COPOLYMERS OF METHACRYLIC ACID AND
ITACONIC ACID DERIVATIVES AS
THERMALLY CROSSLINKABLE ELECTRON RESISTS

A Thesis submitted to

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This thesis is submitted for the degree of Doctor of Philosophy at the University of Stirling, having been submitted for no other degree. It is a record of research undertaken in the Department of Chemistry. This work is wholly original except where due reference is made.

To my parents.

ABSTRACT

This thesis describes the preparation and lithographic evaluation of copolymers of methyl methacrylate, dimethyl itaconate and α-methyl styrene with derivatives of methacrylic acid or itaconic acid as thermally crosslinkable electron resists. A number of promising materials, including copolymers, terpolymers and mixtures of two types of copolymer have been identified, and have been demonstrated to be capable of sub 500nm resolution.

Statistical copolymers have been found to show a general variation in resist properties with copolymer composition. This has been discussed in terms of the variation in the proportion of crosslinking groups present, and in changes in radiation sensitivity and solvent development behaviour with copolymer composition.

It has been shown that the exposure dose required to first solubilise the resist can be very much less than that required for the development of high resolution resist features. Experimental results obtained in this work are compared to a theory originally published to describe the solubilisation of lignin from plant tissues, whereby gel degradation can be conceptually treated as the reverse of network formation.

ACKNOWLEDGEMENTS

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Electron beam resists are polymer materials that have an important application in the manufacture of integrated circuits. The growth in the interest in these materials can be traced to work on poly(methyl methacrylate) (PMMA) as an electron resist material in 1968[1]. A significant increase in the number of publications on new or improved resist materials occurred during the period 1970-1985, although many of these publications reported materials which could offer advantages in only one or two respects.

Thermally crosslinkable electron beam resists were first described in 1973 and have been shown to have a number of important advantages for high resolution lithography, although at the present time they are generally acknowledged to suffer from disadvantages, including a relatively low sensitivity to the exposing electron beam. The major reason for continued research in these materials is the still-present requirement for resist materials capable of high resolution lithography.

Integrated circuits are constructed as a series of overlying layers of conducting and insulating materials intricately interconnected or arranged over a semiconducting substrate. Each layer is normally patterned by first preparing a similar pattern in a thin polymer film, termed a resist, and then transferring the pattern produced in the resist to the underlying material by one of a number of specialised etching processes. The method of first preparing a pattern in a resist film and then transferring this pattern to an underlying material is called lithography.

A number of different lithographic techniques currently exist and each technique can be shown to have particular advantages and

disadvantages. In electron beam lithography the resist material is exposed to a focussed beam of electrons. Exposure of the resist normally leads to changes in solubility or in dissolution rate, and allows either the exposed or unexposed areas of resist to be selectively removed. Once the required pattern has been produced in the resist, it can then be transferred to the underlying substrate. Chemical etching using liquid etchants is commonly used, but dry etching techniques such as plasma or reactive ion etching have advantages for the transfer of very fine resist features. At the present time the major applications of electron beam lithography are in the preparation of mask plates, used in ultra-violet and deep ultra-violet lithography, and in the manufacture of specialised devices by direct write techniques.

1.2 Electron Beam Resist Materials

Electron beam resist materials are generally required to have excellent film forming properties, a high resistance to attack by chemical or dry etching techniques, and a high sensitivity to exposing electrons. For advanced lithography, line resolution and resist-substrate adhesion are additional important requirements. The general properties required of resist materials are discussed in more detail by Thompson.[2]

Positive Resist Materials

The major class of positive acting resists are linear polymers which degrade by main chain scission during exposure to an electron beam. An important feature of these materials is that following exposure of the resist, the exposed areas have a dissolution rate in a

selected solvent 7-20 times greater than the dissolution rate of the unexposed polymer in the same solvent. This allows the selective removal of the exposed areas in a solvent or solvent mixture termed a developer. The selection of a suitable solvent developer is crucial to the successful use of a material in electron beam lithography.

Main chain scission has been shown to proceed in materials of this type with a dependence upon G(s), the radiation chemical yield for main chain scission, defined as the number of main chain scission events per 100eV absorbed energy. For materials which degrade by main chain scission, the molecular weight distribution (MWD) following irradiation has been demonstrated to tend towards a random, or most probable distribution where Mw = 2Mn, regardless of the original MWD.[3]

Irradiation has also been reported to lead to changes in polymer tacticity.[4,5] For PMMA, Thompson[4] reported that irradiation resulted in a decrease in isotactic sequences, and an increase in atactic and syndiotactic sequences. It was suggested that this might result from rapid recombination of chain fragments, in a different arrangement to that originally present, following scission.

The increase in dissolution rate for exposed positive resists has been shown to be related to the reduction in average molecular weight.[6,7] Cooper[8] compared the dissolution rates of PMMA with number average molecular weights between 6,000 and 320,000 $g.mol^{-1}$ prepared by polymer synthesis, and by the exposure of an originally higher molecular weight sample. It was found that the dissolution rate of material prepared by exposure of an originally higher molecular weight sample was approximately 2-3 times greater than the corresponding dissolution rate of material prepared

by laboratory synthesis.   It was therefore suggested that some additional factor, besides the reduction in average molecular weight, was responsible for increased dissolution rates of exposed resist.   It was sugested by Cooper that these results might be due to enhanced rates of solvent penetration in exposed polymer as a result of the release and entrapment of gaseous fragments during irradiation.   This effect has also been postulated by a number of other authors[9-11], most notably by Ouano.[9]

Negative Resist Materials

Negative acting resists become less soluble with exposure to an electron beam as a result of covalent crosslinking.   At a particular absorbed dose, termed the gel dose, an insoluble fraction of resist is first formed.   With increasing exposure, the quantity of crosslinked polymer increases in a non-linear manner towards unity. At the same time the quantity of un-crosslinked polymer, or sol, decreases.   Charlesby[12] has shown that the rate of increase in gel fraction with normalised dose, (D/Dgel), is greatest for polymers with an originally mono-disperse molecular weight distribution.

Negative resists generally have a higher electron sensitivity, ie require a lower exposed dose to provide a lithographically useful resist pattern, compared to positive resists.   The resolution of negative acting resists is generally poorer than that of positive acting resists however, because of the relatively high degree of swelling which can occur during resist development.

1.3 Thermally Crosslinkable Positive Resists (Review)

Thermally crosslinkable electron beam resists were first described by Roberts.[13,14] These materials might now be regarded as part of a more general class of pre-crosslinked resists, since it has also been demonstrated to be possible to prepare crosslinked films by ultra-violet exposure prior to degradative irradiation by an electron beam.[11]

The general principle of operation for pre-crosslinked resists is illustrated in Figure 1. Thermally crosslinkable resists are normally baked in-situ on the surface of the substrate material at temperatures between 160-215°C to produce a lightly crosslinked film prior to irradiation. During electron beam exposure the irradiated areas are degraded, restoring solubility to these regions and allowing their selective removal in a suitable solvent.

The material first described by Roberts consisted of a mixture of two copolymers, poly(methyl methacrylate-co-methacryloyl chloride) and poly(methyl methacrylate-co-methacrylic acid) which were thermally crosslinked to give intermolecular anhydride crosslinks (Figure 2).

A number of variations on the idea of Roberts, including copolymers and terpolymers containing methacrylic acid (MAA) and methacryloyl chloride (MACl) have since been proposed.[15-19]

Roberts has further reported the thermal crosslinking of para or ortho substituted phenol formaldehyde resins with poly(methyl methacrylate-co-methacryloyl chloride),[20] and also a mixture of two copolymers poly(styrene-co-methacrylic acid) and poly(styrene-co-methacryloyl chloride.[20,21] Improved dry etch resistance was claimed for these materials.
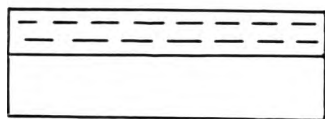
Un-coated wafer
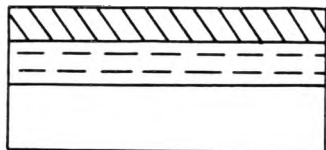
spin-on resist and pre-bake
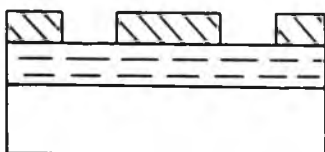
pattern resist
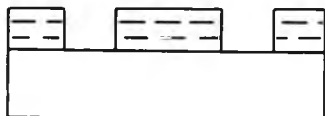
Transfer pattern to underlying film.
Strip Resist

resist

layer to be patterned

substrate material

FIGURE 1   Preparation of Patterned Layer using Pre-crosslinked Resist.
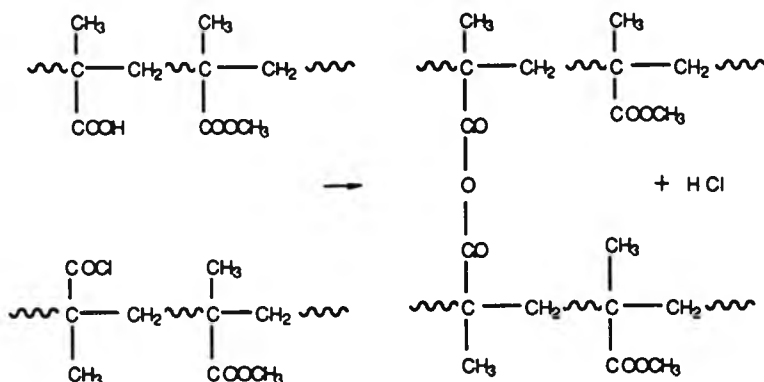
Figure 2: Thermal crosslinking of MMA-co-MAA, MMA-co-MACl
(after Roberts[13,14]).

Matsuda[22] reported the use of poly(methacrylamide) (PMAM) as a single component thermally crosslinkable resist. This material was spun from aqueous solution and pre-baked for 15 minutes at 200°C. Matsuda reported that the C/N ratio, determined by elemental analysis, varied systematically with baking and it was suggested that crosslinking occurred with the formation of a mixture of inter and intra molecular imide linkages. Sensitivity was reported to be ~0.3μC.cm^{-2} with development in an aqueous solution of Na_2SiO_3. Subsequent work by Namaste,[23] however,

found that the crosslinking could not be reproduced, and that many of the properties claimed for this material could not be substantiated. Resist sensitivity was not as good as that initially reported and resolution was said to be poor as a result of resist swelling. MMA-MAM copolymers were found to show reduced swelling, but sensitivity enhancement over PMMA was minimal.

Crosslinked resists based on imide and anhydride structures prepared by an in-situ gas-solid phase reaction at 200°C have also been described.[24]

Tada[25] described the thermal crosslinking of poly(2,2,2 trichloroethyl methacrylate). This material has a number of disadvantages, including a tendency to crosslink with electron exposure at high exposure doses, but has still been made available commercially.

Poly(phenyl methacrylate-co-methacrylic acid) has been reported by Harada[26] to crosslink with reaction occurring between phenyl methacrylate and methacrylic acid repeat units. Anhydride formation as a result of the reaction between two carboxylic acid units is thought not to take place.[27] This material shows high electron sensitivity (~ 5 $\mu C.cm^{-2}$), and also very good resolution. Resist features ~ 0.35-0.20 micrometre were defined at an exposed dose of 65 $\mu C.cm^{-2}$. Dry etch rates were approximately a factor of 2 improved over that of PMMA.

A pre-crosslinked resist prepared from poly(methyl methacrylate-co-glycidyl methacrylate) was reported by Yamashita.[28] This material was cured by exposure to ultra violet radiation and was found to degrade with exposure to an electron beam.

Further thermally crosslinkable resist materials have been

prepared by the crosslinking of a polymer and a lower molecular weight crosslinking agent.[29-37]   Details of these materials are given in Table 1.

Table 1   Pre-crosslinked Resists formed from Mixtures of Polymers and Low Molecular Weight Crosslinking Agents.

