.8mmol) and methacryloyl chloride (9.6g, 9.0ml, 92.2mmol), yield 9.94g (65%). This material (1.98g) was distilled from hydroquinone, bp 80-82°C (1mm Hg)

(Found: C, 60.97; H, 7.19. $C_{10}H_{14}O_4$ requires C, 60.59; H, 7.13%); ν_{max} (liquid film) 2960 (w, C-H), 1724 (s, C=O), 1638 (m, C=C), 1455, 1323, 1296, 1155, 1051, 945, 815 cm^{-1}; δ_H ($CDCl_3$) 1.94 (d, 6H), 4.41 (s, 4H), 4.41 (s, 4H), 5.58 (m, 1H), 6.12 (s, 1H); δ_C ($CDCl_3$) 18.20, 62.41, 125.79, 136.14, 166.91; n_D^{20} 1.4534.

7.5 Azo Initiators

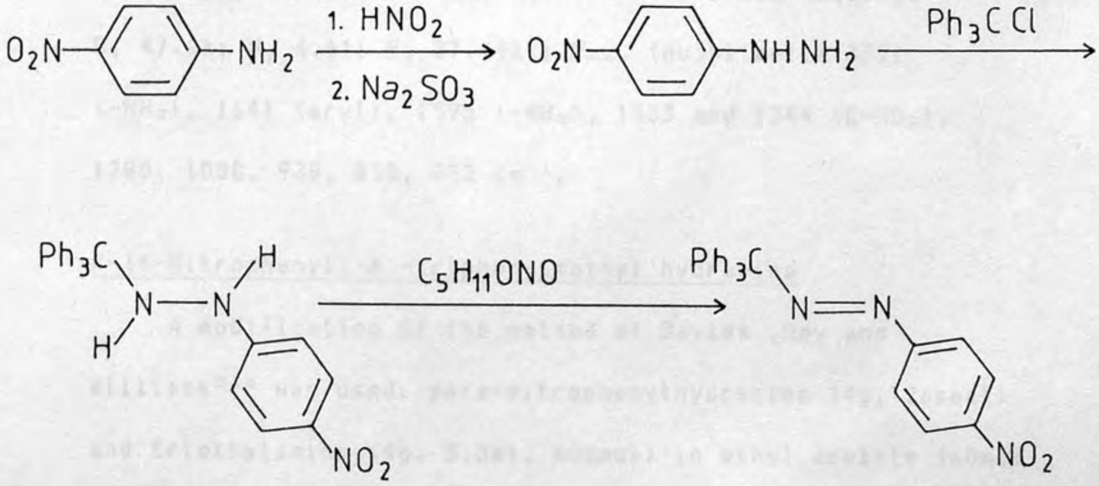
Phenylazotriphenylmethane



Scheme 7.13 Preparation of Phenylazotriphenylmethane (PATM)

A mixture of triphenylmethyl chloride (7.25g, 27mmol) and phenylhydrazine (6.6g, 61mmol) in dry ether (250ml) was allowed to reflux on a water-bath for 3h. After cooling the precipitate of phenylhydrazine hydrochloride was removed by filtration leaving a yellow solution. A solution of bromine in water was slowly added with vigorous shaking until the presence of residual bromine was detected in the aqueous layer using starch-iodide paper. The organic layer was separated, dried ($MgSO_4$) and evaporated to yield the crude product. Crystallization from chloroform and methanol at 0°C gave phenylazotriphenylmethane, 8.29g (80%) as yellow crystals, mp 111° (decomp), [lit[200] 110-112°C].

The *para*-nitro analogue of PATM (pNAT) was prepared in three steps from *para*-nitroaniline, (Scheme 7.14).



Scheme 7.14 The Preparation of *Para*-Nitrophenylazotriphenylmethane (pNAT)

<u>*para*-Nitrophenylhydrazine</u>

para-Nitroaniline (20g, 0.145mol) was warmed with hydrochloric acid (42ml) and water (42ml) until dissolution was complete then cooled in ice to precipitate the hydrochloride. This was diazotized by the addition of sodium nitrite (12g in 24ml of water), filtered and added to an ice-cold mixture of hydrated sodium sulphite (82g, 0.325mol), sodium hydroxide (8g, 0.20mol) and water (200ml), slowly, with stirring. Hydrochloric acid (140ml) was added and the mixture was heated on a water-bath for 3 minutes then allowed to stand overnight. The yellow solid was filtered off and heated for 7 minutes with hydrochloric acid (40ml) on a water-bath. On cooling a red crystalline solid separated. This was collected and dissolved in water (about 100-120ml). The solution was filtered and treated with a saturated solution of sodium acetate. The end-point was determined using universal indicator paper. The free base was obtained by filtration and washed with a little water, yield 10.90g (49%) mp 155-158°C (decomp) [lit[241] 158°C (decomp)] (Found: C, 46.83; H, 4.56; N, 27.39. $C_6H_7N_3O_2$ requires C, 47.06; H, 4.61; N, 27.44%); ν_{max} (nujol mull) 3321 ($-NH_2$), 1641 (aryl), 1595 ($-NH_2$), 1533 and 1344 ($C-NO_2$), 1280, 1088, 938, 838, 752 cm^{-1}.

N-(4-Nitrophenyl)-*N'*-triphenylmethyl hydrazine

A modification of the method of Davies ,Hey and Williams[204] was used. *para*-Nitrophenylhydrazine (4g, 26mmol) and triethylamine (4g, 5.5ml, 40mmol) in ethyl acetate (60ml) was heated to reflux. A solution of triphenylmethyl chloride (7.5g, 27mmol) in ethyl acetate (50ml) was added and the mixture allowed to reflux for 1h. The precipitate of triethylamine hydrochloride was removed by filtration and the solution was concentrated by evaporation. The hydrazine was precipitated by the addition of ethanol, collected, washed with ethanol and dried to yield 8.30g (80%) of yellow crystals, mp 169-174°C (decomp), [lit[204] 170°C] (Found: C, 75.78; H, 5.37; N, 10.46. $C_{25}H_{21}N_3O_2$ requires C, 75.93; H, 5.35; N, 10.63%); ν_{max} (nujol mull) 3291 (w, N-H), 1598 (-NH), 1493, 1355, 1310, 1299, 1269, 1114, 949, 855, 839, 749, 703 cm^{-1}.

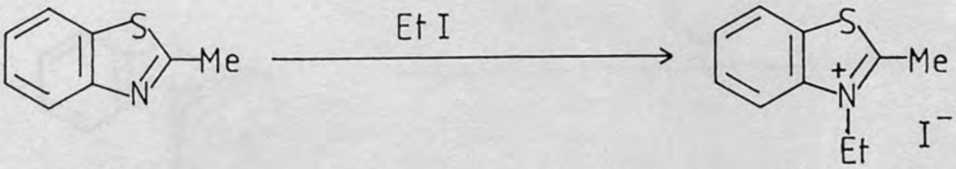
para-Nitrophenylazotriphenylmethane

para-Nitrophenyl triphenylmethyl hydrazine (4g, 10mmol) was suspended in an ethereal solution (100ml) of pentyl nitrite (2.61g, 3.0ml, 22mmol). A few drops of acetyl chloride were added to start the reaction and the mixture was warmed to reflux, brown fumes being evolved. After refluxing for 10 minutes the solid had all dissolved, forming an orange solution.

After removing the heat, the flask was left for 15 minutes as fumes were still being evolved. The ether was removed by rotary evaporation and the resultant damp solid was recrystallized by dissolving in benzene (15ml) adding ethanol (60ml) and leaving in a refrigerator overnight. The fluffy orange needles were collected and washed with ethanol, yield 2.50g, mp 122.5°C (decomp), [lit[204] 120°C (decomp)]. A second crop of crystals was recovered from the mother liquor, 0.89g, mp 120-122°C, total yield 3.39g (85%); (Found: C, 76.56; H, 4.88; N, 10.55. $C_{25}H_{19}N_3O_2$ requires C, 76.32; H, 4.87; N, 10.68%); ν_{max} (nujol mull) 1610 and 1593 (w, aryl), 1527, 1489, 1445, 1347, 859, 757, 731, 701, 640 cm^{-1}.

7.6 Cyanine Dyes

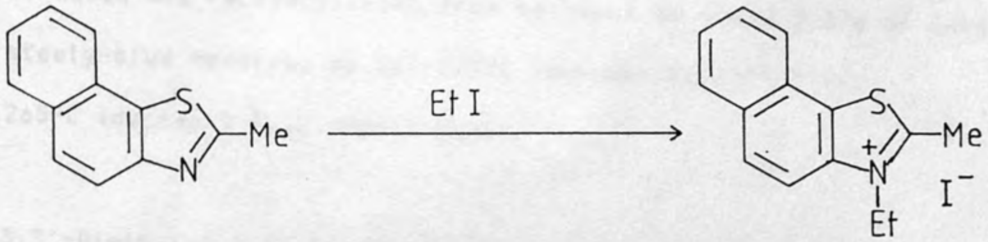
2-Methyl-3-ethyl-benzothiazolium iodide



Scheme 7.15 Quaternization of 2-Methyl Benzothiazole

2-Methylbenzothiazole (3ml, 3.52g, 23.6mmol) and ethyl iodide (3ml, 5.85g, 37.5mmol) were sealed in a tube and suspended in an oil-bath at 100°C for 3 days. The tube was broken open on cooling and the product was collected and washed with ether to yield 6.83g of crude material. This was recrystallized from methylated spirits to yield 5.00g (69%) of the product as colourless needles, mp 195-197°C (decomp) [lit[242] 190-192°C].

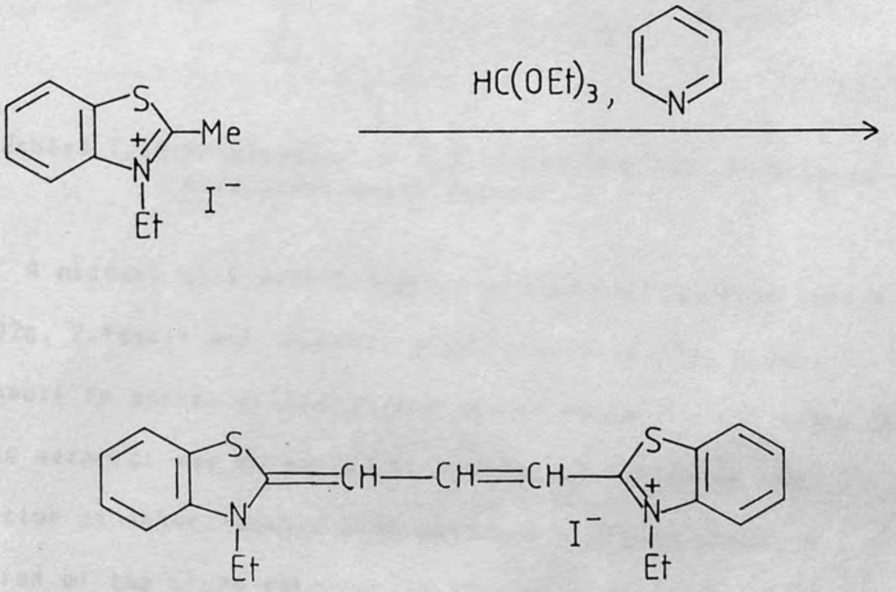
2-Methyl-3-ethyl-α-naphthothiazolium iodide



Scheme 7.16 Quaternization of 2-Methyl-α-Naphthothiazole

In an analogous manner 2-methyl-α-naphthothiazole (1.5g, 7.5mmol) and ethyl iodide (1ml, 1.95g, 12.5mmol) were heated together in a sealed tube. The crude product, 2.56g, was recrystallized from methanol to yield 1.78g (67%) mp 235-236°C (decomp) [lit [243] 235°C (decomp)].

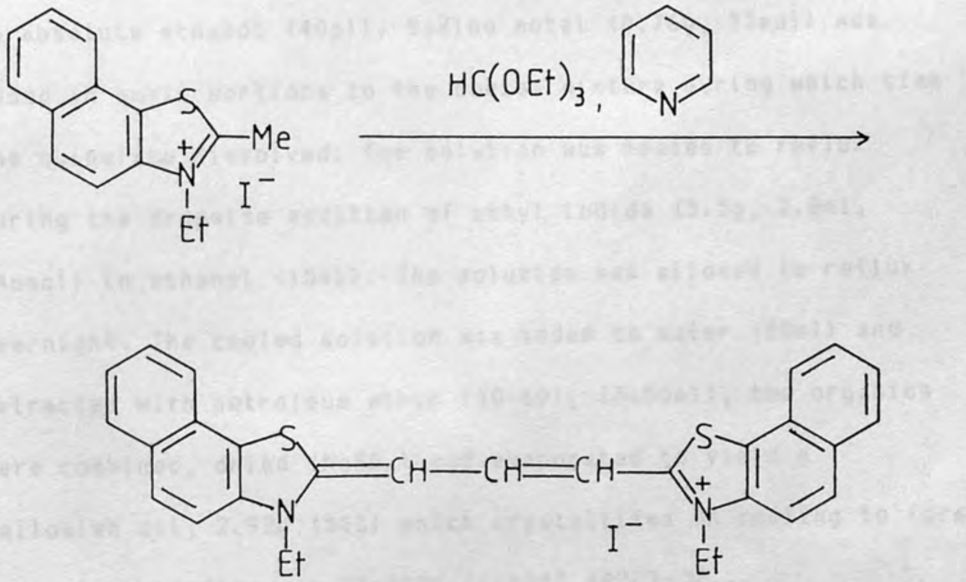
3,3′-Diethyl thiacarbocyanine iodide



Scheme 7.17 Preparation of 3,3′-Diethyl Thiacarbocyanine Iodide

A mixture of 2-methyl-3-ethyl benzothiazolium iodide (3.0g, 9.8mmol) and triethyl orthoformate (0.80g, 0.9ml, 5.3mmol) in pyridine was heated to reflux for 1.5h. The crude material was collected by filtration after the addition of ether, washed with ethanol and then ether. The crude yield was 2.28g (96%), 0.85g of which was recrystallized from methanol to yield 0.57g of long steely-blue needles, mp 267-270°C (decomp) [lit[244] 264-265°C (decomp)] λ_{max} (MeOH) 561nm.