Polymer	Crosslinking Agent	Ref
Poly(MMA-co-MAA)	Epoxy monomers	29
Poly(MMA-co-HEMA)	Hexanedoic acid	30
Poly(αMS-co-MAA)	Mono azido or diazido compound	31
Poly(αMS-co-itaconic acid)	Mono azido or diazido compound	32
Poly(MMA-co-MACl	Neopentylene glycol	33
Poly(MMA-co-vinyl alcohol)	p-azido sulphonyl benzoate	34
Poly(MMA-co-methacrylonitrile)	Tripropylene glycol-diglycidyl ether (TPG)	35
Poly(methacrylonitrile)	2,6-bis(4 azido benzal) cyclohexanone (DABC)	36[a]
Poly(n-butyl methacrylate) (PnBA)	DABC	37[a]
Poly(methyl isopropenyl ketone) (PMIPK)	DABC	37[a]
Poly(MMA-co-MAA)	TPG	37

[a]   cured by uv and/or heat.

1.4 Electron Exposure of Resist Materials

The exposure of electron beam resists is understood to be dependent upon the characteristics of electrons scattered within the resist film. Electron scattering within a resist normally occurs from two main sources; (1) a forward scattering of electrons as they pass through the resist and substrate material, and (2) a backscattering of electrons from the substrate material. It has been estimated that backscattered electrons contribute approximately 40% of the total energy absorbed by a resist film.[38]

For inelastically scattered electrons the primary mechanisms of energy interchange are ionisation and excitation. Ionisation will occur if an inner shell electron has been given sufficient energy to escape from its parent molecule and will result in the formation of secondary electrons. Secondary electrons may have sufficient energies to cause further ionisations or excitations within a limited range, and it is believed that during electron beam irradiation most crosslinking or chain scission events are initiated by the absorption of energy associated with secondary electrons.

The absorbtion of high energy radiation is generally assumed to be non-specific and to depend only upon the electron density of the irradiated material.[3] It is commonly assumed that there is no significant transfer of energy following the initial absorption event. Guillet[39] has highlighted studies showing that the probability of reactions occurring at a carbonyl group is much greater than would be expected from its mass absorption coefficient. This latter result would suggest that it is possible for energy or charge to migrate following the initial absorption event. However, crosslinking or main chain scission can be regarded as obeying the

statistical laws of random distribution throughout the polymer when considered as a whole.

One of the major results of electron scattering within a resist film is that the area of resist which receives a significant electron dose can be much larger than the nominal dimensions of the exposing beam. This effect produces an important limitation to the resolution that can be achieved in practical resist systems since most polymer resist materials are sensitive to both forward and backscattered primary electrons, and also to lower energy secondary electrons. Electron scattering also normally leads to a variation in absorbed energy density at distances away from the nominal position of the beam, and with depth into the resist film. Very high resolution resist materials require that the response of the resist (ie the changes in solubility or dissolution rate) occur abruptly at the edges of exposed features, and therefore over a narrow range of absorbed doses.

Electron scattering within the resist and substrate lead to two further effects:

(1) The cross sectional profile of the developed resist profile is not always vertical, and can show either a positively sloping face or an undercut profile;

(2) The lateral scattering of electrons can result in certain geometries receiving an additional dose as a result of electron scattering from nearby features. This is termed the proximity effect. Proximity effects can lead to distortions in the shapes of developed resist features and results in the actual dose required to expose positive resist features decreasing in the order large areas < closely spaced lines < isolated lines.

1.5 Radiation Chemistry of Methacrylic Acid and Related Materials

Polymers of methacrylic acid and related materials are part of a relatively small number of polymers that degrade by high energy irradiation. This behaviour is in accordance with the generalised rule for vinyl polymers first proposed by Miller,[40] where repeat units of the general structure I degrade, whereas repeat units of the general structure II crosslink.

$$\left(\begin{array}{c} R_1 \\ | \\ -C-CH_2- \\ | \\ R_2 \end{array} \right) \qquad \left(\begin{array}{c} H \\ | \\ -C-CH_2- \\ | \\ R_1 \end{array} \right)$$

I   II
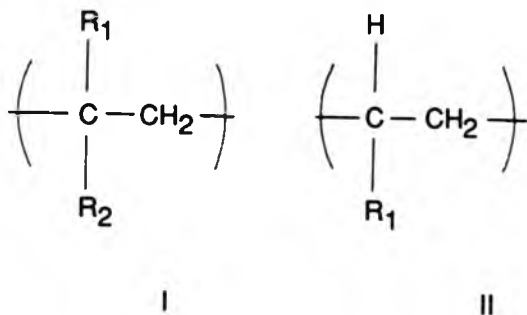
This observation has been found to be correct for most polymers. The notable exception to this rule occurs where side chains contain long methylene sequences or where repeat units are substituted by halogen atoms. For the case of alkyl methacrylates, Graham[41] found that crosslinking occurred in n-heptyl analogues and above. Crosslinking did not take place in n-butyl, n-hexyl or sec-heptyl and sec-octyl materials. Kircher[42] reported that with increasing branching of a butyl side group, (n-butyl, isobutyl, sec-butyl, tert-butyl) there is an increasing tendency for chain scission.

Many materials do not exclusively show one form of behaviour and can show a mixture of both main chain scission and crosslinking over a wide range of absorbed energies.[43]   In other materials, main chain scission can be observed at low doses, and crosslinking observed at high doses.   PMMA has been reported to crosslink during electron exposure at exposed doses greater than 1000 $\mu C.cm^{-2}$ at accelerating voltages of 10 or 14 KV.[1]

The radiation chemistry of polymer materials is normally characterised by the use of G-values.   A G value is defined as the number of chemical events of a particular kind occurring per 100eV of absorbed energy.   G values are commonly reported for main chain scission (Gs), and for crosslinking (Gx).   G values for gas evolution or double bond formation are also sometimes reported.   G values have been found to be independent of polymer molecular weight, but are dependent on temperature.[12]

The radiation chemistry of PMMA has been reviewed by Dole[44] and by Hiroaka.[45]   In separate studies, Kircher, Alexander and Todd report G values for main chain scission of 1.2, 1.64 and 1.1 respectively, with approximately 0.71 to 0.83 $COOCH_3$ side chain breaks per main chain scission.[42,46,47]   These findings have been interpreted as showing that a major mechanism of main chain scission involves scission of the ester side chain, which precedes, and then induces, main chain scission.   Analysis of the volatile materials released during irradiation show that CO, CO_2, CH_4 and $HCOOCH_3$ are the major products.   Gaseous products are thought to be liberated largely as a result of the decomposition of the $COOCH_3$ side chain.   No evidence has been found for the splitting off of α-CH_3 groups.[47]

Hiroaka[45] has described the radiation degradation behaviour of poly(methacrylic acid), poly(t-butyl methacrylate), and poly(methacrylic anhydride). Main chain scission induced by side chain elimination was reported to be a common feature of the behaviour of all of these materials. Radiation chemical yields for a number of other acrylate polymers have been reported (see eg the review by Schnabel,[48] and publications of Harada.[49])

Copolymers of MMA and itaconic acid (III) were reported by

$$COOH$$
$$|$$
$$CH_2$$
$$|$$
$$C = CH_2$$
$$|$$
$$COOH$$
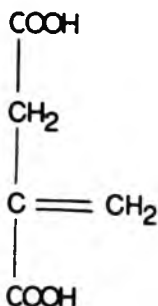
III   Itaconic Acid (Monomer)

Anderson[50] to have increased values of Gs compared to PMMA. Anderson suggested that a similar degradation process involving scission of the acyl side chain(s) was likely in itaconate structures although no experimental evidence supporting this proposal was given. Gs values for other itaconates were found to decrease in the order; poly(itaconic acid) > poly(dimethyl itaconate) > poly(diethyl itaconate) > poly(di-n-butyl itaconate), ie in increasing size of ester substituent.[51]   Mono-alkyl itaconates were found to

have a higher Gs than corresponding di-alkyl itaconates.

Literature values for the radiation chemical yields of poly(dimethyl itaconate) (IV) show some inconsistencies.

$$
\begin{array}{c}
COOCH_3 \\
| \\
CH_2 \\
| \\
\left(\!\!\!- C - CH_2 -\!\!\!\right) \\
| \\
COOCH_3
\end{array}
$$
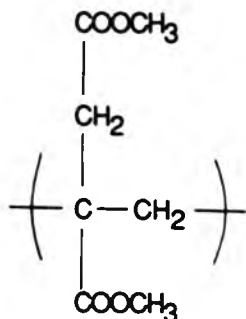
IV   Poly(Dimethyl Itaconate)

Helbert[52] reported Gs = 4.5, but stated that radiation crosslinking took place at higher exposure doses. Harada[49] and Anderson[51] both report lower values of Gs = 1.68, and Gs = 1.75, respectively.

1.6 Development of Positive Electron Beam Resists

The importance of the development step in the production of high resolution resist features is well described in the general review by Thompson.[2]   Inappropriate choice of solvent developer system is known to give a misleading view of the optimum resolution and sensitivity of a resist material.

General features of the dissolution of amorphous polymer

materials have been described by Uebberreitter[53], Tu[54] and Soong.[55]   Uebberreitter considered important factors in the dissolution process to be the relative speeds for the penetration of the solvent into the polymer, and the disentanglement and movement of polymer molecules into the solvent stream.   Except for cases where the molecular weight of the polymer is very low, the penetration of the solvent is normally the faster of the two processes, and leads to the dissolution of the polymer occurring in two stages:

(1)   The penetration of solvent molecules into the polymer to form a swollen gel boundary layer;

(2)   The disentanglement and movement of polymer molecules into the bulk of the solution.

For the case of a two stage dissolution process, Uebberreitter suggested that up to four types of boundary layer (infiltration layer, a solid swollen layer, a gel layer, and a liquid layer) can be present over a thickness corresponding to approximately 10,000 molecular coils.   Uebberreitter reported that the overall thickness of the boundary layer did not show a strong dependence on polymer molecular weight providing the molecular weight was greater than $300\,000$ g.mol^{-1}.   For the case of irradiated positive resist, where the average molecular weight can be much smaller than this, Krasicky[56] found a general dependence of increasing boundary layer thickness with increasing polymer molecular weight.

Temperature was also found to have a strong influence upon the number and type of boundary layers present.   Most pronounced changes are observed in comparison of dissolution phenomena above and below the glass transition temperature of the polymer.[53]

Movement of the boundary layers during dissolution were investigated by Tu and Soong. The most comprehensive treatment has been given by Tu[54] who simulated the dissolution of material where the rate of dissolution was controlled by: (a) the penetration of the solvent into the glassy polymer; and (b) where the rate of dissolution of material is primarily controlled by the rate of disentanglement of polymer molecules. Tu also considered the case of a crosslinked material where the material is insoluble, but the position of the liquid/gel interface can change as a result of swelling.

Empirical expressions for the overall rate of dissolution of positive resist materials are given by several authors (see eg 6,56,57). These expressions are generally complicated and contain a number of adjustable fitting parameters. Complications arise because resist materials can show induction times of up to 50% of the total developing time, and also because dissolution rate can vary with exposed dose, which for exposure by electron beam can vary with depth.

The development of positive electron beam resists is likely to depend upon both kinetic and thermodynamic factors. Reference to the earlier work of Hildebrand[59] shows that for resist development dependent upon thermodynamic factors alone there will always be a partition of a lower molecular weight fraction between solution and swollen polymer phases. The distribution of a given fraction of molecular weight M_i between un-dissolved polymer and a solution of the polymer in a solvent was given by:

$$\frac{V_i^{*}}{V_i'} = \exp^{\alpha M_i} \tag{1}$$

where V_i^{*} = proportion (by volume) of fraction i retained in the polymer, V_i' = proportion of fraction i in solution, α = partition coefficient.

The partition coefficient α depends upon the thermodynamic quality of the solvent, or solvent mixture, and temperature. It can be seen from this expression that discrimination by the solvent between molecules of different molecular weights cannot be expected to be perfectly sharp and that there will always be a distribution of the polymer between phases.

1.7 Sensitivity of Pre-crosslinked Resists

Factors affecting the sensitivity or solvent development of pre-crosslinked resists appear to have received little attention. A largely theoretical paper defining the highest sensitivity attainable for crosslinked positive resists was given by Suzuki,[37] who considered that because the crosslinks introduced during pre-baking etc occupy only a minor part in the overall polymer network, scission of the crosslinks themselves is not important. The degradation of the pre-crosslinked network was therefore assumed to largely depend upon the reduction in weight average molecular weight of the primary chains, given by:

$$Mw' = \frac{1}{1 + \dfrac{Gs \cdot E \cdot Mw}{200 \cdot \rho \cdot N_A}} \tag{2}$$

where

    Mw' = polymer weight average molecular weight following irradiation.

    Mw = primary weight average molecular weight.

    E = absorbed energy density per unit volume.

    N_A = Avogadro's number.

    ρ = Polymer density.

The network was assumed to become fully soluble when the reduction in primary average molecular weight was sufficient to render all portions of the network finite, and therefore soluble in a suitable solvent. The final expression obtained was that:

$$Q \geq \frac{200\ \rho\ N_A\ (\delta - 1)}{(4\ Gc\ Pc + Gs(1 - Pc))A.\ Mw} \qquad (3)$$

where

    δ = number of crosslinked repeat units per primary weight average molecule.

    A = proportionality constant between E and Q.

    Q = exposed dose.

    Gc = radiation chemical yield for scission of the crosslinkages

which, provided that 'Pc' (the ratio of energy absorbed by the crosslinkages to the entire polymer system) is small, can be approximated to:

$$Q \geq \frac{200\ \rho.\ N_A.\ (\delta - 1)}{Gs.\ A.\ Mw} \qquad (4)$$

Changes in the distribution of molecular weights during the degradation of the network were not considered. Experimental results obtained by Suzuki are reproduced in table 2.

Table 2 Comparison between Calculated and Experimental Results for Mixtures of a Polymer and a Crosslinking Agent (reproduced from ref 37).

Sample[a]	Wt% cross-linking agent	Mw g.mol^{-1}	δ (est)	Calculated Sensitivity $\mu C.cm^{-2}$	Experimental Result $\mu C.cm^{-2}$
P(MMA-MAA)	13	77000	1.6	3.7	3.5
and TPG	13	580000	2.2	1.0	1.0
	6.5	580000	2.6	1.3	1.5
Pn B MA	1	110000	2.8	2.0	2.3
and DABC	2	110000	3.8	3.1	7.6
PMIPK	15	180000	4.0	15	510
and DABC	7.5	180000	2.5	6.8	60
	3.8	180000	1.7	3.1	15
	1.9	180000	1.1	0.44	0.51
	1.9	600000	3.3	3.0	4.0

(a) for codes, see table 1.

Suzuki concluded that the predicted values from the theoretical expression, (4), showed fairly good agreement with experimental values except where the DABC content was larger than several percent. Suzuki attributed this disagreement to the radiation

protection effect of aromatic groupings in DABC.   Experimental values given in table 2 were obtained by soaking the exposed resist for 20 hours in acetone or methyl ethyl ketone to obtain the highest sensitivity value possible.

The nature of degraded portions following the exposure of a pre-crosslinked resist does not appear to have been previously considered.   Branched molecules are well known to have differing solubility characteristics from linear molecules, and for the same average molecular weight would be expected to show a lower solubility in any given solvent as a result of the higher number of polymer-polymer contact pairs when compared to the number of polymer-polymer contacts for linear molecules.[60]   Branched molecules will also contain a higher number of end groups for the same average molecular weight.

An additional factor affecting the solvent development of thermally crosslinkable resists is the problem of resist swelling. The swelling of crosslinked resists (both thermally crosslinkable, and negative type materials) is well known to affect the resolution obtainable.   Distortion of resist features normally occurs in two main ways:

(1)   A snake-like distortion of narrow lines where the resist line is heavily swollen but is prevented from longitudinal extension by resist-substrate adhesion;

(2)   The bridging of neighbouring resist lines by fine strings of resist, believed to be due to the resist lines coming into contact during the time they are swollen with solvent.

1.8 Swelling of Crosslinked Polymers

Factors affecting the swelling of a crosslinked network have been discussed by Flory[61] and by Charlesby.[12] Charlesby considered that for a network containing only a small soluble fraction, equilibrium swelling can be adequately described by the simplified Flory-Rehner relationship:

$$q_m^{5/3} = \frac{(0.5-\chi)Mc}{\rho \cdot Mv} \tag{5}$$

where

q_m = equilibrium swelling ratio

χ = Flory-Huggins interaction parameter

Mc = Number average molecular weight between crosslinks

ρ = density of the polymer

Mv = solvent molar volume.

The Flory-Huggins interaction parameter 'χ' is generally regarded as an indication of solvent power.[62] Solvents with little affinity for the polymer network have values of $\chi > 0.5$. Increasing affinity towards the network lowers χ. Important variables in this equation are the average molecular weight between crosslinks, solvent molar volume, and the Flory-Huggins interaction parameter. Experimental measurements confirming the importance of these variables have been made by Hildebrand,[59] and Gee.[63]

For the swelling of a crosslinked network where the density of crosslinking is relatively low, several additional factors must be considered:

(1)   The equilibrium swelling ratio will depend only upon the properties of the gel fraction.   Following its removal, the soluble fraction will not influence the equilibrium swelling ratio;

(2)   At low densities of crosslinking, the effects of network imperfections such as loose ends, chain entanglements and closed loops will be most significant.

For network loose ends, Flory[61] suggested that the equilibrium swelling ratio will be increased by a factor:

$$(1 - \frac{2M_c}{M})$$

where M = primary molecular weight before crosslinking.   This additional consideration suggests that swelling should be reduced for networks formed from the crosslinking of chains with an initially high average molecular weight.

1.9 Thermal Properties of Resist Materials

The glass transition temperature (glass/rubber transition, T_g) has been defined by Boyer[64] as the temperature which marks the freezing in (on cooling) or the unfreezing (on heating) of cooperative molecular motion of chain segments 20-50 main chain atoms in length.   Knowledge of the glass transition temperature is important since resist materials are normally required to be baked above their glass transition temperature to improve resist-substrate adhesion, and also to relieve stresses introduced to the resist film during

resist spinning. Roberts,[14] and Farah[65] have further shown that the pre-bake temperature has an important influence upon the performance of thermally crosslinkable resists (see section 4.7.1).

The onset of thermal degradation normally marks the upper service temperature of any resist material.

1.10 Aims and Objectives of this Work

The major objective of the work described here is the identification of new materials which will operate as thermally crosslinkable electron beam resists. At the present time, the mixture of two copolymers first described by Roberts[13,14] is used by a number of British electronics companies. Although this material has a number of advantages it has the disadvantage of high moisture sensitivity. Hydrolysis of the COCl units in the methacryloyl chloride copolymer is thought to reduce the number of reactive groups available for crosslinking and to lead to a variation in peformance between batches. The exposed dose required for development of the resist is also relatively high (~100 $\mu C.cm^{-2}$). Characteristics that would give any new material a significant advantage over those presently in use are therefore greater electron sensitivity and/or a reduced moisture sensitivity. Continued reductions in the minimum feature sizes of resist patterns also places increasing demands on resist-substrate adhesion.

A number of polymers were therefore investigated to try to find materials which might offer these advantages. Preliminary meetings between the Plessey Company and Professor A Ledwith at the University of Liverpool had suggested that derivatives of itaconic acid, particularly structures containing itaconic anhydride might be most suitable, and so work was initially concentrated on these materials.

CHAPTER TWO

EXPERIMENTAL AND INSTRUMENTATION

2.1 Instrumental and Analytical Techniques

Infrared Spectroscopy

Infrared (ir) analysis of monomer and polymer samples was made using a Shimadzu IR-435 instrument. For routine analysis, monomer and polymer samples were solvent-cast using acetone or chloroform onto NaCl discs and spectra taken with the instrument in its transmission mode. For the quantitative analysis of itaconic anhydride copolymers, absorbance spectra were taken using an expanded wavenumber scale over the range 2000-1500 cm^{-1}, with acetonitrile as the solvent. Spectra were obtained using matched 0.1 mm path length cells.

Nuclear Magnetic Resonance Spectroscopy

Proton nmr spectra were recorded using either a Hitachi Perkin-Elmer R24 (60 MHz) or a Perkin-Elmer R32 (90 MHz) instrument. Both instruments were operated in their standard modes. Samples were prepared as solutions in deuterated chloroform or deuterated acetone, with tetramethylsilane (TMS) as the internal reference.

Membrane Osmometry

Number average molecular weights were measured using a Knauer membrane osmometer and detecting bridge at $35\,^{\circ}C$. Membranes (Sartorius, regenerated cellulose) were conditioned to methyl ethyl ketone (MEK). The concentrations of polymer solutions used were in the range 3-10 $g.dm^{-3}$.

Number average molecular weights were calculated using the following expression:

$$Mn \sim \frac{RT}{(\pi/C) \to O}$$ (6)

where:

R = universal gas constant ($8.314 \ J.K^{-1}.mol^{-1}$)

T = temperature (308K)

π = osmotic pressure ($Kg.m^{-1}.s^{-2}$)

C = concentration (g. dm^{-3} = Kg. m^{-3})

and π = $\rho.g. \Delta h$

ρ = density of the polymer solution ($Kg.m^{-3}$)

g = acceleration due to gravity ($9.81 \ m.s^{-1}.s^{-1}$)

Δh = pressure expressed in m of solvent

The value of $(\pi/C) \to O$ was obtained from the extrapolation of experimentally measured values of $\Delta h/C$ to zero concentration using a linear least squares regression. No significant curvature of the $\Delta h/C$ plots was noted. The density of the solution at $35^{o}C$ (308K) was assumed to be the same as that of the pure solvent at that temperature.

Potentiometric Titration

Potentiometric titration was carried out using a Corning-Eel Model 7 pH meter with a glass combination electrode at $20^{o}C$ (393K).

Differential Scanning Calorimetry

Glass transition temperatures (Tg) were measured using a

Perkin-Elmer DSC-2 instrument. A nitrogen atmosphere was used with a heating rate of $20^{\circ}.\text{min}^{-1}$. The glass transition temperature was noted as the temperature corresponding to the intersection of lines extending the ΔCp trace of the glassy region and the region of maximum slope at the discontinuity.

Thermogravimetric Analysis

A Perkin-Elmer model TGS-2 driven by the Perkin-Elmer DSC-2 temperature programmer was used to measure the thermal stability of selected polymers. A nitrogen atmosphere was used with a heating rate of $20^{\circ}\text{C}.\ \text{min}^{-1}$. The sample (ca 5-10 mg) was normally prepared as a slightly compacted powder.

Elemental Analysis

A model 1106 Carlo-Elba Elemental Analyser was used for all work. C, H, and N were determined directly. O was obtained by difference.

2.2 Preparation and Characterisation of Materials
2.2.1 Purification of commercial solvents.

Unless otherwise stated, solvents used in this work were of laboratory grade and were used as supplied. Acetone used for infrared spectroscopy was of "Analar" grade. Solvents used for the purification and fractionation of itaconic anhydride copolymers were dried using the standard procedures. This precaution was taken in order to minimise the hydrolysis of itaconic anhydride during the preparation of the copolymers. Solvents used for solution polymerisation were distilled prior to use.

2.2.2 Purification of commercial monomers.

Methyl Methacrylate (MMA)

Methyl methacrylate (Aldrich 99%) was washed with several portions of 10% NaOH solution, and then with water to remove the inhibitor. The monomer was then dried over magnesium sulphate and distilled. The first fraction was rejected. Bp = 100°C.

Itaconic Anhydride (IT. ANH)

Itaconic anhydride (Fluka, 97%) was recrystallised from a mixture of 80:20 benzene:hexane. The recrystallised sample was then re-dissolved in chloroform at 25°C and reprecipitated in petroleum ether. Infrared analysis showed the material prepared in this way was free of COOH impurity. The as-supplied material was found to contain approximately 10% itaconic acid.