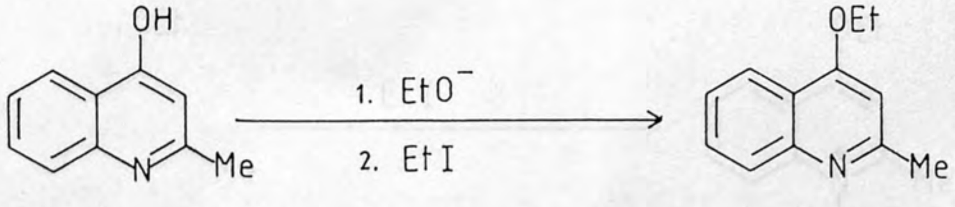
3,3'-Diethyl-6,7,6',7'-dibenzothiacarbocyanine iodide



Scheme 7.18 Preparation of 3,3'-Diethyl-6,7,6',7'-Dibenzothiacarbocyanine Iodide

A mixture of 2-methyl-3-ethyl-α-naphthothiazolium iodide (1.02g, 2.9mmol) and triethyl orthoformate (0.27g, 0.3ml, 1.8mmol) in pyridine (10ml) were heated to reflux for 1.5h. The crude material was collected by filtration following the addition of ether, washed with methanol and then ether. A portion of the crude material (0.38g) was retained and the remainder was recrystallized from methanol to yield fine greenish-black needles, mp 288-292°C (decomp) [lit[243] 294°C] λ_{max} (MeOH) 596nm.

4-Ethoxy-2-methyl quinoline

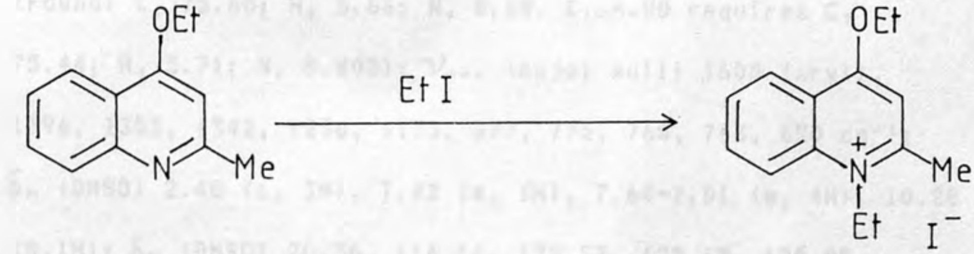


Scheme 7.19 O-Ethylation of 4-Hydroxy-2-Methyl Quinoline

4-Hydroxy-2-methyl quinoline (5g, 31.4mmol) was suspended in absolute ethanol (40ml). Sodium metal (0.76g, 33mol) was added in small portions to the cooled mixture during which time the quinoline dissolved. The solution was heated to reflux during the dropwise addition of ethyl iodide (5.5g, 2.8ml, 34mmol) in ethanol (15ml). The solution was allowed to reflux overnight. The cooled solution was added to water (50ml) and extracted with petroleum ether (40-60), (3x50ml), the organics were combined, dried ($MgSO_4$) and evaporated to yield a yellowish oil, 2.92g (50%) which crystallized on cooling to form colourless needles, mp 27-31°C [lit[245] 48°C]; ν_{max} (nujol mull) 1610, 1598, 1568, 1510, 1423, 1345, 1235, 1188, 1160, 1117, 1027, 818, 765 cm^{-1}; δ_H ($CDCl_3$) 1.37 (t, 3H), 2.52 (s, 3H), 3.87 (q, 2H), 6.23 (s, 1H), 8.11-7.16 (m, 4H).

This material was used in the next step without further purification.

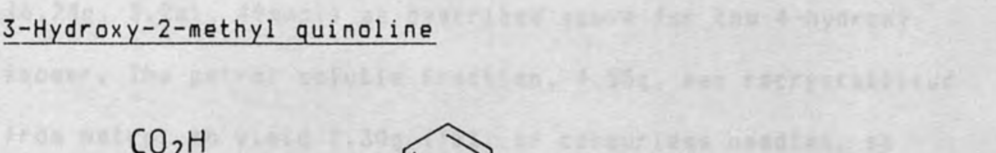
1-Ethyl-4-ethoxy-2-methyl quinolinium iodide



Scheme 7.20 Quaternization of 4-Ethoxy-2-Methyl Quinoline

The oil (2.92g, 15.6mmol) from the previous preparation was refluxed overnight with excess ethyl iodide (5-10ml). The crude product was obtained by filtration after the addition of ether to yield 3.37g of air-dried material. This product was recrystallized from water using decolourizing charcoal to yield 1.97g (37%) of near colourless needles, mp 211-214°C (decomp) [lit^{246} 205°C] (Found: C, 48.90; H, 5.27; N, 3.96. $C_{14}H_{18}INO$ requires C, 48.99; H, 5.30; N, 4.08%); ν_{max} (nujol mull) 1601 (aryl), 1576, 1529, 1425, 1304, 1270, 1134, 1017, 871, 785, 775 cm^{-1}.

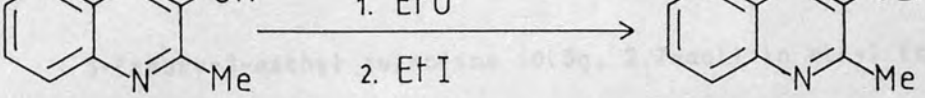
3-Hydroxy-2-methyl quinoline



Scheme 7.21 Decarboxylation of 3-Hydroxy-2-Methyl Quinoline-4-Carboxylic Acid

3-Hydroxy-2-methyl quinoline-4-carboxylic acid (15g, 74mmol) was heated to reflux in pyridine (100ml) until evolution of gas ceased. The product was obtained by the addition of water and dried over P_2O_5 to yield 9.84g (84%) of cream-coloured crystalline material, mp 261-264°C (decomp) [lit^{247} 260°C] (Found: C, 75.60; H, 5.66; N, 8.88. $C_{10}H_9NO$ requires C, 75.44; H, 5.71; N, 8.80%); ν_{max} (nujol mull) 1605 (aryl), 1396, 1355, 1342, 1236, 1175, 877, 775, 760, 743, 620 cm^{-1}; δ_H (DMSO) 2.48 (s, 3H), 7.42 (s, 1H), 7.64-7.81 (m, 4H), 10.28 (S,1H); δ_C (DMSO) 20.36, 114.11, 125.57, 125.65, 125.95, 127.84, 128.54, 141.86, 149.65, 151.99.

3-Ethoxy-2-methyl quinoline

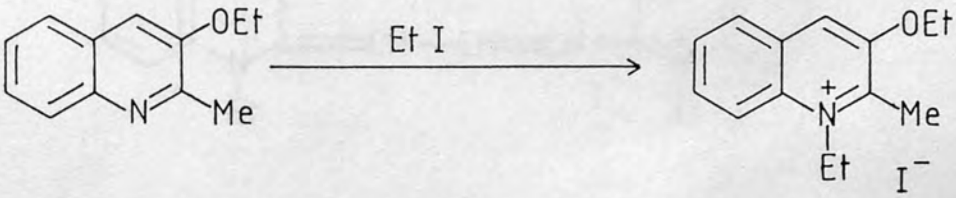


Scheme 7.22 O-Ethylation of 3-Hydroxy-2-Methyl Quinoline

3-Hydroxy-2-methyl quinoline (6g, 38mmol) in ethanol (50ml) was treated with sodium metal (0.86g, 38mmol) and ethyl iodide (6.24g, 3.2ml, 40mmol) as described above for the 4-hydroxy isomer. The petrol soluble fraction, 4.55g, was recrystallized from petrol to yield 1.30g (18%) of colourless needles, mp 68-71°C [lit^{247} 68-69°C]; (Found: C, 77.33; H, 7.03; N, 7.30. $C_{12}H_{13}NO$ requires C, 76.96; H, 7.01; N, 7.48%); ν_{max} (nujol mull) 1606 (aryl), 1500, 1436, 1392, 1355, 1323, 1233, 1175, 1147, 1120, 1039, 851, 829, 776, 754, 616 cm^{-1}; δ_H ($CDCl_3$) 1.45 (t, 3H), 2.63 (s, 3H), 4.02 (q, 2H), 7.13 (s, 1H), 7.35-8.01 (m, 4H); δ_C ($CDCl_3$) 14.91, 20.85, 63.84, 111.52, 126.17, 126.56 (2 peaks unresolved), 128.59, 128.77, 142.85, 151.65, 153.38.

Further extraction of the aqueous portion with chloroform yielded 2.13g of a crystalline material, after crystallization from methanol having mp 197-204°C (decomp) (probably 1-ethyl-3-hydroxy-2-methyl quinolinium iodide).

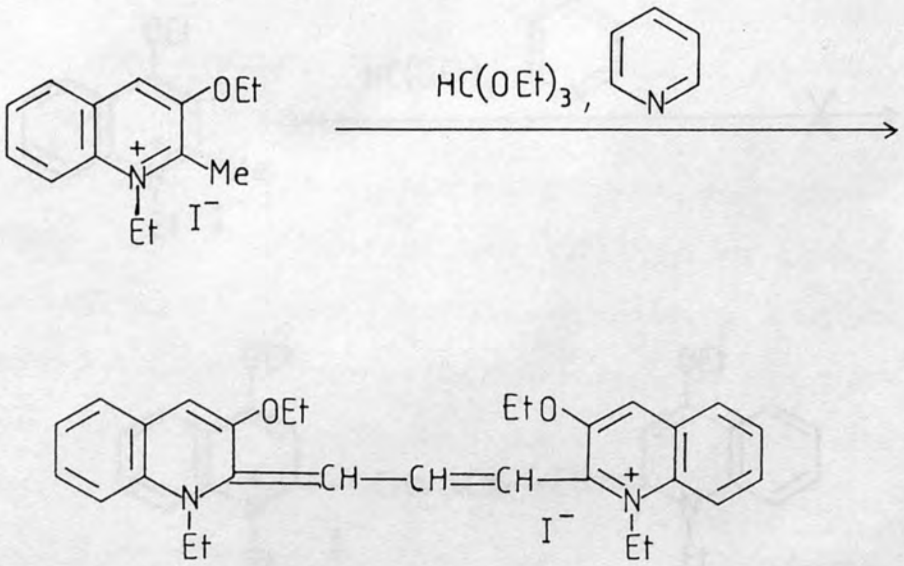
<u>1-Ethyl-3-ethoxy-2-methyl quinolinium iodide</u>



Scheme 7.23 Quaternization of 3-Ethoxy-2-Methyl Quinoline

3-Ethoxy-2-methyl quinoline (0.5g, 2.7mmol) in ethyl iodide (5-10ml) was heated to reflux for 96h. The crude material was collected by filtration, after the addition of ether, as a yellow powder. Recrystallization from ethanol gave yellow plates, 0.57g (62%) mp 213-215°C (decomp); (Found: C, 48.13; H, 5.34; N, 3.90. $C_{14}H_{18}INO$ requires C, 48.99; H, 5.30; N, 4.08%); ν_{max} (nujol mull) 3506, 1608 (aryl), 1511, 1346 ,1331, 1273, 1227, 1197, 1111, 1029, 920, 779, 657 cm^{-1}; δ_H (DMSO) 1.43 (t, 3H), 1.47 (t, 3H), 2.93 (s, 3H), 4.32 (q, 2H), 4.99 (q, 2H), 7.81-8.65 (m, 5H); δ_C (DMSO) 13.50, 14.25, 15.45, 48.14, 66.13, 118.73, 122.13, 128.49, 129.07, 129.20, 131.73, 133.23, 150.73, 154.92.