α-Methyl Styrene (α-MS)

α-Methyl styrene (Aldrich 99%) was prepared as for MMA. Following drying, the monomer was distilled under reduced pressure. Bp 50°C at 10 mm Hg.

Dimethyl Itaconate (DMI)

Dimethyl itaconate (Fluka, 97%) was purified by distillation. Bp = 85°C at 10 mm Hg pressure.

2-Hydroxyethyl Methacrylate (HEMA)

2-Hydroxyethyl methacrylate (Aldrich, 97%) was purified by fractional distillation under reduced pressure. The bp of the fraction collected was 67°C at 3.5 mm Hg pressure. Macret[66] reported that commercial HEMA monomer can contain small amounts of ethylene glycol, ethylene glycol dimethacrylate, and methacrylic acid. HEMA prepared for this work was therefore analysed using thin layer chromatography (TLC). The solvent used was a 50:50 mixture of diethyl ether and n-hexane. Pre-coated silica gel plates (F_{254}) were supplied by Merck. The distilled HEMA showed only a single spot at Rf 0.3 when developed under an ultra violet lamp or using an iodine tank. The monomer was found to be 96.4% pure when analysed by titration of COOH groups following acetylation (Section 2.2.5).

Methacrylic Acid (MAA)

Methacrylic acid (Aldrich, 98.5%) was distilled under reduced pressure. Bp = 64°C at 10 mm Hg pressure. Precautions to be observed in the handling of this monomer are detailed by Sandler.[67]

Methacrylamide (MAM)

Methacrylamide (Aldrich, 98%) was recrystallised twice from hot chloroform. Mp = 109-110°C

2.2.3 Preparation of Monomethyl Itaconate (MMI)

Monomethyl itaconate (V) was prepared following the procedure of Baker[68]. Mp = 68-70°C, nmr (table 3).

$$COOCH_3 \quad ^c$$
$$|$$
$$CH_2{}^d$$
$$|$$
$$C{=}CH_2{}^{a,b}$$
$$|$$
$$COOH$$

MMI (V)

$$CO.O.CO.CH_3{}^d$$
$$|$$
$$C{=}CH_2{}^{a,b}$$
$$|$$
$$CH_3{}^c$$
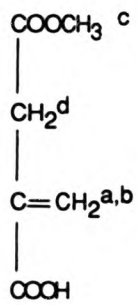
ACMP (VI)

2.2.4 Preparation of 1-Acetoxy carboxy, 2 methylene propanoate (ACMP)

17.5 cm^3 (0.305 mol) acetic acid, 42.5 cm^3 (0.305 mol) triethylamine and 500 cm^3 dry benzene were placed together in a 1 dm^3 round bottomed flask. 31.94g (0.305 mol) methacryloyl chloride (Fluka, 97%, distilled prior to use) in 70 cm^3 dry benzene was added dropwise while stirring. The mixture was left stirring for ~12 hours. The solids were removed by vacuum filtration and the liquid was concentrated using a rotary evaporator. The concentrated liquid product was distilled under reduced pressure using a rotary oil vacuum pump and 'Kugelrohr' short path length distillation apparatus.
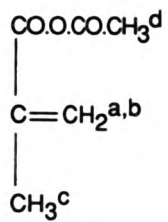
ir C=O 1790 and 1727 cm^{-1}. nmr (table 3).

TABLE 3 nmr data for MMI and ACMP monomers V, VI

V	Proton	Position	Integral
	a,b	6.5, 5.8	1,1
	c	3.7	3
	d	3.4	2

VI	Proton	Position	Integral
	a,b	6.1, 5.7	1,1
	c	1.85	3
	d	2.1	3

2.2.5 Preparation and Characterisation of Copolymers
General Procedure

Copolymerisations were carried out using bulk or solution techniques. Solution techniques were generally adopted where the monomers were not miscible in one another at room temperature. The presence of oxygen during polymerisation did not appear to have any adverse effects except for slight reductions in the average molecular weight. Where control over the average molecular weight was required, dissolved gases were removed from the monomers by repeated freeze thaw operations before sealing the polymerisation flask under vacuum. All copolymerisations were deliberately terminated at low percentage conversion to minimise composition drift.

Poly(itaconic anhydride-co-methyl methacrylate)

IT ANH-co-MMA copolymers were prepared using bulk and solution polymerisation techniques with α,α'-azoisobutyronitrile (AIBN) as the initiator. AIBN was recrystallised twice from methanol prior to use.

2,4 and 6 mol % feed composition copolymers were prepared by solution copolymerisation in p-dioxane at 60°C. The initiator concentration was 0.45 mol % (0.074g. dm^{-3} of solvent). The total monomer concentration was 0.67 mol.dm^{-3}. Polymerisation times and percentage conversions are given in table 4. Following copolymerisation, approximately half the solvent was removed with gentle heating using a rotary evaporator, and the polymer was precipitated into 500 cm^3 methanol. The polymer was redissolved in MEK and precipitated two further times into 500 cm^3 diethyl ether.

Further compositions of IT.ANH-co-MMA were prepared by bulk copolymerisation at 70°C. The materials shown in table 5 were prepared by first dissolving the monomers at 70°C before adding 0.5 mol % AIBN and sealing the polymerisation vessel with a serum cap. Polymerisation time was 3-20 minutes. Polymers were precipitated into 300-400 cm^3 methanol or diethyl ether according to composition. Copolymers of feed compositions less than 50 mol % itaconic anhydride were precipitated into methanol, dissolved in MEK and reprecipitated two further times into diethyl ether. Copolymers of feed compositions greater than 50 mol % itaconic anhydride were precipitated into diethyl ether, dissolved in MEK and reprecipitated two further times in a 1:1 mixture of diethyl ether and hexane.

Copolymers shown in table 6 were prepared by bulk polymerisation at 70°C in the absence of dissolved gases. The reaction flasks were charged with the required ingredients, evacuated by repeated freeze-thaw cycles and sealed under vacuum. The polymers were recovered and reprecipitated as before.

All samples were dried at 60°C under vacuum for >48 hours and then at 140°C for 15-20 minutes in a convection oven. Heating the copolymers at more than 90°C in a vacuum oven was found to cause thermal crosslinking.

Fractionation

Copolymers of 2,6,11,15 and 21 mol % feed IT.ANH were fractionated by fractional precipitation. Ethyl acetate was used as the solvent, and cyclohexane or a mixture of 80:20 cyclohexane and ethyl acetate as the precipitant. After the supernatent was

removed, each settled fraction was dissolved in MEK and reprecipitated into diethyl ether. Mn values for each of the fractions collected are given in table 6.

Homopolymerisation of Itaconic Anhydride.

Itaconic anhydride was polymerised in bulk at $70^{\circ}C$ using 0.5 mol % AIBN as the initiator. Polymerisation time was two hours. The polymer was precipitated into diethyl ether, dissolved in MEK and reprecipitated two further times in diethyl ether. % conv = 16%.

Characterisation of IT.ANH-co-MMA Copolymers.

The composition of IT.ANH-co-MMA copolymers was determined using the method of Sharabash.[69] Mixtures of poly(itaconic anhydride) and poly(methyl methacrylate) (BDH) were prepared to give solutions of concentration 75g. dm^{-3} (0.150g in 2 cm^{3}) in distilled acetonitrile. Infrared absorption spectra were taken between 2000 and 1500 cm^{-1} using an expanded wavenumber scale. The peak area of the absorption at 1864 cm^{-1} due to the C=O stretching of itaconic anhydride was measured for each composition and used to construct a standard curve of peak area versus mixture composition. Solutions of the same total concentration in acetonitrile were then prepared for copolymer samples, and the peak area determined for each composition. The composition of the copolymers was then obtained from the standard curve. It is assumed in this technique that the area of the absorption at 1864 cm^{-1} is the same for both a mixture of two homopolymers and for a copolymer of the same composition. Copolymer compositions are given alongside their respective feed compositions in tables 4-6.

TABLE 4 IT.ANH-co-MMA Copolymers Prepared by
Solution Copolymerisation in Dioxane at 60°C.

Feed mol % IT.ANH	Polym. Time h	wt% conv.	Comp mol % IT.ANH
2	5	14	5
4	5	13	10
6	5	11	14

TABLE 5 IT.ANH-co-MMA Copolymers Prepared by Bulk
Copolymerisation at 70°C.

Feed mol % IT.ANH	Polym. Time min	wt% conv.	Comp mol% IT.ANH
4	9	2	15
10	10	4	30
20	9	8	39
30	11	5	50
40	3	0.3	61
60	8	6	67
70	11	3	71
80	10	4	88
90	11	3	93

TABLE 6 IT.ANH-co-MMA Copolymers Prepared by Bulk Copolymerisation in Evacuated and Sealed Off Flasks at 70°C.

Feed mol % IT.ANH	AIBN mol %	Polym.Time min	wt % conv.	Comp mol % IT.ANH	Mn g.mol^{-1}	Fraction
2	0.1	20	10	10	396000	2
					227000	3
6	0.1	18	11	24	444000	2
					187000	3
11	0.1	19	10	33	216000	(a)
					444000	2
					155000	3
15	0.022	25	3		282000	(b)
15	0.076	13	4		235000	(b)
15	0.155	13	8		186000	(b)
15	0.221	11	7		156000	(b)
15	0.349	11	9		100000	(b)
15	0.500	10	14		54000	(b)
21	0.02	24	5		186000	(a)
					118000	2
21	0.05	24	9		530000	1
					111000	2
21	0.10	20	14	46	104000	(a)
					424000	1
					166000	1
					145000	3
					108000	4

(a) = Molecular weight before fractionation.
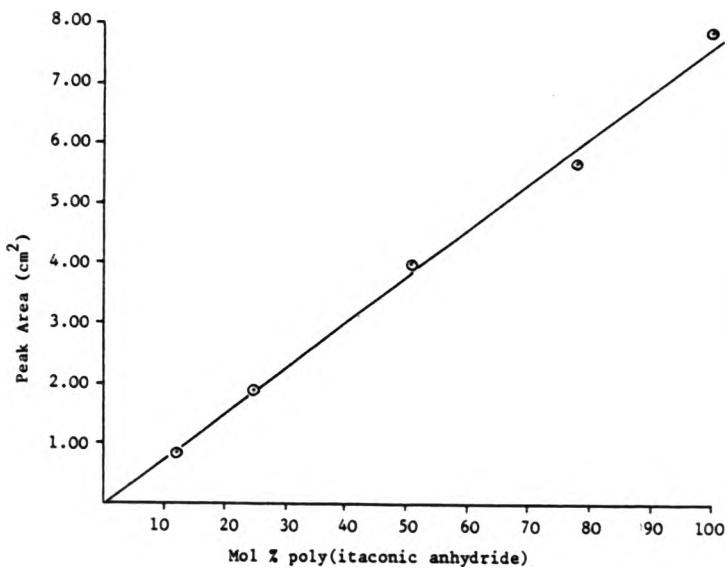(b) = Not fractionated.

FIGURE 3   Standard curve of the Area of the Carbonyl Peak at 1864 cm^{-1}
in Mixtures of Poly(itaconic anhydride) and Poly(methyl methacrylate)

TABLE 7   Data for Standard Curve.

Poly(IT.ANH) g	Poly(MMA) g	IT.ANH mol%	Peak Area cm^2
0.02	0.13	12.08	0.93
0.04	0.11	24.51	1.89
0.08	0.07	50.52	4.00
0.12	0.03	78.13	5.87
0.15	0	100	7.84

Poly(itaconic anhydride-co-dimethyl itaconate)

IT.ANH-co-DMI copolymers were prepared in evacuated and sealed glass flasks by solution copolymerisation in benzene at 70°C. The initiator concentration (AIBN) was 0.08 mol % (0.985 g.dm^{-3} of solvent).   Total monomer concentration was 7.5 mol.dm^{-3}.   2,6,12 and 25 mol % feed copolymers were recovered by precipitation into methanol.   These polymers were dissolved in MEK, and re-precipitated two further times into diethyl ether.   A 35 mol % feed copolymer precipitated from solution during polymerisation, and was recovered in a 1:1 mixture of petroleum ether and methanol. This material was dissolved in MEK and reprecipitated two further times in the same mixture.   Polymers were dried at 60°C under vacuum and at 140°C for 15 minutes in a convection oven. Polymerisation details are given in table 8.

The composition of IT.ANH-co-DMI copolymers was determined by quantitative infrared analysis using the same procedure as that described for poly(IT.ANH-co-MMA).   Experimental measurements and the standard curve are presented in table 9 and figure 4. Copolymer compositions are given alongside their respective feed compositions in table 8.
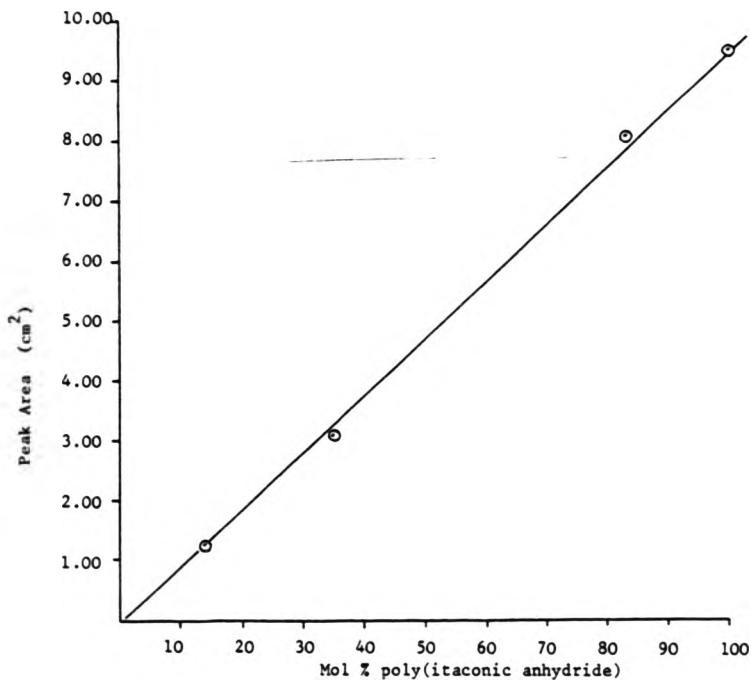
FIGURE 4   Standard Curve of the Area of the Carbonyl Peak at 1864 cm^{-1}
in Mixtures of Poly(itaconic anhydride) and Poly(dimethyl itaconate).

TABLE 9   Data for Standard Curve.

Poly(IT.ANH)	Poly(DMI)	IT.ANH	Peak Area
g	g	mol%	cm^2
0.01	0.065	14.19	1.27
0.025	0.05	34.96	3.08
0.062	0.014	83.05	8.05
0.075	0	100	9.49

TABLE 8   IT.ANH-co-DMI Copolymers Prepared by Solution
Copolymerisation in Benzene at 70°C.

Feed mol % IT.ANH	Polym. time h	wt% conv.	Comp. mol % IT.ANH
2	6.2	9	7
6	5.4	8	19
12	4.4	8	25
25	3.5	6	35
35	2.8	11	49

Poly(Itaconic anhydride-co-α-methyl styrene).

IT.ANH-co-αMS copolymers were prepared by bulk
copolymerisation in evacuated and sealed glass flasks at 70°C.
Copolymers were precipitated into chloroform, dissolved in MEK and
re-precipitated two further times in chloroform.   Polymerisation
details are given in table 10.   The copolymer composition was
determined by elemental analysis.

Theor. for 49% IT.ANH-co-αMS = %C 73.34; %H 6.17; %O 20.04.   Found %C 73.82;
%H 6.40; %O 19.78.

TABLE 10   IT.ANH-co-αMS Copolymers Prepared by Bulk
Copolymerisation at 70°C.

Feed mol % IT.ANH	AIBN mol %	Polym.time h	wt% conv.	Comp mol % IT.ANH	Mn g.mol^{-1}
15	0.3	3	5	49	89000
15	1.0	3	7		83000
15	1.3	0.9	4		79000

Poly(2-hydroxyethyl methacrylate-co-methyl methacrylate)

HEMA-co-MMA copolymers were prepared by solution copolymerisation in p-dioxane at 60°C. Initiator concentration (AIBN) was 0.493 g.dm^{-3} of solvent. Total monomer concentration was 0.67 mol.dm^{-3}. Following polymerisation the contents of the reaction vessel were concentrated with a minimum amount of heating using a rotary evaporator. The polymers were precipitated into diethyl ether, dissolved in MEK and re-precipitated two further times into diethyl ether. The polymers were dried under vacuum at 60°C, and then at 140°C for 15 minutes in a convection oven. Copolymerisation details are given in table 11.

TABLE 11   HEMA-co-MMA Copolymers Prepared by Solution Copolymerisation in p-dioxane at 60°C.

Feed mol % HEMA	Polym. Time h	% conv.
2	5	17
4	5	19
6	5	16

The composition of HEMA-co-MMA copolymers was determined using an adaptation of the procedure described by Vogel.[70] An acetylating reagent was prepared by taking 56.438g acetic anhydride (Aldrich, 98%) and making this up to 250 cm^3 with pyridine which had been distilled, and then dried over potassium hydroxide.

3.5 cm^3 acetylating reagent and a further 3 cm^3 of pyridine were added to 0.344-0.956g of copolymer and left overnight to dissolve. This solution was heated on a steam bath for one hour to ensure reaction of the alcohol functional groups with acetic anhydride. 25 cm^3 of 1:3 water:pyridine mixture was then added and the solution heated for a further 10-15 minutes to hydrolyse remaining acetic anhydride. The solution was then cooled in ice and titrated with 1M NaOH.

A blank determination was made in the absence of alcohol functions. 25 cm^3 of the 1:3 water:pyridine mixture was added to 3.5 cm^3 acetylating reagent and heated on a steam bath as before. The mixture was cooled in ice and titrated with 1M NaOH. Copolymer

composition (% HEMA) was calculated from the difference in the number of moles of NaOH consumed in the titration of the sample and in the blank.

Experimental results for the titration of the blank, a sample of HEMA monomer, and for copolymers of HEMA-co-MMA are shown in table 12. The blank determination yielded 15.15×10^{-3} mol acetic acid from 7.739×10^{-3} mol acetic anhydride, suggesting the acetic anhydride used was 97.9% pure. HEMA monomer (prepared as detailed in section 2.2.2) was found to be 96.4% pure. 6.5% and 12% feed copolymers shown in table 12 were originally prepared by Professor A Ledwith at Liverpool University.

TABLE 12 Experimental Quantities for the Characterisation of HEMA-co-MMA Copolymers.

Sample	Qty	Equivalence Point (cm^3 1M NaOH)		Composition
	g	Exp.	Calc.	% ROH
Acetylating reagent	3.5 cm^3	15.15	15.47	
HEMA monomer	0.3443g	12.60	12.83	96.4
2% feed HEMA-co-MMA	0.5787g	14.95		3.5
4% feed HEMA-co-MMA	0.9558g	14.65		5.3
6.5% feed HEMA-co-MMM	0.5374g	14.6		10.6
12% feed HEMA-co-MMA	0.4299g	14.47		16.6

Itaconic anhydride:2-hydroxyethyl methacrylate:methyl methacrylate Terpolymers.

Terpolymerisation of IT.ANH, HEMA and MMA was attempted using solution polymerisation in benzene and in p-dioxane at $60^{\circ}C$. Polymerisation in benzene using total monomer concentrations of 1.25 and 0.75 $mol.dm^{-3}$ of solvent, with 0.45 mol % (0.92 $g.dm^{-3}$) AIBN gave an insoluble product which precipitated from solution. Improved results were obtained with p-dioxane.

Polymers with 5, 10, 20 and 35 mol % feeds of IT.ANH and HEMA (balance MMA) were prepared using a total monomer concentration of 0.5 $mol.dm^{-3}$ of dioxane with 0.45 mol % (0.92 $g.dm^{-3}$) AIBN. The contents of the polymerisation flask were concentrated with minimum heating using a rotary evaporator and precipitated into diethyl ether. The polymers were dissolved in MEK and reprecipitated two further times into diethyl ether before drying in vacuo. Polymerisation details are given in table 13. Infrared absorptions characteristic of alcohol, anhydride and ester functional groups were present in the spectra of the polymers prepared. No attempt was made at quantitative analysis.

TABLE 13 IT.ANH-HEMA-MMA Terpolymers

Feed composition (mol %)			Polym. time	wt %
IT.ANH	HEMA	MMA	h	conv.
5	5	90	5.9	9
10	10	80	8.3	32
20	20	60	5.9	6
35	35	30	6.6	17

Poly(monomethyl itaconate-co-methyl methacrylate.

MMI-co-MMA copolymers were prepared by solution copolymerisation in benzene at 70°C using AIBN as the initiator. Polymerisation details are given in table 14. Copolymers of feed compositions less than 25 mol % MMI were recovered by precipitation into methanol. Copolymers with feed compositions greater than 25 mol % MMI were recovered by precipitation into diethyl ether. All compositions were purified by dissolving in MEK and reprecipitating two further times in 300-400 cm^3 diethyl ether. Polymers were dried under vacuum at 60°C for 48 hours and at 140°C for 15 minutes in a convection oven.

The composition of MMI-co-MMA copolymers was determined by potentiometric titration of COOH units on MMI repeat units with NaOH. 25 cm^3 of 80:20 isopropyl alcohol:distilled water mixture was added to 0.050-0.228 g of copolymer and left overnight to dissolve. The solution was then titrated with 0.01M NaOH. Copolymer composition (mol % MMI) was determined directly from the number of moles of NAOH consumed at the equivalence point. A blank determination using 0.1012 g PMMA with 25 cm^3 80:20 isopropyl alcohol:distilled water yielded an equivalence point of 0.8×10^{-5} mol COOH which was not considered significant. Experimental results for the titration of MMI-co-MMA copolymers are shown in table 15.

TABLE 14 MMI-co-MMA Copolymers Prepared by Solution Copolymerisation in Benzene at 70°C.

Feed	AIBN	Total Monomer Conc. in Benzene	Polym.Time	wt %	Mn
mol % MMI	mol % (g.dm⁻³ Benzene)	mol. dm⁻³	min	conv.	g.mol⁻¹
2.3	.125 (8.55)	42	27	8	$>10^6$
5	.01 (0.68)	42	90	11	333000
5	.08 (5.47)	42	25	8	114000
5	.20 (13.68)	42	40	21	
6	.40 (13.13)	20	15	8	
8	.125 (5.13)	25	35	23	
9	.275 (11.29)	25	10	6	115000
13	.40 (13.13)	20	15	7	
15.6	.125 (8.55)	42	30	10	
18	.150 (6.15)	25	20	13	95000
23	.125 (8.55)	42	25	9	
27	.40 (13.13)	20	15	7	184000
50	.125 (5.13)	8	22	2	
51	.40 (9.19)	14	15	7	
70	.125 (5.13)	4	26	0.4	
90	.125 (5.13)	4	80	2	

TABLE 15 Experimental Quantities for the Characterisation
of MMI-MMA Copolymers.

Feed mol % MMI	Weight g	End point cm^3 0.01M NaOH	Comp. mol % MMI
2.3	0.1000	2.1	2
5	0.1000	3.75	4
9	0.0865	6.2	7
15.6	0.1000	11.9	13
18	0.1025	12.8	13
23	0.1000	16.5	18
50	0.0500	15.2	35
70	0.0247	10.8	54
90	0.2280	118.0	67

Poly(1-acetoxy carboxy, 2 methylene propanoate)-co-MMA.

ACMP-co-MMA copolymers were prepared by solution polymerisation in p-dioxane.   Attempts at copolymerisation at 55°C and 70°C in bulk, and copolymerisation in benzene at 55°C were unsuccessful due to the formation of an apparently crosslinked gel.