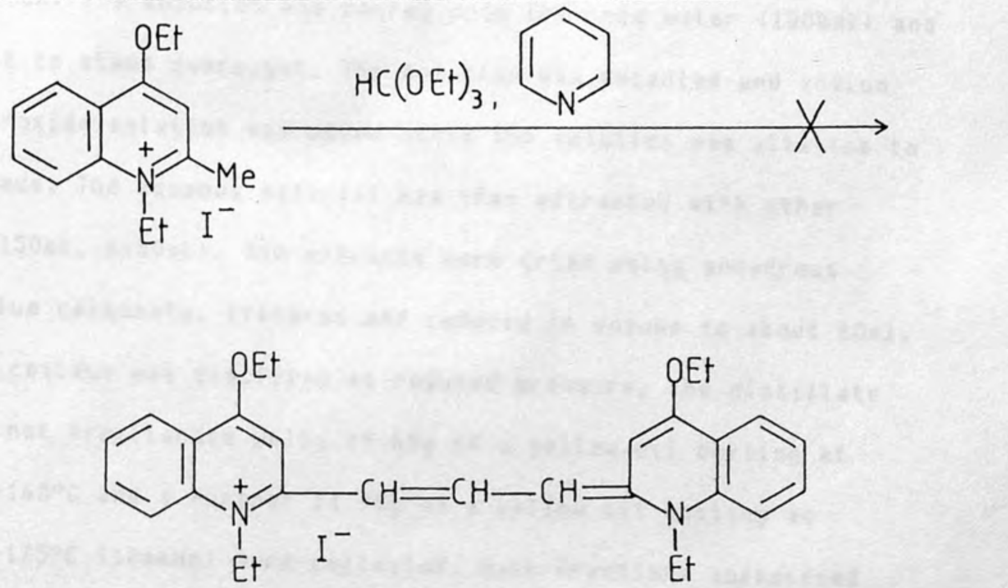
1,1'-Diethyl-3,3'diethoxy-2,2'-carbocyanine iodide



Scheme 7.24 Preparation of 1,1'-Diethyl-3,3'Diethoxy-2,2'-Carbocyanine Iodide

1-Ethyl-3-ethoxy-2-methyl quinolinium iodide (0.3g, 0.87mmol) and triethyl orthoformate (0.65g, 0.73ml, 4.4mmol) in pyridine (5ml) was heated to reflux on an oil-bath for 1.5h. The crude material, 0.30g, was obtained by filtration after the addition of ether. Recrystallization from methanol gave 0.14g (56%) of green-gold metallic needles, mp 230-231°C. λ_{max}(MeOH) 631nm (Found: C, 60.96; H, 5.81; N, 4.74. $C_{29}H_{33}IN_2O_2$ requires C, 61.26; H, 5.86; N, 4.93%); ν_{max} (nujol mull) 1614 (aryl), 1527, 1500, 1422, 1393, 1263, 1192, 1157, 1129, 1106, 1080, 1049, 964, 841 cm^{-1}; δ_H (DMSO) 1.39 (t, 3H), 1.43 (t, 3H), 4.28 (q, 2H), 4.53 (q, 2H), 6.41 (q, 2H), 7.33-7.81 (m, 10H), 9.55 (t, 1H); δ_C (DMSO) 12.49, 13.98, 44.42, 65.36, 106.07, 113.54, 115.69, 124.21, 124.60, 127.53, 129.48, 134.61, 145.34, 150.68, 153.54.

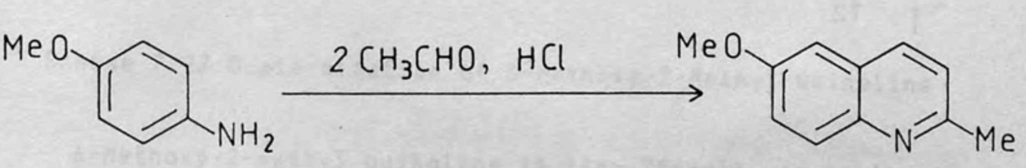
1,1'-Diethyl-4,4'diethoxy-2,2'-carbocyanine iodide



Scheme 7.25 Attempted Preparation of 1,1'-Diethyl-4,4'Diethoxy-2,2'-Carbocyanine Iodide

1-Ethyl-4-ethoxy-2-methyl quinolinium iodide was similarly treated with triethyl orthoformate in both refluxing pyridine and 2,6-lutidine. Despite the formation of colour in the solution, no crystalline product was obtained on addition of ether, only a dark tarry substance.

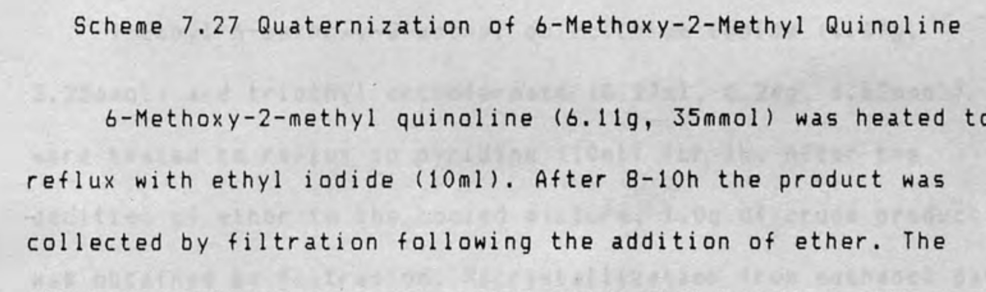
6-Methoxy-2-methyl quinoline



Scheme 7.26 Preparation of 6-Methoxy-2-Methyl Quinoline

para-Anisidine (57g, 0.46mol) in hydrochloric acid (184ml) was cooled on an ice-bath with stirring during the dropwise addition of acetaldehyde (53g,67ml, 1.2mol). After the addition was complete the solution was gently warmed to reflux for 3h. The solution was poured onto ice-cold water (1000ml) and left to stand overnight. The solution was decanted and sodium hydroxide solution was added until the solution was alkaline to litmus. The aqueous material was then extracted with ether (1x150ml, 6x50ml). The extracts were dried using anhydrous sodium carbonate, filtered and reduced in volume to about 60ml. The residue was distilled at reduced pressure. The distillate did not fractionate well, 19.69g of a yellow oil boiling at 148-163°C and a further 11.98g of a yellow oil boiling at 163-175°C (10mmHg) were collected. Both fractions solidified partially on cooling and recrystallization gave 8.14g (10%) of pure material as colourless cubes, mp 63-66°C [lit[248] 65-67°C]; ν_{max} (nujol mull) 1625, 1603, 1566, 1500, 1345, 1308, 1234, 1168, 1113, 1031, 883, 834 cm^{-1}; δ_H (CDCl$_3$) 2.71 (s, 3H), 3.91 (s, 3H), 7.02-7.98 (m, 5H).

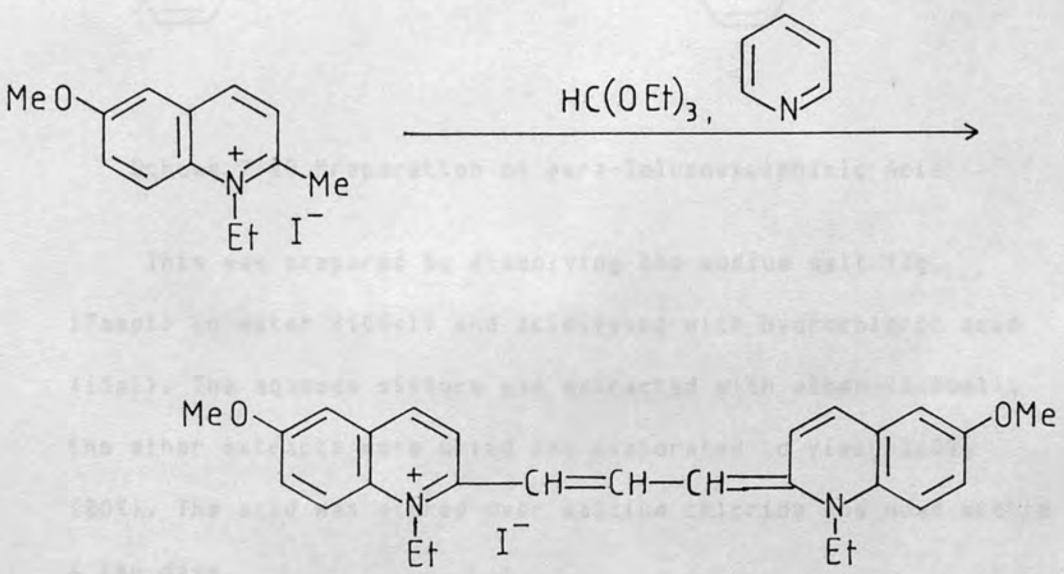
1-Ethyl-6-methoxy-2-methyl quinolinium iodide



Scheme 7.27 Quaternization of 6-Methoxy-2-Methyl Quinoline

6-Methoxy-2-methyl quinoline (6.11g, 35mmol) was heated to reflux with ethyl iodide (10ml). After 8-10h the product was collected by filtration following the addition of ether. The ethereal washings were evaporated and heated together with more ethyl iodide for a further 8-10h when the collection procedure was repeated. The combined crude material was recrystallized. The first batch (from water) was obtained as 2.03g of yellow crystals, mp 193-197°C. The second batch, from methanol/ ethyl acetate, was 4.71g, mpt. 200-201°C (decomp). Combined yield 6.74g (58%); (Found: C, 47.48; H, 4.85; N, 4.13. $C_{13}H_{16}INO$ requires C, 47.43; H, 4.90; N, 4.26%); ν_{max} (nujol mull) 1609, 1583, 1520, 1491, 1341, 1283, 1254, 1225, 1160, 1085, 1069, 1025, 879, 843 cm^{-1}; δ_H (DMSO) 1.58 (t, 3H), 3.01 (s, 3H), 3.85 (s, 3H), 4.80 (q, 2H), 7.22- 8.61 (m, 5H).

6,6'-Dimethoxy-1,1'-diethyl-2,2'-carbocyanine iodide

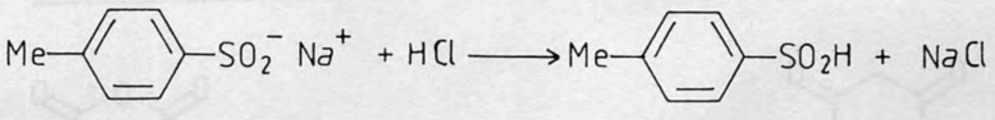


Scheme 7.28 Preparation of 6,6'-Dimethoxy-1,1'-Diethyl-2,2'-Carbocyanine Iodide

1-Ethyl-6-methoxy-2-methyl quinolinium iodide (1.07g, 3.25mmol) and triethyl orthoformate (0.27ml, 0.24g, 1.62mmol) were heated to reflux in pyridine (10ml) for 1h. After the addition of ether to the cooled mixture, 1.0g of crude product was obtained by filtration. Recrystallization from methanol gave 0.06g (7%) of fine green needles, mp 316-317°C (decomp). Dye remaining in the mother liquor decomposed on standing to a reddish solution. ν_{max} (nujol mull) 1612, 1543, 1417, 1352, 1311, 1276, 1261, 1231, 1170, 1157, 1144, 1131, 1030 cm^{-1}; δ_H (DMSO) 1.34 (t, 3H), 3.80 (s, 6H), 4.4 (q, 2H), 6.4 (d, 2H), 7.3-8.3 (m, 8H), 8.5 (t, 1H).

7.7 Co-initiators

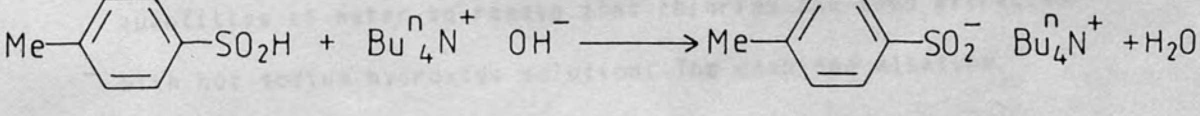
para-Toluenesulphinic acid



Scheme 7.29 Preparation of *para*-Toluenesulphinic Acid

This was prepared by dissolving the sodium salt (3g, 17mmol) in water (100ml) and acidifying with hydrochloric acid (15ml). The aqueous mixture was extracted with ether (3x50ml), the ether extracts were dried and evaporated to yield 2.09g (80%). The acid was stored over calcium chloride and used within a few days.

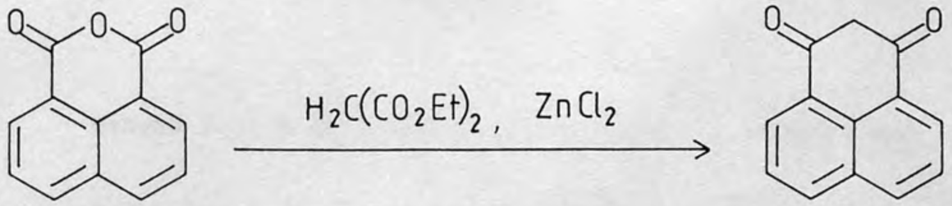
Tetrabutylammonium *para*-toluenesulphinate



Scheme 7.30 Preparation of Tetrabutylammonium *para*-Toluenesulphinate

The sulphinic acid, prepared as described above from 20g (0.11mol) of the sodium salt, was dissolved in water (50ml). Tetrabutylammonium hydroxide (approximately 72ml of a 40% solution in water) was added until the mixture was neutral to pH paper. The water was removed by rotary evaporation to give a viscous liquid. This was extracted back into chloroform (150ml), filtered and evaporated to give a hygroscopic material which was used without further treatment.