Soluble polymers were prepared by copolymerisation in dioxane at 55°C using 0.45 mol % (.58 g.dm^{-3} solvent) AIBN as the initiator.   The total concentration of monomer was 0.83 g.dm^{-3}.   Following copolymerisation, the contents of the reaction vessel were concentrated using a minimum amount of heating on a rotary evaporator and precipitated into dry methanol.   The polymers were then dissolved

in MEK and reprecipitated two further times into dry diethyl ether. Polymers were dried at 60°C under vacuum and at 140°C for 15 minutes in a convection oven.   Polymerisation details are given in table 16.

TABLE 16 ACMP-co-MMA Copolymers prepared by Solution Copolymerisation in p-dioxane at 55°C.

Feed mol % ACMP	Polym.Time h	wt % conv.	Mn g.mol^{-1}
5	5.7	12	
10	4.4	4	
15	5	11	155000
20	6.3	12	210000
30	3.8	11	

The composition of ACMP-co-MMA copolymers was determined by back titration of carboxylic acid groups following the hydrolysis of ACMP repeat units.   0.1844-0.623 g of copolymer was taken and dissolved in 25 cm^3 distilled pyridine.   6 cm^3 distilled water was added, and the solution heated for one hour on a steam bath.   The solution was then cooled in ice and titrated with 0.1M NaOH.   A single end point was observed at pH 9-10.   Mol % ACMP was determined from the number of moles of NaOH consumed at the equivalence point with

the assumption that the hydrolysis of the anhydride yields 2 moles COOH:

$$RCO.O.CO.CH_3 + H_2O \xrightarrow{\text{pyridine, } 100^{\circ}C} RCOOH + CH_3COOH \quad (6)$$
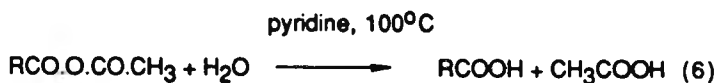
A control experiment using 0.9796 g PMMA (BDH, Mn 530000 g.mol^{-1}) showed that hydrolysis of the ester group of MMA did not occur under these conditions. Experimental results for the titration of ACMP-co-MMA copolymers are shown in table 17. By interpolation, the composition of feed 10 mol % (ACMP)-co-MMA was estimated to be 9 mol % ACMP.

TABLE 17 Experimental Quantities for the Characterisation of ACMP-co-MMA Copolymers.

Feed mol % ACMP	Weight g	End Point cm^3 0.1M NaOH	Comp Mol % ACMP
PMMA (control)	0.9796	<1.0	
5	0.2167	1.95	5
15	0.1844	4.85	14
20	0.6236	18.13	15
30	0.5943	39.2	36

Poly(methacrylic acid-co-methyl methacrylate).

MAA-co-MMA copolymers were prepared by bulk copolymerisation at 70°C using AIBN as the initiator. Polymerisation details are given

in table 18.   The polymers were recovered by precipitation into diethyl ether.   The materials were then re-dissolved in MEK and reprecipitated two further times into diethyl ether.   Samples were dried under vacuum at 60°C and then at 140°C for 15 minutes in a convection oven.

TABLE18 MAA-co-MMA Copolymers prepared by Bulk Copolymerisation at 70°C.

Feed mol % MAA	AIBN mol %	Polym.Time min	wt % conv.
2	.45	28	5
4.6	.45	24	8
6	.45	24	7

The composition of MAA-co-MMA copolymers was determined by titration of MAA repeat units with NaOH.   25 cm^3 of 80:20 isopropyl alcohol:distilled water mixture was added to 0.1029-0.1050 g of copolymer and left overnight to dissolve.   The solution was then titrated with 0.01M NaOH.   Copolymer composition (mol % MAA) was determined directly from the number of moles of NaOH consumed at the equivalence point.   Experimental measurements for the titration of MAA-co-MMA copolymers are given in table 19.

TABLE 19 Experimental Quantities for the Characterisation of MAA-co-MMA Copolymers.

Feed mol % MAA	weight g	End Point cm^3 0.01M NaOH	Comp mol % MAA
2	0.1046	3.5	3
4.6	0.1050	6.0	6
6	0.1029	8.4	8

Poly(methacrylamide-co-methyl methacrylate)

MAM-co-MMA copolymers with feed compositions between 5 and 25 mol % MAM were prepared by bulk copolymerisation at 70°C with 0.1 mol % AIBN. A copolymer of 50 mol % feed MAM was prepared by solution polymerisation in p-dioxane at 70°C. Total concentration of monomers in p-dioxane was 40 mol.dm^{-3}. Copolymers with feed compositions of less than 20 mol % MAM were recovered by precipitation into methanol. These materials were redissolved in MEK and reprecipitated two further times into 300-400 cm^3 methanol. Copolymers with feed compositions greater than 20 mol % MAM could not be reprecipitated into methanol. In all cases only a small quantity of material was recovered. Polymerisation details are given in table 20.

TABLE 20 Copolymers of MAM-co-MMA prepared by Bulk and Solution Copolymerisation at 70°C.

Feed mol % MAM	Polym.Time min	wt% conv.
5	15	10
9	20	11
15	15	8
20	24	a
25	24	
50	15	

(a)   figure not obtained due to difficulty in reprecipitation.

The composition of MAM-co-MMA copolymers was determined by elemental analysis.   Results are presented in table 21.

TABLE 21 Elemental Analysis of MAM-co-MMA Copolymers.

Feed mol % MAM	Found %N	%C	%H	Calc. Comp. mol % MAM
5	0	59.22	8.13	0
9	0.68	58.63	8.13	4
15	1.04	58.63	8.13	7
20	2.03	54.83	8.13	15
50	5.68	55.99	7.91	38

2.2.6 Preparation and Evaluation of Resist Materials.

76mm diameter, un-oxidised silicon wafers were baked at 170°C for several hours to remove surface moisture. The wafers were allowed to cool and were blown with dry nitrogen to remove contaminating particles. Polymer materials were dissolved in a suitable solvent to give a concentration of 100-200 g.dm^{-3}.

Spin Coating

Resist films were prepared by spin coating using a two speed Headway Research photo resist spinner. Resist solutions were filtered by passing through a 0.2 or 0.5 micrometre filter before being deposited onto the surface of the wafer. The wafer was spun at 500 rpm for 30 seconds to distribute the resist evenly over the surface of the wafer, and then rapidly accelerated to 2000-4000 rpm to give a thin, even film. The final spin speed was adjusted to give a film thickness of ~0.5 micrometre.

Resist Pre-Baking

Unless otherwise stated, all resist films were baked at 170°C in a normal atmosphere using a fan assisted convection oven.

Exposure of the Resist

Resist samples were exposed using a Cambridge Instruments Electron Beam Microfabricator (EBMF-2). The accelerating voltage used was 20KV. Beam currents were in the range 0.2-5 nA. The EBMF-2 instrument utilises a beam with a Gaussian current density distribution and operates by a vector scan technique. The electron beam is scanned in a boustrophedon fashion to expose each pattern

feature and is blanked for the period of time during which it is moved to begin the next exposure. The focussed beam can be deflected over a maximum area of 1x1 mm without unnaceptable distortion. Patterns larger than 1mm^2 are exposed by the sequential exposure and butting together of 1 mm^2 fields. The wafer is moved under the beam by an X-Y table under computer control. The position of the stage is measured by laser interferometry and any error in the required XY table position is corrected for by adjusting the position of the beam before exposure. The 1mm^2 exposure field is divided into 8192 x 8192 exposure points. The distance between adjacent exposure points is 125 nm. The beam diameter is normally of the order of 60-150 nm depending on the type of source used and the accelerating voltage.

Resist Test Pattern

The resist test pattern consists of a column of 16 rectangles, 86 x 100 micrometre, and an array of 10 columns by 16 rows of special test patterns. The test patterns comprise isolated lines, 1:1 lines and spaces, 1:2 lines and spaces, gap features between large exposed areas and a narrow line next to a large block, figure 5 (detail).

The exposure dose given to each pattern is varied from row 1 to row 16. Typically the exposure settings are pre-selected to cover a ten fold increase in exposure dose. Each column consists of features of the same nominal dimensions. The ten columns in the complete array cover a range of pattern dimensions 0.125 to 4.0 micrometre.

FIGURE 5   Resist Test Pattern (detail).

2.3 Development of Resist Materials

Exposed patterns were developed by gently agitating the exposed resist in a solvent or solvent mixture at room temperature (20-22°C). Commonly, two beakers of developing solvent were used. The sample was removed from the first beaker and transferred to the second beaker after a prescribed time. Samples were normally rinsed in isopropyl alcohol (IPA) for 30 seconds. Following rinsing, samples were blown dry with filtered nitrogen and then post baked at ~100°C by placing them on a thermostatically controlled hot plate.

2.4 Resist Thickness Measurements

The thickness of spun films following pre-baking, and thickness of resist remaining after solvent development were measured using a Rank Taylor Hobson Talystep 1. Resist thickness following baking was measured by traversing the stylus over a groove prepared in the resist film using a scalpel blade. Resist thickness remaining following development was measured by traversing the column of 80x100 micrometre rectangles in the resist test pattern. Normalised remaining thickness is defined as

$$N_T = \frac{T}{T_o} \qquad (7)$$

where T   = thickness of resist remaining after solvent development

T_o = original resist thickness.

2.5 Measurement of Resist Sensitivity and Contrast

Sensitivity and contrast are measured from plots of normalised remaining thickness versus exposure dose following resist development and post baking. Throughout this work sensitivity is defined as the minimum dose required for the complete removal of resist from an exposed rectangular area 80x100 micrometre. Contrast (γ) is defined as the slope of a line drawn from the dose corresponding to zero remaining thickness and intercepting the normalised remaining thickness curve at $T/T_o = 0.5$. γ is then obtained from

$$\gamma = \left[\log_{10} \frac{D_{1.0}}{D_o} \right]^{-1} \tag{8}$$

where $D_{1.0}$ and D_o are defined as shown in figure 6.
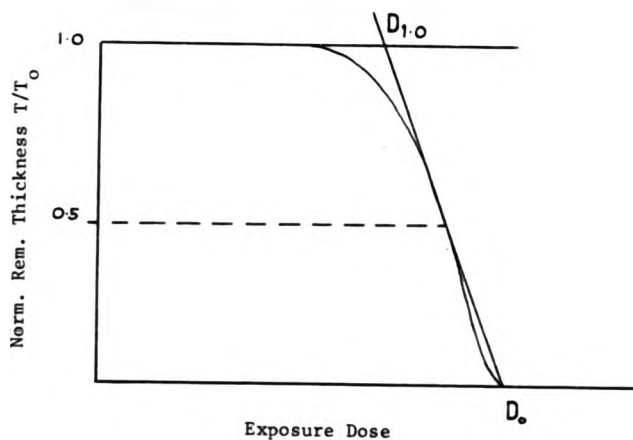
FIGURE 6: Typical curve showing measurement of resist contrast (γ).

Resist contrast is a measure of the rate of change in normalised remaining thickness with exposure dose. It is generally accepted that contrast values of more than 1.0-1.5 are required for high resolution lithography.

2.6 SEM and Optical Microscopy

Optical microscopy was performed using a Lietz Ergolux optical microscope. Selected samples were also examined using a Cambridge Instruments 150 Scanning Electron Microscope (SEM). This facility was provided by Plessey Research (Caswell) Ltd. Acknowledgement is due to Mr N Griffin, Mrs C Miller-Tate and Mrs J Hewitt for all SEM micrographs.

2.7 Oxygen Plasma Etching

The dry etch resistance of selected samples was measured using a Plasma Technology PE80 Parallel plate etcher under the following conditions:

Working Pressure	350 millitorr
Base Pressure	10 millitorr
Etch Gas	Oxygen
Flow Rate	50 std. cm^3 per min
Power Input	200 watts
Reflected Power	~0 (watts)

The etch time was 1 minute.