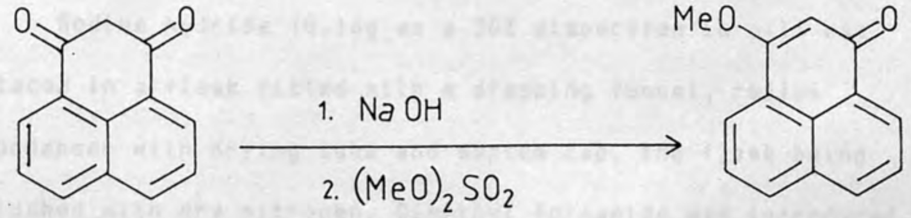
Perinaphth-1,3-indandione[249]



Scheme 7.31 Preparation of Perinaphth-1,3-indandione

Naphthalic anhydride (60g, 0.30mol), zinc chloride (60g, 0.44mol) and diethyl malonate (120ml, 126.6g, 0.79mol) were placed in a three-necked flask fitted with stirrer, thermometer and reflux condenser, The mixture was stirred and heated to 170°C when a vigorous reaction set in. The mixture was allowed to reflux for a further hour after all signs of vigorous reaction had ceased. Water was added to the cooled mixture and the sticky precipitate collected. This was washed with large quantities of water to remove zinc chloride and then extracted with hot sodium hydroxide solution. The combined alkaline extracts were acidified with hydrochloric acid. The crude product separated as a yellow-brown precipitate, yield 47g (79%). A portion of this material was chromatographed on silica gel, eluting with 2% methanol in chloroform. The product obtained from the column was then precipitated from its sodium salt as a further purification step. ν_{max} (nujol mull) 2580, 1862 (broad, enol OH), 1629 (weak, carbonyl), 1579, 1515, 1338, 1311, 1239, 1214, 1164, 834, 772, 687 cm^{-1}.

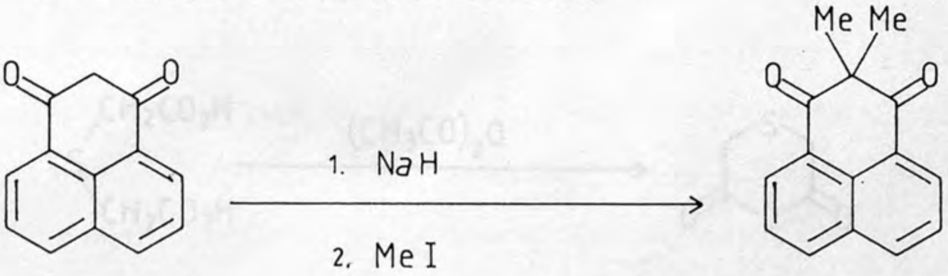
3-Methoxyphenalenone



Scheme 7.32 O-Methylation of Perinaphth-1,3-indandione

Crude perinaphth-1,3-indandione (53g) was suspended in methanol (400ml) in a flask fitted with two dropping funnels and reflux condenser. Solutions of sodium hydroxide (30g) in water (100ml) and dimethyl sulphate (85ml) in methanol (100ml) were added alternately, in portions, with stirring. The mixture was heated to reflux for 5h and the methanol was then distilled out to leave a wet solid. The dried residue was extracted with chloroform and the extracts chromatographed on alumina, eluting with petroleum ether/chloroform. 3-Methoxyphenalenone (11.16g, 20%) was obtained by evaporation of the column fractions. A sample was recrystallized four times from methanol to yield yellow crystals, mp 145-146°C [lit[E14] 144-144.5°C]; (Found: C, 79.54; H, 4.84. $C_{14}H_{10}O_2$ requires C, 79.99; H, 4.79%); ν_{max} (nujol mull) 1637 (carbonyl), 1620 (C=C), 1580, 1562, 1413, 1348, 1236, 1218, 1163, 832, 774 cm^{-1}; δ_H ($CDCl_3$) 3.96 (s, 3H), 6.07 (s, 1H), 8.60-7.29 (m, 6H).

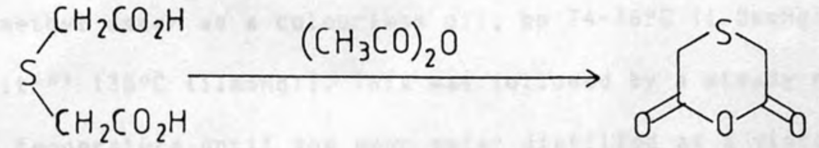
2,2-Dimethylperinaphth-1,3-indandione



Scheme 7.33 C-Methylation of Perinaphth-1,3-indandione

Sodium hydride (0.16g as a 50% dispersion in oil) was placed in a flask fitted with a dropping funnel, reflux condenser with drying tube and septum cap, the flask being flushed with dry nitrogen. Dimethyl formamide was introduced and removed by syringe in several portions to wash the hydride free of oil. To the ice-cold hydride was added crude perinaphth-1,3-indandione (5g) as a solution in DMF. After all signs of gas evolution had ceased, methyl iodide (1.6ml) was added and the mixture was allowed to stand for several days. Water was added to the flask, cautiously at first, and the aqueous mixture was then repeatedly extracted with chloroform. The extracts were combined, washed with water (3x50ml), dried and evaporated. Absorption on alumina and elution with petrol (bp 40-60) gave a pale yellow oil which crystallized readily. Recrystallization from methanol gave 0.80g (14%) of 2,2-dimethylperinaphth-1,3-indandione as pale yellow needles, mp 90-92°C [lit^{250} 100.5-101°C]; (Found: C, 79.9; H, 5.4. $C_{15}H_{12}O_2$ requires C, 80.33; H 5.40%); ν_{max} (nujol mull) 1698, 1673 (carbonyl), 1578, 1505, 1313, 1174, 1041, 842, 780 cm^{-1} δ_H ($CDCl_3$) 1.52 (s, 6H), 8.49-7.59 (m, 6H).

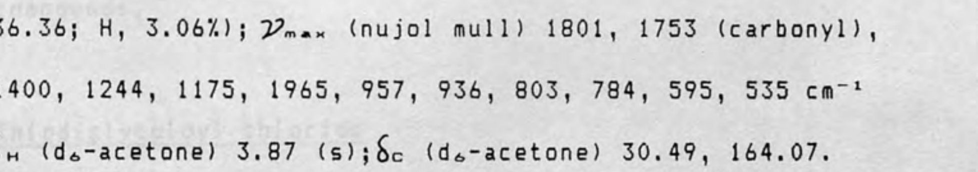
Thiodiglycolic anhydride



Scheme 7.34 Preparation of Thiodiglycolic Anhydride

Thiodiglycolic acid (20g, 0.13mol), was heated to reflux in freshly redistilled acetic anhydride (25ml, 27g, 0.26mol). After 1.5h the flask was set-up for distillation and the volume of solvent was reduced to about 10ml. Cooling in ice caused the anhydride to separate as colourless needles, collected by filtration and washed with dry ether, yield 13.22g, mp 99-101°C [lit[251] 102°C]. Reconcentration of the residue and cooling yielded a further 1.82g of material. Total yield 15.04g (85%); (Found: C, 36.51; H, 3.06; $C_4H_4O_3S$ requires C, 36.36; H, 3.06%); ν_{max} (nujol mull) 1801, 1753 (carbonyl), 1400, 1244, 1175, 1965, 957, 936, 803, 784, 595, 535 cm^{-1} δ_H (d_6-acetone) 3.87 (s); δ_C (d_6-acetone) 30.49, 164.07.

Monomethyl thiodiglycolate



Scheme 7.35 Reaction of Thiodiglycolic Anhydride and Methanol

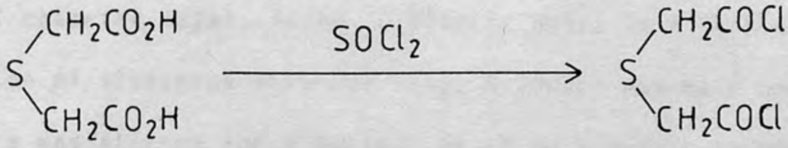
Thiodiglycolic anhydride (6.32g, 48mmol) in methanol (25ml) was heated to reflux on a water-bath for 6h. Removal of the solvent left a brownish oil, 7.89g, which was distilled at reduced pressure. The first fraction was a small amount of the dimethyl ester as a colourless oil, bp 74-76°C (1.5mmHg), [lit[251] 135°C (11mmHg)]. This was followed by a steady rise in temperature until the mono ester distilled as a viscous colourless oil, bp 120-121°C (1.5mmHg) [lit[252] 178-185°C (25mmHg)], yield 4.49g (57%).

Diester: ν_{max} (liquid film) 2955, 1741 (carbonyl), 1438, 1412, 1384, 1196, 1158, 1009, 931, 880, 708, 593 cm^{-1}; δ_H (CDCl$_3$) 3.48 (s, 4H), 3.82 (s, 6H); δ_C (CDCl$_3$) 33.56, 52.42, 170.19; n_D^{20} 1.4748.

Monoester: ν_{max} (liquid film) 3200 (broad, OH), 1734 (C=O), 1439, 1412, 1389, 1304, 1200, 1163, 1007 cm^{-1}; δ_H (CDCl$_3$) 3.45 (s, 4H), 3.75 (s, 3H), 10.80 (s, 1H); δ_C (CDCl$_3$) 33.56, 52.61, 170.64, 175.00; n_D^{20} 1.4955.

No satisfactory analyses could be obtained for these compounds.

Thiodiglycoloyl chloride



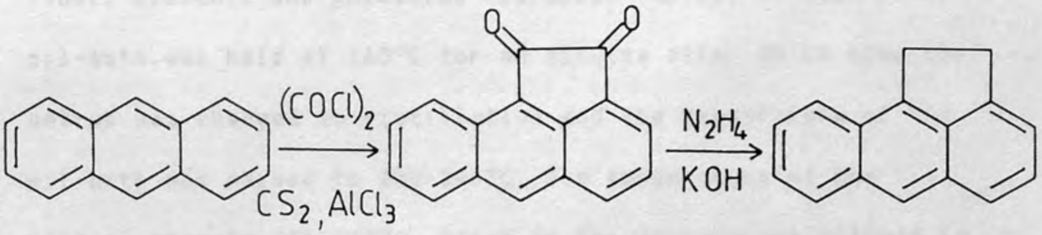
Scheme 7.36 Preparation of Thiodiglycoloyl Chloride

Thiodiglycolic acid (20g, 0.13mol) and thionyl chloride (22ml, 35g, 0.29mol) were allowed to reflux for 2h on an oil-bath. Distillation at reduced pressure gave the acid chloride as a yellowish oil, bp 78-84°C (1.5mmHg) [lit[253]

69-71°C (0.4mmHg)], yield 13.88g (56%); (Found: C, 25.97; H, 2.20. $C_4H_4Cl_2O_2S$ requires C, 25.69; H, 2.16%); ν_{max} (liquid film) 1795 (carbonyl), 1372, 1170, 1013, 964, 706, 639, 557 cm^{-1}; δ_H ($CDCl_3$) 3.87 (s); δ_C ($CDCl_3$) 45.04, 170.32; n_D^{20} 1.4528.

7.8 Sensitizers

Aceanthrene was prepared in two steps from anthracene via aceanthrenequinone, (Scheme 7.38).



Scheme 7.38 Preparation of Aceanthrene

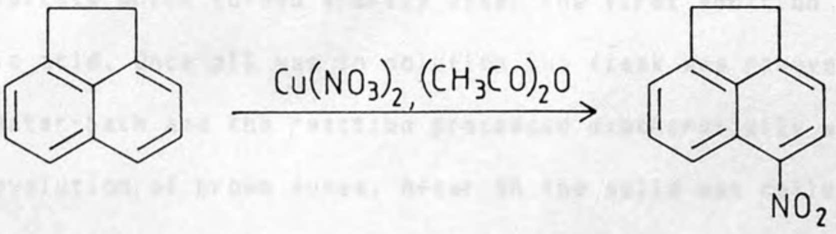
Aceanthrenequinone

Anthracene (20g, 0.11mol) in carbon disulphide (150ml) was cooled on an ice-bath with stirring before the addition of aluminium chloride (16g, 0.12mol) and the dropwise addition of oxalyl chloride (32ml, 46.6g, 0.37mol). After 2h a further addition of aluminium chloride (14g, 0.10mol) was made and the mixture was stirred for a further 4h in an ice-bath before being left overnight at room temperature. Ice-cold dilute hydrochloric acid was added to the mixture and when all signs of reaction had ceased the carbon disulphide was removed by distillation using gentle heating on a water-bath. The product was collected by filtration, washed with water, sodium hydroxide solution and then again with water. The air-dried residue was then extracted with benzene in a soxhlet apparatus. Aceanthrenequinone was collected by filtration from the concentrated extracts, 16.7g (64%) as a red crystalline material, mp 271-274°C, [lit^{245} 214°C]; (Found: C, 82.76; H, 3.49. $C_{16}H_8O_2$ requires C, 82.75; H, 3.47%) ν_{max} (nujol mull) 1737, 1703 (carbonyl), 1574 (aryl), 1281, 1085, 1012, 918, 753 cm^{-1}.

Aceanthrene

Aceanthrenequinone (4g, 17mmol) in diethylene glycol (140ml) was stirred during the addition of hydrazine hydrate (48ml, 0.82mol) and potassium hydroxide (28.8g, 0.51mol). The oil-bath was held at 160°C for 45 minutes after which time the set-up was changed to distillation and the temperature of the oil-bath was raised to 220-240°C. The temperature of the mixture rose to 205-210°C. After 3h the mixture was allowed to cool, poured onto water (400ml), and acidified (HCl). The filtrate, solid and distillate were all extracted with chloroform and the organics were washed with sodium hydroxide solution and evaporated. The brown solid (2.13g) was dissolved in a small amount of chloroform and applied to a column prepared from 120g of alumina and eluted with petrol (bp 40-60). The product was obtained by evaporation of the petroleum ether fractions and recrystallized (ethanol) as 0.57g (16%) of yellow plates, mp 118-119°C, [lit^{255} 113-4°C]; (Found: C, 93.58; H, 5.96. $C_{16}H_{12}$ requires C, 94.08; H, 5.92%); ν_{max} (nujol mull) 1619, 1575, 1528, 1345, 892, 874, 846, 772, 758, 743, 733, 503 cm^{-1}; δ_H ($CDCl_3$) 3.44 (t, 2H), 3.51 (t, 2H), 7.14-8.06 (m, 7H);

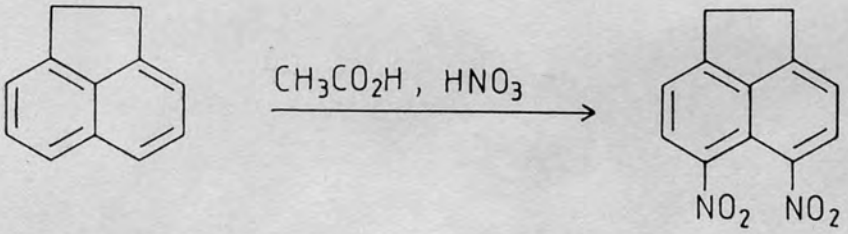
5-Nitroacenaphthene



Scheme 7.39 Mononitration of Acenaphthene

Copper nitrate (8g) in acetic anhydride (100ml) was stirred on a water-bath at 30°C during the addition of acenaphthene (10g, 65mmol). The solution was stirred for a further 50 minutes during which time heat was evolved. The solution was filtered from the residue of copper acetate. Water (50ml) was added to precipitate the organic product as fluffy yellow crystals. The product was washed with 50% acetic acid solution and dried to yield 18.6g, which was recrystallized from alcohol as yellow needles, 9.85g (76%); mp 104-105.5°C [lit[256] 106°C]; (Found: C, 72.35; H, 4.53; N, 7.21. $C_{12}H_9NO_2$ requires C, 72.35; H, 4.55; N, 7.03%); ν_{max} (nujol mull) 1616, 1595 (aryl), 1509 (nitro), 1422, 1329 (nitro), 1214, 901, 838, 775, 737 cm-1; δ_H ($CDCl_3$) 3.38 (s,4H), 7.18-8.50 (m, 5H).

4,5-Dinitroacenaphthene



Scheme 7.40 Dinitration of Acenaphthene

Acenaphthene (10g, 65mmol) in glacial acetic acid (80ml) was stirred during the dropwise addition of concentrated nitric acid (40ml). The mixture was warmed to redissolve the precipitate which formed shortly after the first addition of nitric acid. Once all was in solution the flask was removed from the water-bath and the reaction proceeded exothermically with the evolution of brown fumes. After 4h the solid was collected by filtration, washed with acetic acid, then water and dried to yield 9.7g of crude material. This product was boiled with toluene (50ml) for 2 minutes, filtered from the hot solvent and washed with a little cold toluene. Drying gave 5.51g (35%). Recrystallization of a 2g portion from benzene gave 0.91g as yellow needles, mp 220-223°C [lit[256] 220-224°C]; Found: C, 59.32; H, 3.28; N, 11.46. $C_{12}H_8N_2O_4$ requires C, 59.02; H, 3.30; N, 11.47%); ν_{max} (nujol mull) 1623, 1597, 1581 (aryl), 1516 (nitro), 1436, 1357, 1338 (nitro), 1143, 1066, 874, 862, 802, 745 cm^{-1}; δ_H ($CDCl_3$) 3.57 (s, 4H), 7.46, 7.55, 8.24, 8.33 (q, 4H).

8. Experimental II: Sensitization and Imaging

8.1 General Details and Instrumentation

Light Sources

A 100W mercury vapour lamp was used to provide UV irradiation of samples.

A 5mW He-Ne laser was used when monochromatic illumination at 633nm was required.

An argon ion laser (Coherent) with an output of 400mW at 458nm was used in PATM-sensitized, high resolution imaging experiments.

Spin Coating

A Headway Research vacuum chuck spinner with timer was used to spin-coat 50x50cm glass blanks for imaging purposes.

Surface Profiles

A Talystep (Rank Taylor Hobson) surface profile measuring instrument was used to examine the surface of developed gratings.

Microscopy

A stereo microscope with Nomarski[229] interference contrast illumination (Vickers Instruments) was used to examine exposed and developed gratings.

Photographs were taken using Ilford FP4 35mm film or Polaroid positive-negative film and printed on Ilford Ilfospeed Multigrade II.

Scanning Electron Microscopy

Gratings were examined by electron microscopy by the staff of the Electron Microscope Unit, R.H.B.N.C., Egham.

8.2 Sensitization Experiments

A series of qualitative experiments were carried out with the aim of finding initiators and initiator combinations effective at bringing about free radical photopolymerizations and hence photocross-linking of derivatized polymers. Possible combinations were dissolved in the presence of monomer (acrylamide) or cross-linkable polymer in small clear glass sample tubes and exposed to sunlight on a window-sill. Some of these compositions were also tested at 633nm by holding a similarly prepared tube in the beam of a helium-neon laser in a darkened room.

Tube experiments were carried out on solutions of polymer (MP59) in 2-methoxyethanol, acrylamide in 2-methoxyethanol and mixtures of acrylamide and *N,N'*-methylene-*bis*-acrylamide in aqueous solution. Generally combinations of a dye and a second substance were employed. Control experiments were also performed in which one or both substances were absent or light was excluded. Some single substance initiators were also found in which case comparison was made with a tube kept in the dark.

The sensitized cross-linking of the photocycloaddition polymer supplied by Ciba-Geigy, (Mu 1271/2316), the active group of which is a dimethylmaleimide, was also investigated. Free radical initiator combinations were tried as well as a range of likely triplet sensitizers. An unsensitized sample was used as a control.

8.3 Imaging Experiments Using PATM as Initiator

In the investigation of the imaging properties of new batches of photopolymer a consistent procedure was adopted for the preparation of sensitized plates using phenylazotriphenylmethane (PATM) as initiator. This material is known to decompose both thermally[205] and photochemically,[182] with the loss of nitrogen, to form phenyl and triphenylmethyl radicals.

In a typical experiment; polymer (1g) was dissolved in 2-methoxyethanol (10ml) and PATM (approximately 0.1-0.2g) was added. The solution was agitated to dissolve most of the PATM and then filtered through a millipore 0.5 micron filter using nitrogen pressure. The sensitized solution was handled under yellow safe-lighting and stored in bottles covered in black tape. Solutions were refigerated for long-term storage.

Sensitized coatings were prepared by spin-coating onto clean flat glass substrates (50x50x5mm) using a Headway Research vacuum chuck spinner. Some of the solution was applied as a pool in the centre of the plate, the plate was then spun for 40 seconds at a speed of 2000 rpm. As PATM is thermally labile it was not considered wise to bake sensitized plates so coatings were dried *in vacuo* at room temperature for 30 minutes prior to use.

8.3.1 Low Resolution Imaging

Investigations of polymers and processing conditions were carried out by recording low resolution binary images. In a typical procedure a sensitized plate, coated side up, was covered by a 1:1 linear diffraction grating (chromium on glass) of pitch 2, 10, 40 or 100 lines per millimetre (l mm^{-1}) and

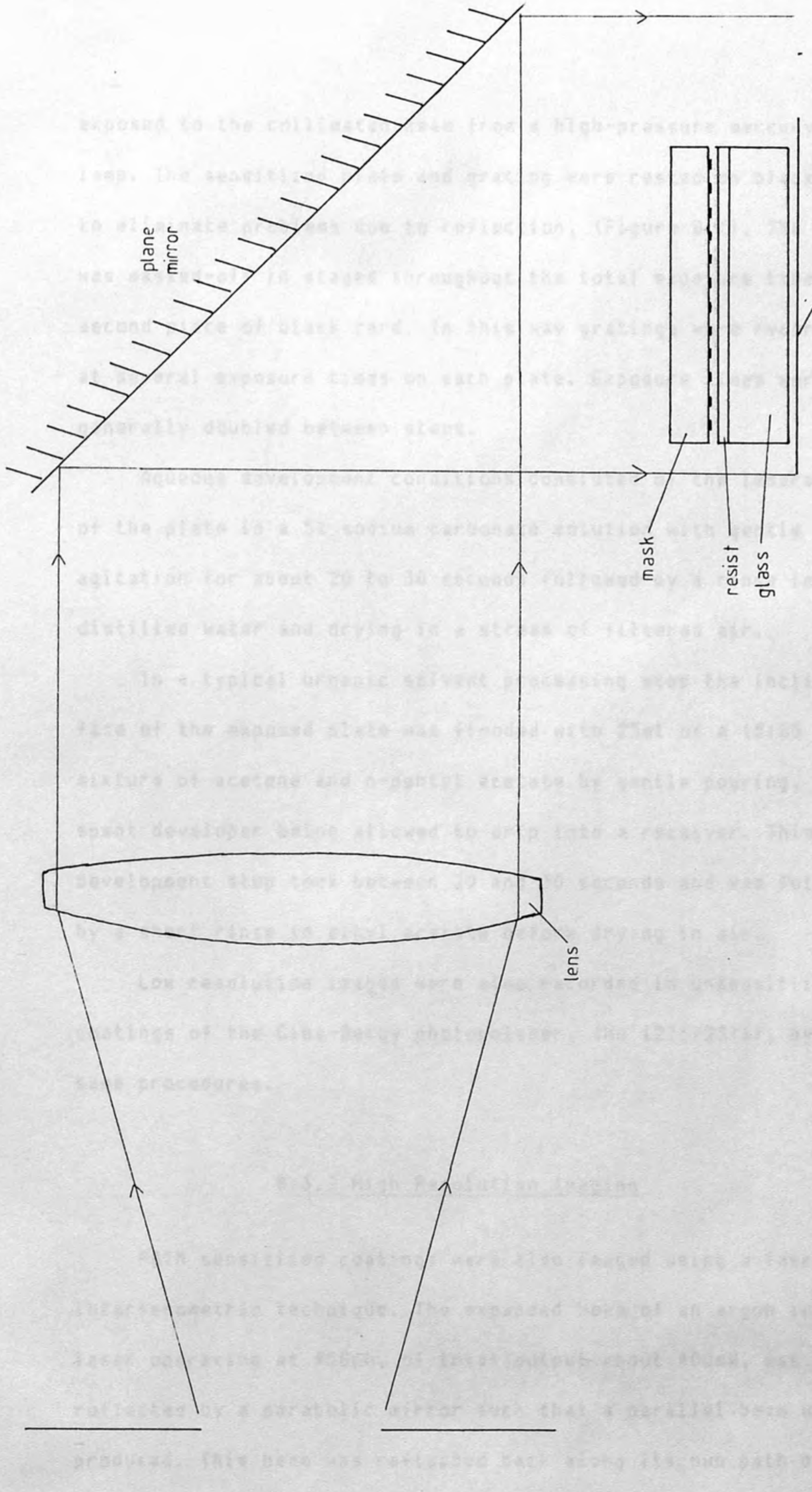


Figure 8.1 Recording of Low Resolution Images

exposed to the collimated beam from a high-pressure mercury lamp. The sensitized plate and grating were rested on black card to eliminate problems due to reflection, (Figure 8.1). The light was masked-off in stages throughout the total exposure time by a second piece of black card. In this way gratings were recorded at several exposure times on each plate. Exposure times were generally doubled between steps.

Aqueous development conditions consisted of the immersion of the plate in a 5% sodium carbonate solution with gentle agitation for about 20 to 30 seconds followed by a rinse in distilled water and drying in a stream of filtered air.

In a typical organic solvent processing step the inclined face of the exposed plate was flooded with 25ml of a 15:85 mixture of acetone and n-pentyl acetate by gentle pouring, the spent developer being allowed to drip into a receiver. This development step took between 20 and 30 seconds and was followed by a short rinse in ethyl acetate before drying in air.

Low resolution images were also recorded in unsensitized coatings of the Ciba-Geigy photopolymer, (Mu 1271/2316), by the same procedures.