All results are reported as the thickness of resist removed (in nm) per min.

CHAPTER THREE

RESULTS

3.1 Reactivity Ratios for the Copolymerisation of IT.ANH-co-MMA

The terminal model for free radical copolymerisation proposed by Mayo and Lewis[71] postulates that the rate of addition of a monomer to a growing polymer chain is independent of chain length, and depends only on the nature of the terminal radical unit. Four possible propagation steps were recognised:

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1\cdot$$

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_2\cdot$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2\cdot$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_1\cdot$$
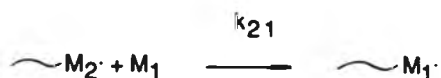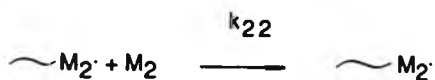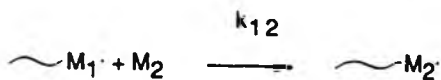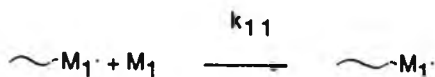
k_{11} and k_{22} are the rate constants for self propagation. k_{12} and k_{21} are the rate constants for cross propagation. Reactivity ratios, r_1 and r_2 are defined from the ratio of the rate constants as below:

$$r_1 = \frac{k_{11}}{k_{12}} \qquad\qquad r_2 = \frac{k_{22}}{k_{21}} \qquad\qquad (9)$$

Values of r_1 and r_2 can be obtained from measurements of copolymer composition over a range of monomer feeds provided that copolymerisations are restricted to a sufficiently low degree of conversion so that the monomer feed composition remains essentially unchanged.[72]

Experimentally determined values of copolymer composition over a range of feed compositions for copolymers of IT.ANH-co-MMA are shown in figure 7. Experimental values are taken from tables 5 and 6. The dotted lines represent the best fit to the experimental points using a non-linear least squares fitting procedure.[*] This analysis was performed using a BBC Microcomputer and provides values for the reactivity ratios r_1 and r_2. For the system IT.ANH-co-MMA r_1 and r_2 were found to be 0.99 ± 0.4 and 0.18 ± 0.07 respectively. The product $r_1.r_2 = 0.18$.

3.2 Reactivity Ratios for the Copolymerisation of MMI-co-MMA

Experimentally determined values of copolymer composition over a range of feed compositions for copolymers of MMI-co-MMA are shown in figure 8. Experimental values are taken from table 15. Reactivity ratios were determined as before, and r_1 and r_2 were found to be 0.20 ± 0.14 and 1.09 ± 0.05 respectively. The product $r_1.r_2 = 0.22$.

3.3 Error in Experimental Results

Within the limitations discussed in more detail by O'Driscoll,[72] it would appear that the terminal model can be fitted to the experimental data quite well. Experimental error is likely in both the measurement of feed composition and in the measurement

[*] see W.H Press, Numerical Recipies (The Art of Scientific Computing)
p 523 Pub Cambridge University Press (1986)
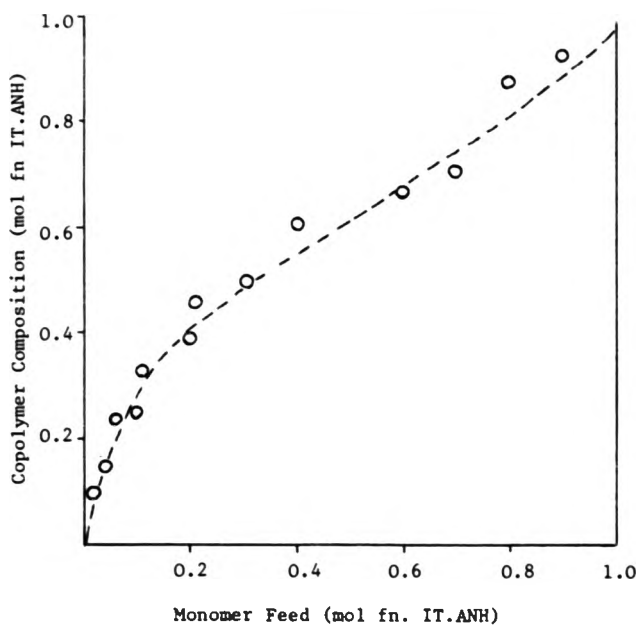
FIGURE 7 Copolymer Composition Curve for Bulk Copolymerisation of
IT.ANH-co-MMA at 70°C.

(o) Experimental Data   (---) non linear least squares
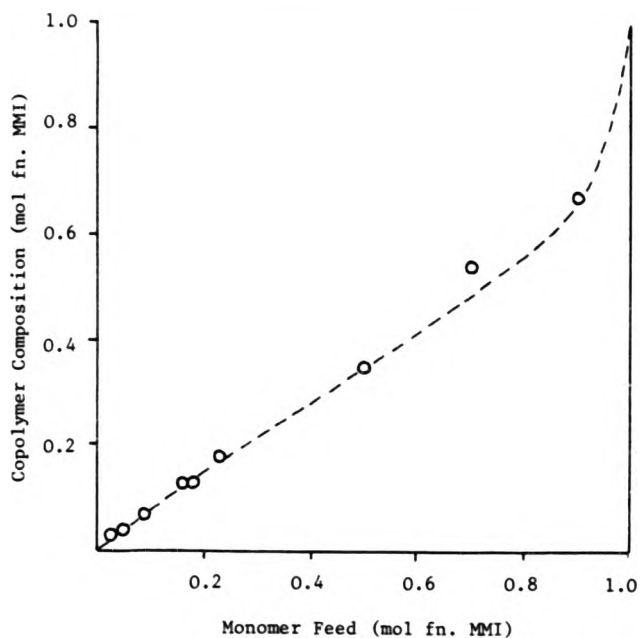
fit (terminal model)

FIGURE 8   Copolymer Composition Curve for Copolymerisation of MMI-co-MMA
in Benzene at 70°C.

(o) Experimental Data   (---) Non   linear least squares
fit (terminal model).

of copolymer composition and this must be considered to introduce a joint error in the values of the reactivity ratios given.

For copolymers of IT.ANH, Sharabash[69] reported that determination of the copolymer compositions by infrared analysis gave results within $\pm$2-3%, but in extreme cases $\pm$7% of values determined by elemental analysis. There did not appear to be any systematic differences between values obtained by infrared and elemental analysis. For copolymers of MMI-co-MMA the likely error due to uncertainty in the end point during titration of copolymers corresponds to differences in copolymer composition of approximately 2-3%.

3.4   Other Copolymers

Data for other copolymers investigated in this work are incomplete and therefore cannot be used to establish reactivity ratios. Examination of the experimental measurements for IT.ANH-co-DMI, HEMA-co-MMA, ACMP-co-MMA, MAA-co-MMA and MAM-co-MMA suggest that these are statistical copolymerisation reactions. Reactivity ratios for the compolymerisation of HEMA-co-MMA, MMA-co-MMA and MAM-co-MMA have been reported previously.[73]

3.5   Number Average Molecular Weight as a Function of Initiator Concentration for Copolymers of IT.ANH-co-MMA, MMI-co-MMA and IT.ANH-co-αMS

Experimentally determined values of the number average molecular weight as a function of initiator concentration are shown in figures 9 and 10 for copolymers of IT.ANH-co-MMA and MMI-co-MMA. Experimental values are taken from tables 6 and 14. The data
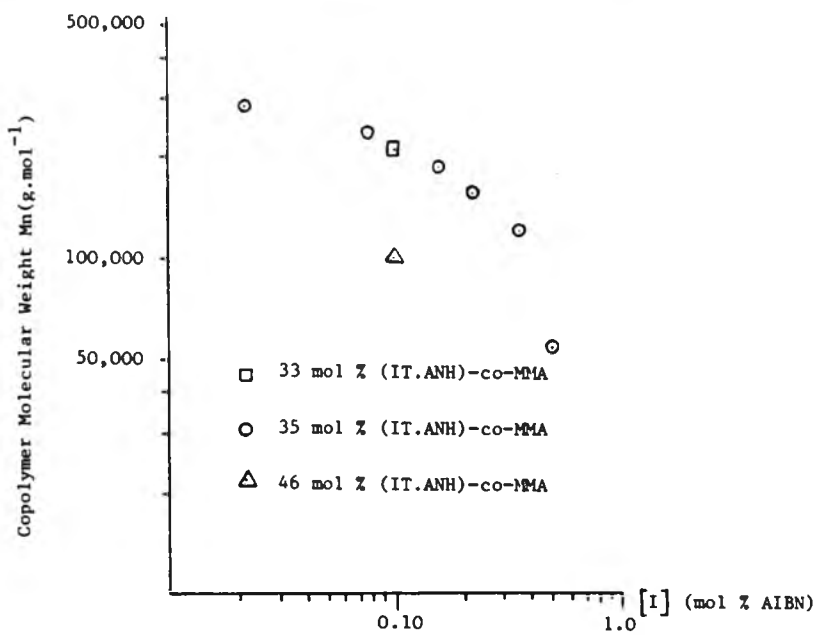
FIGURE 9   Copolymer Molecular Weight as a function of Initiator Conc. for
            IT.ANH-co-MMA.
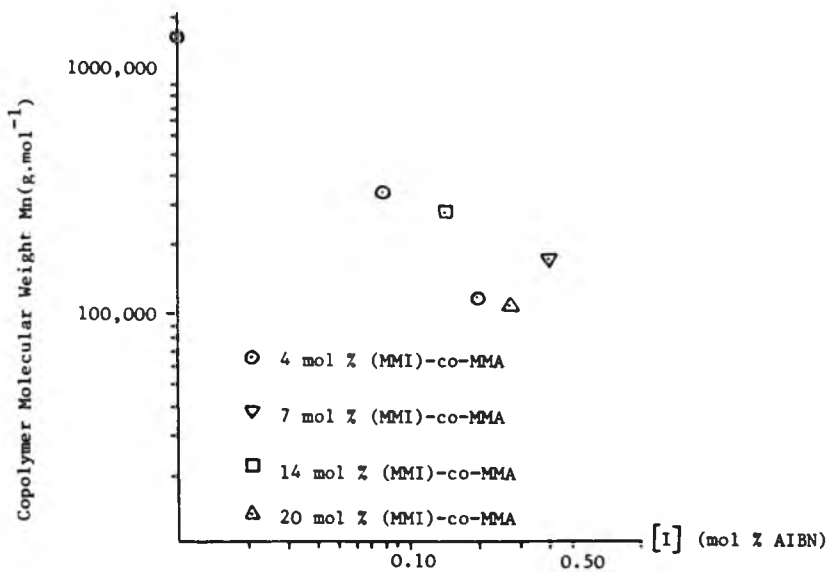
FIGURE 10   Copolymer Molecular Weight as a function of Initiator Conc. for
             MMI-co-MMA.

are presented in the form of a double log plot as results for both systems cover several orders of magnitude.

The results show that for both types of copolymer, initiator concentration has a significant influence on the molecular weight of polymer prepared. For copolymers of IT.ANH-co-MMA variation in initiator concentration over the range 0.02-0.50 mol % AIBN produced changes in number average molecular weight between 282000 and 54000 g.mol^{-1}. The experimental values for 33-35 mol % IT.ANH copolymers appear to fall on a common curve. For this composition of copolymer it does not appear possible to obtain copolymer molecular weights very much greater than 280000 g.mol^{-1} by variation in initiator concentration alone. Some further experiments at a lower polymerisation temperature (60°C) showed that higher molecular weights could be prepared, but the values obtained did not show a singular dependence on initiator concentration. This may have been due to incomplete dissolution of itaconic anhydride monomer at this temperature.

Copolymers of MMI-co-MMA show a variation in average molecular weight between >10^{6} and 114000 g.mol^{-1} with variation in initiator concentration between 0.01 and 0.275 mol %.

Determination of number average molecular weights of copolymers of IT.ANH-co-αMS show molecular weight to be virtually independent of initiator concentration (table 10).