8.3.2 High Resolution Imaging

PATM sensitized coatings were also imaged using a laser interferometric technique. The expanded beam of an argon ion laser operating at 458nm, of total output about 400mW, was reflected by a parabolic mirror such that a parallel beam was produced. This beam was reflected back along its own path by a plane mirror producing a static standing wave pattern of fringe spacing $\lambda/2$, the fringes being perpendicular to the direction of propagation of the beam. The coated substrate was set in the

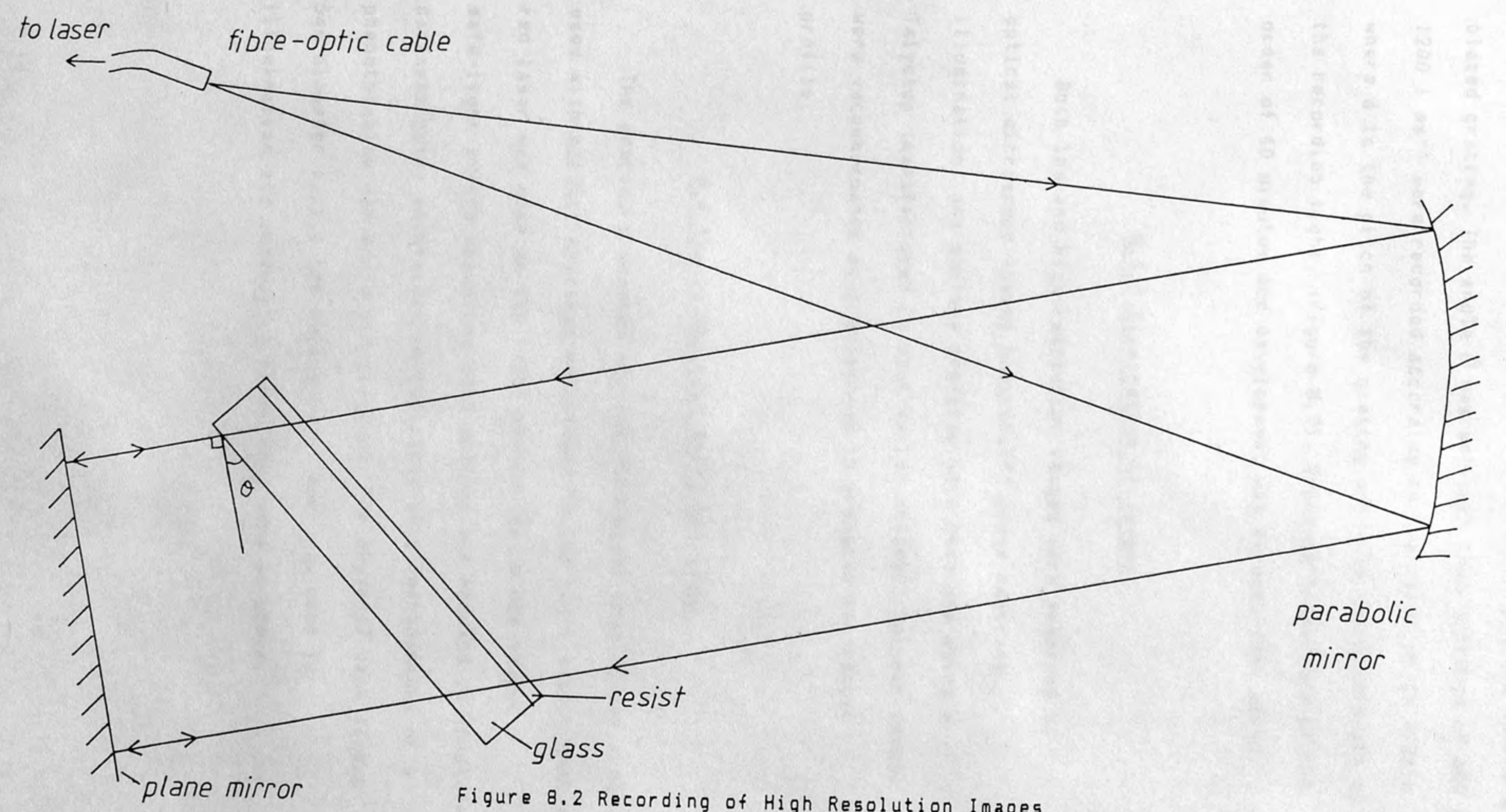


Figure 8.2 Recording of High Resolution Images

beam at an angle so as to intersect the fringes and record a blazed grating. The angle θ was set such that gratings of 600 or 1200 l mm^{-1} were recorded according to the relation d= λ/2sin where d is the pitch of the grating and λ is the wavelength of the recording light, (Figure 8.2). Exposure times were of the order of 40 minutes and development was as described above.

8.3.3 Examination of Images

Both low and high resolution images were examined by optical microscopy (using Nomarski[229] phase contrast illumination) and surface profiles were recorded using a Talystep (manufactured by Rank Taylor Hobson). Polymer images were vacuum-coated with aluminium to preserve the resist profile.

8.4 Images Recorded Using Red Light

The procedure adopted for low resolution imaging was also used with polymer coatings sensitized to red light except that a red laser was used as the light source. As no convenient safe-light exists solutions were made-up and handled in complete darkness only. Initiators investigated were combinations of a phenothiazine dye and a 1,3-diketone. The expanded beam (about 5mm diameter) of a 5mW Helium-Neon laser was used for illumination and processing conditions were as above.

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APPENDICES

Appendix 1(a):- Analysis of Copolymer nmr Spectra

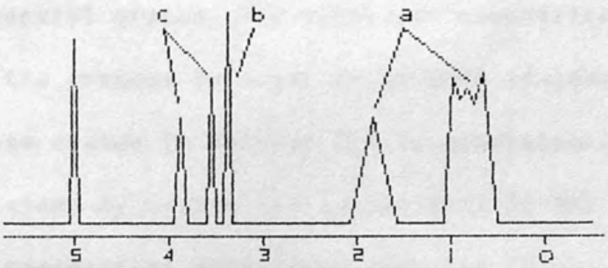
The listing that follows is a BASIC program for the Sinclair ZX-Spectrum microcomputer. The program calculates the monomer ratios of methyl methacrylate, methacrylic acid, hydroxyethyl methacrylate copolymers. It was used to calculate the compositions of MP1, MP10, MP14, MP37 and the MPX copolymer series from spectra run both at 250 and 400MHz. The results of these analyses are presented in Chapter 2.

The listing is followed by a copy of the screen output for a typical run, the data for which comes from the integrals of the 400MHz nmr spectrum of MP1 in deuteromethanol solution.

```
  10 REM COPOLYMER COMPOSITION F
ROM N.M.R.
  50 CIRCLE 230,79,2.5: PLOT 190
,82: DRAW 0,-5: PLOT 149,82: DRA
W 3,0: DRAW 0,-2: DRAW -3,0: DRA
W 0,-2: DRAW 3,0: PLOT 109,82: D
RAW 3,0: DRAW 0,-4: DRAW -3,0: P
LOT 110,80: DRAW 1,0
  60 PLOT 71,78: DRAW 0,4: DRAW
-3,-3: DRAW 3,0: PLOT 32,82: DRA
W -3,0: DRAW 0,-2: DRAW 3,0: DRA
W 0,-2: DRAW -3,0
  70 PRINT AT 0,8;"c": PLOT 68,1
66: DRAW 18,-17: PLOT 68,166: DR
AW 6,-28
  80 PRINT AT 0,13;"b": PLOT 106
,166: DRAW -7,-18
  90 PRINT AT 0,21;"a": PLOT 170
,166: DRAW -12,-30: PLOT 170,166
: DRAW 28,-20
 100 PLOT 0,87: DRAW 255,0: FOR
i=0 TO 5: PLOT 230-i*40,87: DRAW
 0,-3: NEXT i
 110 PLOT 0,92: DRAW 28,0: DRAW
2,70: DRAW 2,-70
 120 DRAW 40,0: DRAW 3,40: DRAW
3,-40
 130 DRAW 8,0: DRAW 2,55: DRAW 2
,-55
 140 DRAW 3,0: DRAW 2,80: DRAW 2
,-80
 150 DRAW 50,0: DRAW 10,40: DRAW
 10,-40
 160 DRAW 20,0: DRAW 4,55: DRAW
3,-8: DRAW 3,4: DRAW 3,-6: DRAW
4,12: DRAW 6,-57
 170 DRAW 40,0
 190 PRINT AT 12,0
 200 PRINT "Integral of groups o
n the main  polymer chain. (a)
=";: INPUT a: PRINT a''
 210 PRINT "Integral of MMA meth
yl group (b)  =";: INPUT b: PRIN
T b''
 220 PRINT "Integral of HEMA met
hylene      groups (c)  =";: INP
UT c: PRINT c''
 230 LET y=1.25*(c/a): LET z=(5*
b)/(3*a): LET x=1-(y+z): LET y=(
INT (y*100+.5))/100: LET z=(INT
(z*100+.5))/100: LET x=(INT (x*1
00+.5))/100
 240 PRINT "Molar ratios:-"'
 250 PRINT "      MMA = ";z;"  (z
)"'''"     MAA = ";x;"  (x)"'''"
  HEMA = ";y;"  (y)"
 260 PRINT '''"AGAIN? Y/N"
 270 IF INKEY$="" THEN GO TO 270
```

```
280 LET i$=INKEY$: IF i$="y" OR
i$="Y" THEN RUN
290 IF i$="n" OR i$="N" THEN ST
OP
300 GO TO 270
```

Sample output:



```
Integral of groups on the main
polymer chain. (a)   =178
Integral of MMA methyl group (b)
  =32.5
Integral of HEMA methylene
groups (c)   =71
Molar ratios:-
       MMA = 0.3   (z)
       MAA = 0.2   (x)
      HEMA = 0.5   (y)

AGAIN? Y/N
```

Appendix 1(b):- Analysis of Derivatized Copolymer nmr Spectra

The listing that follows is a BASIC program for the Sinclair ZX-Spectrum microcomputer. This program uses the data calculated by the program of Appendix 1(a), and integrals measured from the nmr spectra of derivatized (methacrylate ester) copolymers, to calculate the extent of reaction of the polymer hydroxyl groups. The copolymer composition data is stored in the program in a series of DATA statements from line 1000. As was stated in Section 2.4.2, consistency of data has been maintained by basing the analysis of 250MHz spectra on the copolymer composition determined from the 250MHz spectrum of the base copolymer and similarly comparing 400MHz spectra. On the basis of the integrals of the vinyl protons, the methyl methacrylate methyl group and the hydroxyethyl methacrylate methylene protons (marked "b", "c" and "d" in figure 2.2) the percentage of hydroxyl groups esterified is calculated by both methods 1 and 2, (Section 2.4.2).

```
  10 REM Extent of esterificatio
n of polymers from NMR data
  100 PRINT AT 1,3;"Select option
:-";AT 4,5;"1.  Kings (250 MHz)"
;AT 6,5;"2.  QMC   (400 MHz)"
  110 IF INKEY$="" THEN GO TO 110
  120 LET I$=INKEY$: IF I$<>"1" A
ND I$<>"2" THEN GO TO 110
  130 LET I=VAL I$: CLS
  140 PRINT AT 1,3;"Select base p
olymer:-";AT 4,5;"3.  MP 1";AT 6
,5;"4.  MP 10";AT 8,5;"5.  MP 14
";AT 10,5;"6.  MP 37"
  150 IF INKEY$="" THEN GO TO 150
  160 LET I$=INKEY$: IF I$<>"3" A
ND I$<>"4" AND I$<>"5" AND I$<>"
6" THEN GO TO 150
  170 LET J=VAL I$: CLS
  180 RESTORE 987+I*10+J: READ x,
y,z
  190 PRINT AT 2,0;"Vinyl proton
integral ";: INPUT d: PRINT d
  200 PRINT AT 4,0;"HEMA -CH2- pr
oton integral ";: INPUT c: PRINT
 c
  210 PRINT AT 6,0;"MMA methyl pr
oton integral ";: INPUT b: PRINT
 b
  220 LET M1=(150*d*z)/(b*y): LET
 M1=100*M1+.5: LET M1=INT M1: LE
T M1=M1/100
  230 PRINT AT 10,3;"Method 1   ";
M1;"%"
  240 LET R=(4*y)/(3*z): LET R1=c
/b: LET M2=100*(R-R1)/R
  250 LET M2=100*M2+.5: LET M2=IN
T M2: LET M2=M2/100
  260 PRINT AT 14,3;"Method 2   ";
M2;"%"
  270 PRINT AT 20,0;"Repeat with
same parameters? Y/N"
  280 IF INKEY$="" THEN GO TO 280
  290 IF INKEY$="n" THEN RUN
  300 CLS : GO TO 190
1000 DATA 13,55,32
1001 DATA 21,49,30
1002 DATA 25,50,25
1003 DATA 27,58,15
1010 DATA 19,51,30
1011 DATA 25,48,27
1012 DATA 23,52,25
1013 DATA 32,56,12
```

Appendix 2:- Treatment of Viscometry Results

The listing that follows is a BASIC program for the Sinclair ZX-Spectrum microcomputer and Sinclair (or compatible) Printer. The underlined characters appearing in lines 2100, 2230, 2250, 2350 and 5010 should be entered in graphics mode and represent user defined characters created by the subroutine at line 9000.

This program takes the experimental data from the viscometry experiments and calculates the specific and reduced viscosities at each of the concentrations used. The specific viscosity divided by concentration and the logarithm of the reduced viscosity divided by concentration are both plotted against concentration[1] using a standard least squares line fitting routine.[2] The common intercept of these two graphs at the Y-axis is the intrinsic viscosity. In practice the intercepts do not coincide exactly so the mean of both plots is calculated and quoted.

The program listing is followed by the output generated by the analysis of the viscometry data for the copolymer series, the results of which are tabulated in Section 2.4.5.

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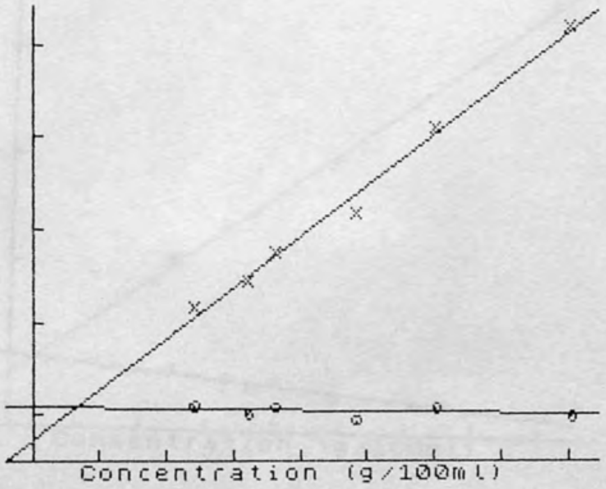
```
 100 REM Program to determine th
e intrinsic viscosity of a polym
r solution
 110 GO SUB 9000
 200 INPUT "Enter a title for th
ese data ";w$
 220 INPUT "Number of data point
s? ";a
 240 INPUT "Temperature/K? ";k
 250 DIM c(a): DIM t(a): DIM y(a
): DIM r(a): DIM i(a)
 280 INPUT "Time for solvent onl
y (seconds) ";t0
 300 FOR i=1 TO a: PRINT "Point
number ";i': PRINT "Concentratio
n in g/100ml  ";: INPUT c(i): PR
INT c(i)
 310 PRINT "Time in seconds ";:
INPUT t(i): PRINT t(i)'': NEXT i
 410 FOR i=1 TO a: LET r(i)=((t(
i)-t0)/t0)/c(i): LET i(i)=(LN (t
(i)/t0))/c(i): NEXT i
 500 FOR i=1 TO a: LET y(i)=r(i)
: NEXT i: GO SUB 1000
 540 LET m1=m: LET c$=b$: LET b1
=ABS b: LET d12=d2
 570 FOR i=1 TO a: LET y(i)=i(i)
: NEXT i: GO SUB 1000
 610 GO TO 2000
1000 LET b$="-": LET x1=0: LET y
1=0: LET xy=0: LET x2=0
1050 FOR i=1 TO a: LET x1=x1+c(i
): LET y1=y1+y(i): LET xy=xy+c(i
)*y(i): LET x2=x2+c(i)*c(i): NEX
T i
1110 LET j=a*x2-x1*x1: IF j<>0 T
HEN GO TO 1160
1130 CLS : PRINT "No solution fo
und": STOP
1160 LET m=(a*xy-x1*y1)/j: LET m
=INT (1e6*m+.5)/1e6: LET b=(y1*x
2-x1*xy)/j: IF ABS b=b THEN LET
b$="+"
1200 LET d=0: LET b=INT (1e6*b+.
5)/1e6: LET d2=0
1230 FOR i=1 TO a: LET d=d+y(i)-
m*c(i)-b: LET d2=d2+(y(i)-m*c(i)
-b)*(y(i)-m*c(i)-b): NEXT i: LET
 d2=INT (1e6*d2+.5)/1e6: RETURN
2000 REM printout
2100 LPRINT w$''"Temperature ";k
;" K"'''"Solvent flow time ";t0'
'" T      C          Asp/C"'"
             (expt)  (calc)"
2150 LET set=1: GO SUB 3000
2230 LPRINT '"Asp (CBO)=";b1
2250 LET set=2: LPRINT '" T
C          LN(Ar)/C"'"
     (expt)  (calc)": GO SUB 300
0
```

```
2350 LPRINT '"LN(Ar) (CBO)=";b
2370 LPRINT '"Sums of deviations
 squared ="'"plot 1 =";d12'"plot
 2 =";d2''"Mean intrinsic viscos
ity ="'(b+b1)/2;" dl/g"'''
2490 GO TO 4000
3000 FOR i=1 TO a
3010 IF set=1 THEN LET y=r(i)
3020 IF set=1 THEN LET yc=m1*c(i
)+b1
3030 IF set=2 THEN LET y=i(i)
3040 IF set=2 THEN LET yc=m*c(i)
+b
3045 LET y=(INT (y*1e4+.5))/1e4
3047 LET yc=(INT (yc*1e4+.5))/1e
4
3050 LPRINT t(i);TAB 7;c(i);TAB
15;y;TAB 23;yc: NEXT i: RETURN
4000 LET xh=-1e38: LET xl=1e38:
LET yh=xh: LET yl=xl: CLS
4040 FOR i=1 TO a
4050 IF r(i)>yh THEN LET yh=r(i)
4060 IF i(i)>yh THEN LET yh=i(i)
4070 IF c(i)>xh THEN LET xh=c(i)
4080 IF c(i)<xl THEN LET xl=c(i)
4090 IF i(i)<yl THEN LET yl=i(i)
4100 IF r(i)<yl THEN LET yl=r(i)
4110 NEXT i
4111 IF b1<yl THEN LET yl=b1
4112 IF b<yl THEN LET yl=b
4113 IF b1>yh THEN LET yh=b1
4114 IF b>yh THEN LET yh=b
4120 LET y=m1*xh+b1: IF y>yh THE
N LET yh=y
4130 LET y=m*xh+b: IF y>yh THEN
LET yh=y
4140 LET xl=0: LET xax=xh-xl: LE
T xh=xh+.05*xax: LET xl=xl-.05*x
ax: LET xax=xh-xl
4160 LET yax=yh-yl: LET yh=yh+.0
5*yax: LET yl=yl-.05*yax: LET ya
x=yh-yl
4210 LET y=(((m1*xl+b1)-yl)/yax)
*175
4212 LET yt=(((m1*(xl+1*xax)+b1)
-yl)/yax)*175
4214 PLOT 0,y: DRAW 255,yt-y
4220 LET y=(((m*xl+b)-yl)/yax)*1
75
4222 LET yt=(((m*(xl+1*xax)+b)-y
l)/yax)*175
4224 PLOT 0,y: DRAW 255,yt-y
4260 FOR i=1 TO a: LET x=((c(i)-
xl)/xax)*255: LET y=((r(i)-yl)/y
ax)*175: PLOT x,y: DRAW 2,2: DRA
W -4,-4: DRAW 2,2: DRAW 2,-2: DR
AW -4,4: LET y=((i(i)-yl)/yax)*1
75: PLOT x,y: CIRCLE x,y,2: NEXT
 i
```

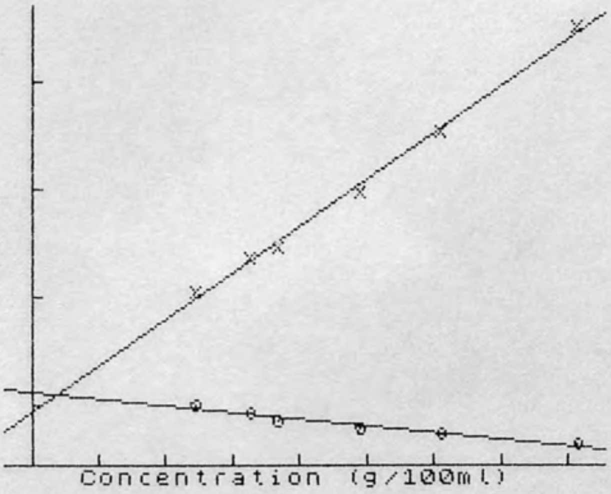
```
4700 PLOT 0,0: DRAW 255,0: LET x
=((0-xl)/xax)*255: PLOT x,0: DRA
W 0,175
4780 FOR i=.5 TO xh STEP .5: LET
 x=((i-xl)/xax)*255: PLOT x,1: D
RAW 0,3: NEXT i
4840 LET x=((0-xl)/xax)*255: FOR
 i=(INT (yl*50)+1)/50 TO yh STEP
 .02: LET y=((i-yl)/yax)*175: PL
OT x+1,y: DRAW 3,0: NEXT i: COPY

5010 LPRINT "    Concentration (
g/100ml)"'''"Y axis:-     Asp/C (
crosses) or"'"           LN(Ar)/C
(circles)"'
5050 LPRINT '"Y axis scale ";(IN
T (50*yl)+1)/50;" to ";(INT (50*
yh))/50;'"step 0.02"''"X axis sc
ale 0.0 TO  ";(INT (xh*2))/2'"st
ep 0.5"
8999 STOP
9000 REM user defined graphics
9010 RESTORE 9100: FOR i=USR "a"
 TO USR "a"+15: READ j: POKE i,j
: NEXT i: RETURN
9100 DATA 0,88,36,36,36,4,4,2,0,
8,4,2,255,2,4,8
```

```
MP1 in 2-methoxyethanol

Temperature 298 K

Solvent flow time 150.6

 T       C              ηsp/C
                   (expt)   (calc)
310.7  4.029     0.2639   0.2628
260.6  3.022     0.2417   0.2407
232    2.418     0.2235   0.2275
209.3  1.813     0.215    0.2142
201.3  1.612     0.2088   0.2098
187.6  1.209     0.2032   0.201

ηsp  (C→0)= 0.17453

 T      C              LN(ηr)/C
                   (expt)   (calc)
310.7  4.029     0.1797   0.1798
260.6  3.022     0.1815   0.1802
232    2.418     0.1787   0.1805
209.3  1.813     0.1815   0.1808
201.3  1.612     0.18     0.1808
187.6  1.209     0.1817   0.181

LN(ηr), (C→0)=0.181535

Sums of deviations squared =
plot 1 =.000024
plot 2 =6E-6

Mean intrinsic viscosity =
0.1780325 dl/g
```



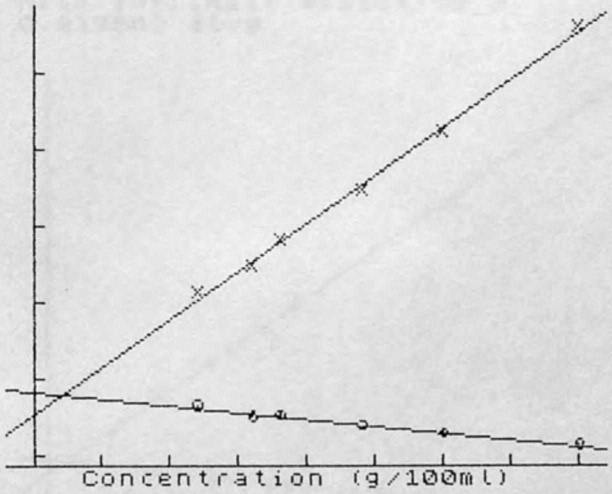
```
Y axis:-     ηsp/C (crosses) or

           LN(ηr)/C (circles)

Y axis scale 0.18 to 0.26
step 0.02

X axis scale 0.0 TO  4
step 0.5
```

```
MP10 in 2-methoxyethanol

Temperature 298 K

Solvent flow time 150.5

 T        C              ηsp/C
                    (expt)   (calc)
304     4.076     0.2502   0.249
256.6   3.057     0.2306   0.2313
231.2   2.445     0.2193   0.2207
208.2   1.834     0.209    0.2101
201.3   1.63      0.2071   0.2066
187.5   1.223     0.201    0.1995

ηsp  (C→0)= 0.178324

 T        C             LN(ηr)/C
                    (expt)   (calc)
304     4.076     0.1725   0.1721
256.6   3.057     0.1745   0.1746
231.2   2.445     0.1756   0.1761
208.2   1.834     0.177    0.1776
201.3   1.63      0.1784   0.1781
187.5   1.223     0.1797   0.1791

LN(ηr)  (C→0)=0.18214

Sums of deviations squared =
plot 1 =8E-6
plot 2 =1E-6

Mean intrinsic viscosity =
0.180232 dl/g
```



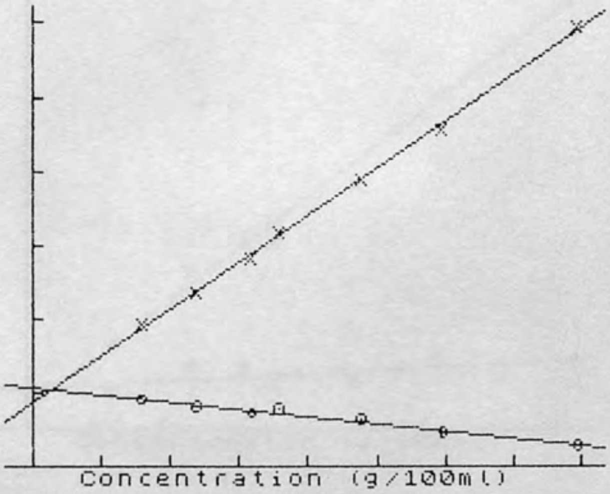
```
Y axis:-     ηsp/C (crosses) or

         LN(ηr)/C (circles)

Y axis scale 0.18 to 0.24
step 0.02

X axis scale 0.0 TO  4
step 0.5
```

```
MP14 in 2-methoxyethanol

Temperature 298 K

Solvent flow time 150.7

 T        C               ηsp/C
                      (expt)    (calc)
339.7   4.012      0.3126    0.3112
279.9   3.009      0.2849    0.2861
248.5   2.407      0.2696    0.271
220.4   1.805      0.2562    0.2559
211.1   1.605      0.2497    0.2509
194.7   1.203      0.2427    0.2408

ηsp  (C→0)= 0.210655

 T        C              LN(ηr)/C
                      (expt)    (calc)
339.7   4.012      0.2026    0.2023
279.9   3.009      0.2058    0.2059
248.5   2.407      0.2078    0.208
220.4   1.805      0.2106    0.2102
211.1   1.605      0.21      0.2109
194.7   1.203      0.2129    0.2123

LN(ηr)  (C→0)=0.216586

Sums of deviations squared =
plot 1 =.00001
plot 2 =2E-6

Mean intrinsic viscosity =
0.2136205 dl/g
```



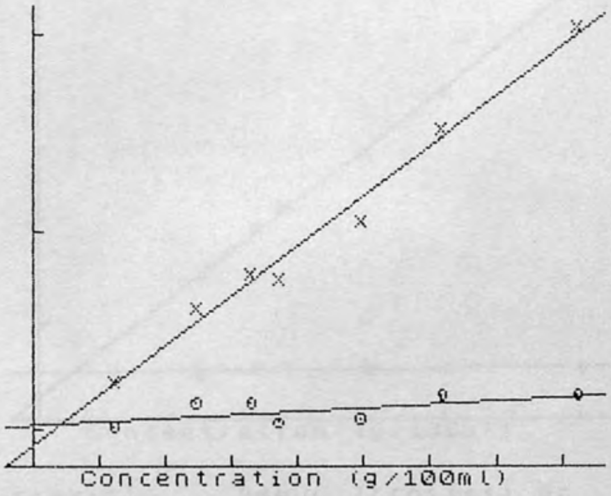
```
Y axis:-    ηsp/C (crosses) or

         LN(ηr)/C (circles)

Y axis scale 0.2 to 0.3
step 0.02

X axis scale 0.0 TO  4
step 0.5
```

```
MP37 in 2-methoxyethanol

Temperature 298 K

Solvent flow time 149.9

 T        C                 ηsp/C
                      (expt)    (calc)
339.7   3.971       0.3189    0.3179
280     2.978       0.2914    0.2928
249.2   2.383       0.278     0.2777
220.5   1.787       0.2636    0.2626
210.9   1.588       0.2563    0.2576
194     1.191       0.247     0.2475
178.3   0.794       0.2386    0.2375

ηsp  (C→0)= 0.217383

 T        C               LN(ηr)/C

                      (expt)    (calc)
339.7   3.971       0.206     0.2063
280     2.978       0.2098    0.2102
249.2   2.383       0.2133    0.2125
220.5   1.787       0.216     0.2148
210.9   1.588       0.215     0.2156
194     1.191       0.2165    0.2171
178.3   0.794       0.2185    0.2187

LN(ηr)  (C→0)=0.221743

Sums of deviations squared =
plot 1 =7E-6
plot 2 =3E-6

Mean intrinsic viscosity =
0.219563 dl/g
```



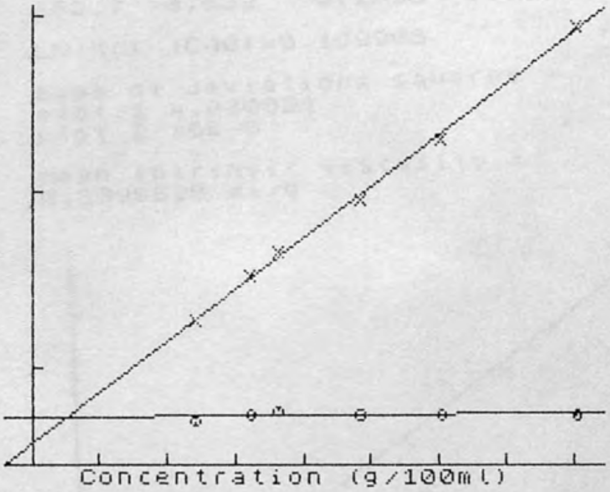
```
Y axis:-     ηsp/C (crosses) or

             LN(ηr)/C (circles)

Y axis scale 0.22 to 0.32
step 0.02

X axis scale 0.0 TO  4
step 0.5
```

```
MPX20 in 2-methoxyethanol

Temperature 298 K

Solvent flow time 153
 T        C                 ηsp/C
                      (expt)    (calc)
254.3  4.118      0.1608   0.1599
224    3.088      0.1503   0.1495
206.3  2.471      0.141    0.1433
191.3  1.853      0.1351   0.137
187.2  1.647      0.1357   0.1349
178    1.235      0.1323   0.1308
164.8  0.618      0.1248   0.1245

ηsp  (C→0)= 0.118271

 T       C                LN(ηr)/C
                      (expt)    (calc)
254.3  4.118      0.1234   0.1234
224    3.088      0.1234   0.1226
206.3  2.471      0.121    0.1222
191.3  1.853      0.1206   0.1217
187.2  1.647      0.1225   0.1216
178    1.235      0.1225   0.1213
164.8  0.618      0.1202   0.1208

LN(ηr)  (C→0)=0.120369

Sums of deviations squared =
plot 1 =.000013
plot 2 =6E-6

Mean intrinsic viscosity =
0.11932 dl/g
```



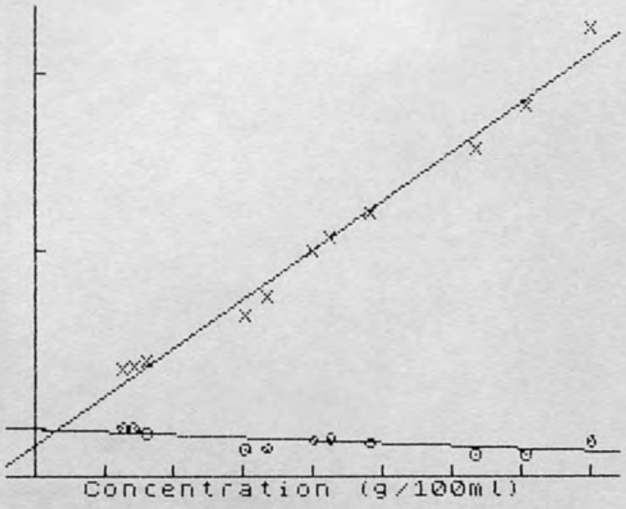
```
Y axis:-     ηsp/C (crosses) or

         LN(ηr)/C (circles)

Y axis scale 0.12 to 0.16
step 0.02

X axis scale 0.0 TO  4
step 0.5
```

```
MPX25 in 2-methoxyethanol

Temperature 298 K

Solvent flow time 150.8

 T       C               ηsp/C
                    (expt)   (calc)
259.6   4.032   0.1789   0.1786
226.6   3.024   0.1662   0.1668
208.9   2.419   0.1593   0.1597
192.7   1.814   0.1532   0.1526
187.4   1.613   0.1505   0.1503
177.3   1.209   0.1454   0.1455

ηsp (C→0)= 0.131391

 T       C              LN(ηr)/C
                    (expt)   (calc)
259.6   4.032   0.1347   0.1349
226.6   3.024   0.1347   0.1347
208.9   2.419   0.1347   0.1347
192.7   1.814   0.1352   0.1346
187.4   1.613   0.1347   0.1346
177.3   1.209   0.1339   0.1345

LN(ηr)  (C→0)=0.134359

Sums of deviations squared =
plot 1 =1E-6
plot 2 =1E-6

Mean intrinsic viscosity =
0.132875 dl/g
```



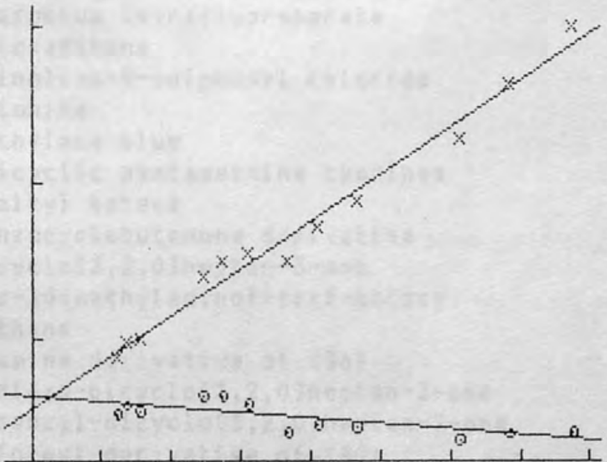
```
Y axis:-    ηsp/C (crosses) or

          LN(ηr)/C (circles)

Y axis scale 0.14 to 0.18
step 0.02

X axis scale 0.0 TO  4
step 0.5
```

```
MPX30 in 2-methoxyethanol

Temperature 298 K

Solvent flow time 148.9

 T       C               ηsp /C
                   (expt)    (calc)
259.3   4.004     0.1852    0.1823
241.7   3.533     0.1764    0.1771
229.7   3.161     0.1717    0.173
207.7   2.403     0.1643    0.1647
199.9   2.12      0.1616    0.1616
196.6   2.002     0.16      0.1603
187.4   1.668     0.155     0.1566
183.1   1.502     0.1529    0.1548
166.5   0.801     0.1476    0.147
164.4   0.707     0.1472    0.146
162.7   0.632     0.1466    0.1452

ηsp  (C→0) = 0.138199

 T       C                LN(ηr) /C
                   (expt)    (calc)
259.3   4.004     0.1385    0.1373
241.7   3.533     0.1371    0.1376
229.7   3.161     0.1371    0.1379
207.7   2.403     0.1385    0.1383
199.9   2.12      0.1389    0.1385
196.6   2.002     0.1388    0.1386
187.4   1.668     0.1379    0.1388
183.1   1.502     0.1377    0.1389
166.5   0.801     0.1395    0.1394
164.4   0.707     0.1401    0.1394
162.7   0.632     0.1402    0.1395

LN(ηr)  (C→0) =0.139906

Sums of deviations squared =
plot 1 =.000021
plot 2 =6E-6

Mean intrinsic viscosity =
0.1390525 dl/g
```



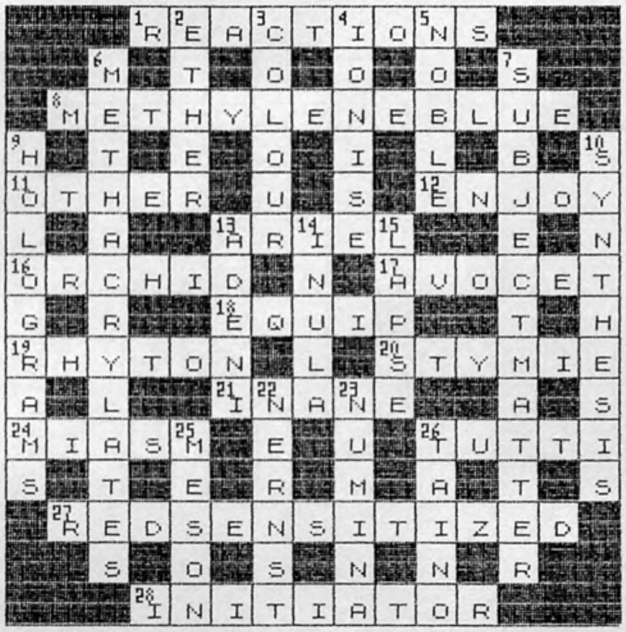
```
Y axis:-     ηsp /C (crosses) or

         LN(ηr) /C (circles)

Y axis scale 0.14 to 0.18
step 0.02

X axis scale 0.0 TO  4
step 0.5
```

```
MPX40 in 2-methoxyethanol

Temperature 298 K

Solvent flow time 149

 T       C             ηsp/C
                   (expt)   (calc)
264.7   3.882    0.2      0.1977
247.3   3.425    0.1926   0.1922
233.8   3.064    0.1857   0.1879
210.7   2.329    0.1778   0.1791
202.4   2.055    0.1744   0.1758
195.6   1.839    0.1701   0.1732
188.6   1.553    0.1711   0.1698
183.7   1.37     0.17     0.1676
179.7   1.226    0.1681   0.1658
167.5   0.776    0.16     0.1604
165.3   0.685    0.1597   0.1593
163.4   0.613    0.1577   0.1585

ηsp (C→0) = 0.151118

 T       C           LN(ηr)/C
                   (expt)   (calc)
264.7   3.882    0.148    0.1471
247.3   3.425    0.1479   0.1478
233.8   3.064    0.147    0.1483
210.7   2.329    0.1488   0.1493
202.4   2.055    0.1491   0.1497
195.6   1.839    0.148    0.15
188.6   1.553    0.1518   0.1504
183.7   1.37     0.1528   0.1507
179.7   1.226    0.1528   0.1509
167.5   0.776    0.1508   0.1515
165.3   0.685    0.1516   0.1516
163.4   0.613    0.1505   0.1517

LN(ηr)  (C→0) =0.152613

Sums of deviations squared =
plot 1 =.000037
plot 2 =.000019

Mean intrinsic viscosity =
0.1518655 dl/g
```



```
Y axis:-     ηsp/C (crosses) or
         LN(ηr)/C (circles)

Y axis scale 0.16 to 0.2
step 0.02

X axis scale 0.0 TO  4
step 0.5
```

Appendix 3:- Structure Index



■	■	■	1 R	2 E	A	3 C	T	4 I	O	5 N	S	■	■	■
■	■	6 M	■	T	■	O	■	O	■	O	■	7 S	■	■
■	8 M	E	T	H	Y	L	E	N	E	B	L	U	E	■
9 H	■	T	■	E	■	O	■	I	■	L	■	B	■	10 S
11 O	T	H	E	R	■	U	■	S	■	12 E	N	J	O	Y
L	■	A	■	■	13 A	R	14 I	E	15 L	■	■	E	■	N
16 O	R	C	H	I	D	■	N	■	17 A	V	O	C	E	T
G	■	R	■	■	18 E	Q	U	I	P	■	■	T	■	H
19 R	H	Y	T	O	N	■	L	■	20 S	T	Y	M	I	E
A	■	L	■	■	21 I	22 N	A	23 N	E	■	■	A	■	S
24 M	I	A	S	25 M	■	E	■	U	■	26 T	U	T	T	I
S	■	T	■	E	■	R	■	M	■	A	■	T	■	S
■	27 R	E	D	S	E	N	S	I	T	I	Z	E	D	■
■	■	S	■	O	■	S	■	N	■	N	■	R	■	■
■	■	■	28 I	N	I	T	I	A	T	O	R	■	■	■