3.6 Glass Transition Temperatures and Thermogravimetric Analysis

3.6.1 IT.ANH-co-MMA

The glass transition temperatures of IT.ANH-co-MMA copolymers for copolymer compositions 15-66 mol % IT.ANH are presented in table 22 and figure 11. Attempts to determine the glass transition temperature of a copolymer containing 94 mol % IT.ANH were unsuccessful, and no reproducible value was obtained below 200°C (473K). It was later found that samples of this composition show significant weight loss between 180-230°C (450-500K), and it is suspected that thermal degradation takes place prior to the glass transition temperature.

Table 22 Glass Transition Temperatures of IT.ANH-co-MMA Copolymers

Comp	Tg		Tg 170°C 1hr (see text)	
mol % IT.ANH	K	(°C)	K	(°C)
15	397	(124)	399	(126)
30	401	(128)	402	(129)
38	406	(133)	407	(134)
45	410	(137)	417	(144)
54	420	(147)	430	(157)
66	433	(160)	437	(164)
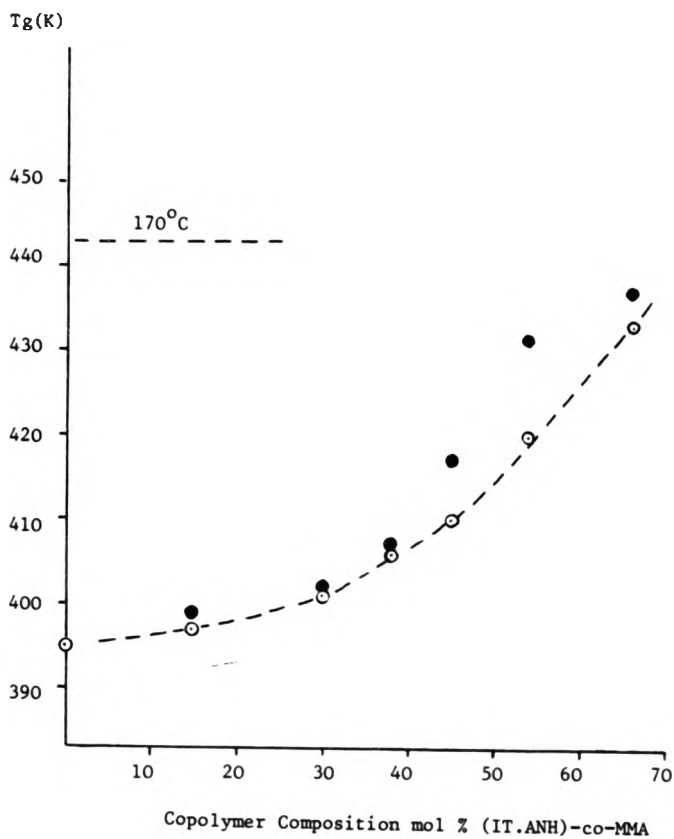
FIGURE 11   Glass Transition Temperature versus Copolymer Composition. IT.ANH-co-MMA.

Glass transition temperatures of IT.ANH-co-MMA copolymers were also re-measured after heating the samples for one hour at 170°C (443K), and the experimental values shown as solid points in figure 11, are given in table 22. Following this procedure all samples were found to be insoluble and are presumed to be crosslinked. It can be seen that samples of copolymer composition 15-38 mol % (IT.ANH) do not show any significant change in Tg with baking, while samples of composition 45-54 mol % (IT.ANH) show a small increase in glass transition temperature. The change in glass transition temperature is apparently reduced again for the copolymer containing 66 mol % (IT.ANH)-co-MMA.

To investigate possible changes in the structure of IT.ANH-co-MMA copolymers with baking, infrared spectra of 28 and 46 mol % (IT.ANH) samples were taken after baking for various lengths of time at 170°C and 200°C. No discernible changes in infrared spectra were found for samples baked for one hour at 170°C. Baking the 28 mol % (IT.ANH)-co-MMA sample for one hour at 200°C resulted in a small increase in absorption between 3000-3500 cm^{-1}, and a relative reduction in the intensity of carbonyl absorptions at 1864 cm^{-1} and 1785 cm^{-1}.

Thermogravimetric Analysis

TGA thermograms showing residual weight fraction as a function of furnace temperature for copolymers of composition 30-94 mol % (IT.ANH), plus TGA thermograms of P(MMA) and P(IT.ANH) homopolymers are presented in figure 12. P(MMA) homopolymer shows complete volatilization between 580-700K (317-427°C). IT.ANH-co-MMA copolymers show a more complex behaviour with an
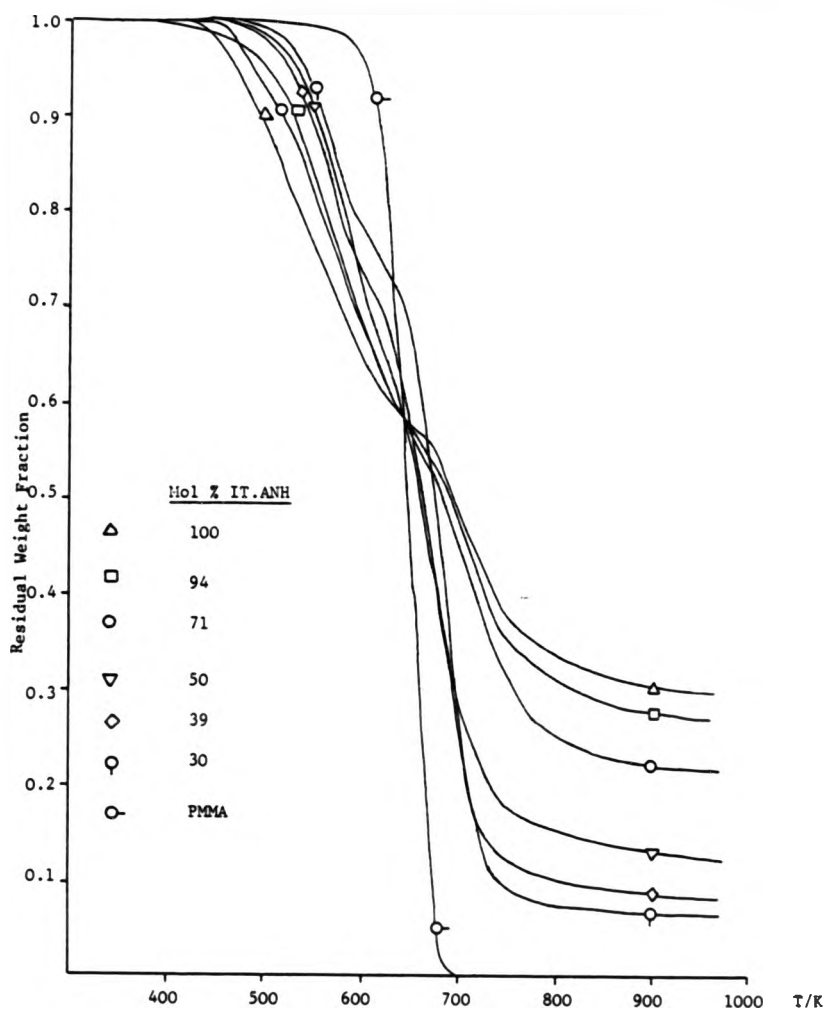
FIGURE 12   TGA Thermograms for IT.ANH-co-MMA Copolymers.
Heating Rate 20 K.min^{-1}.   N$_2$ Atmosphere.

inflexion in the TGA thermograms at a residual weight fraction of 0.8-0.6, plus a residue increasing in proportion to the mol % (IT.ANH) present in the copolymer. The onset of thermal degradation takes place at a lower temperature with increasing mol % (IT.ANH). The onset of thermal degradation of P(IT.ANH) homopolymer occurs at ~425K (152°C). The thermal degradation of P(MMA) has been reviewed by Madorski,[74] and will not be commented on here.

3.6.2 IT.ANH-co-DMI

The glass transition temperatures of IT.ANH-co-DMI copolymers with copolymer composition 7-49 mol % (IT.ANH) are presented in table 23 and figure 13. The glass transition temperature of P(DMI) homopolymer has been previously reported[75,76] to be 368-372K (95-99°C). No significant changes in the glass transition temperature was noted for samples baked for one hour at 170°C.

Table 23 Glass Transition Temperatures of IT.ANH-co-DMI
Copolymers

Comp	T_g	
mol % IT.ANH	K	(°C)
7	369	(96)
19	382	(109)
25	390	(117)
35	405	(132)
49	412	(139)
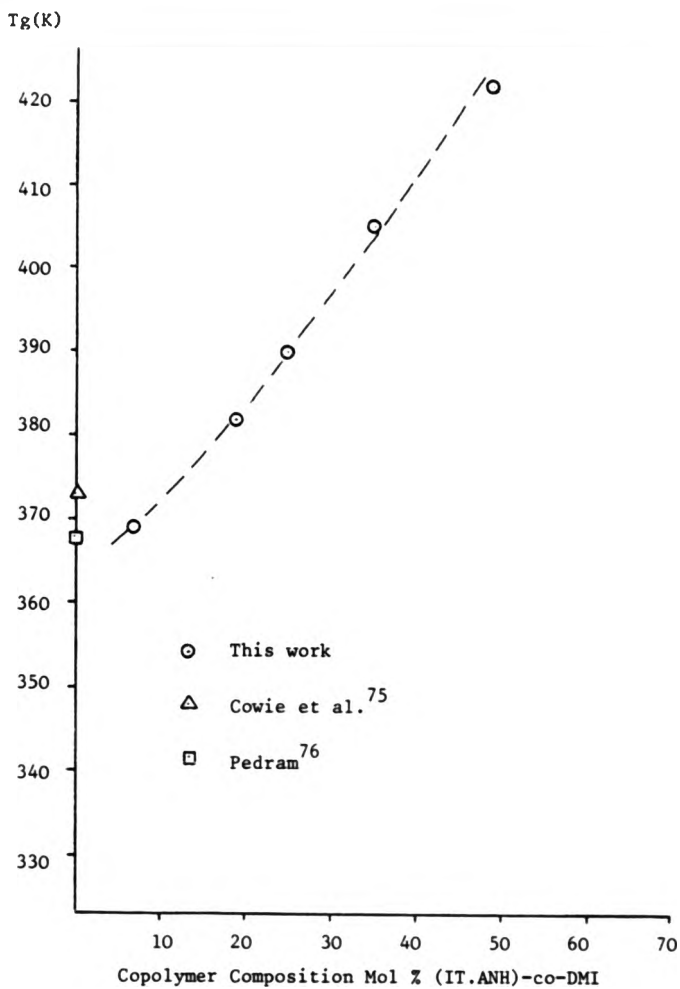
FIGURE 13   Glass Transition Temperature versus Copolymer Composition.

IT.ANH-co-DMI.

Thermogravimetric   Analysis

TGA thermograms for P(DMI) and IT.ANH-co-DMI copolymers with composition 7-49 mol % (IT.ANH) are shown in figure 14. P(DMI) can be seen to completely volatilize over the temperature range 600-680K (327-407°C).   Copolymers of IT.ANH-co-DMI show reduced thermal stability with increasing mol % (IT.ANH) in the copolymer composition.   The residue at 900K is greatest for P(IT.ANH) homopolymer.

3.6.3 IT.ANH-co- αMS

The glass transition temperature of 51 mol % (IT.ANH)-co-αMS (Mn 79000) was found to be 486K (213°C).   Baking above the glass transition temperature (230°C for 30 minutes) did not result in any significant change in Tg.   The sample remained soluble following baking.

Thermogravimetric   Analysis

The TGA thermogram for 51 mol % (IT.ANH)-co-αMS is shown in figure 15.   It can be seen that a small weight loss occurs prior to the onset of thermal degradation at ~540K (267°C).   This may be due to the escape of volatiles such as water or residual solvent at temperatures approaching the glass transition temperature.   A small residue remains at 800-850K (527-577°C).

P(α MS) homopolymer has been reported previously to degrade by main chain scission followed by un-zipping of chain fragments to monomer.[77]
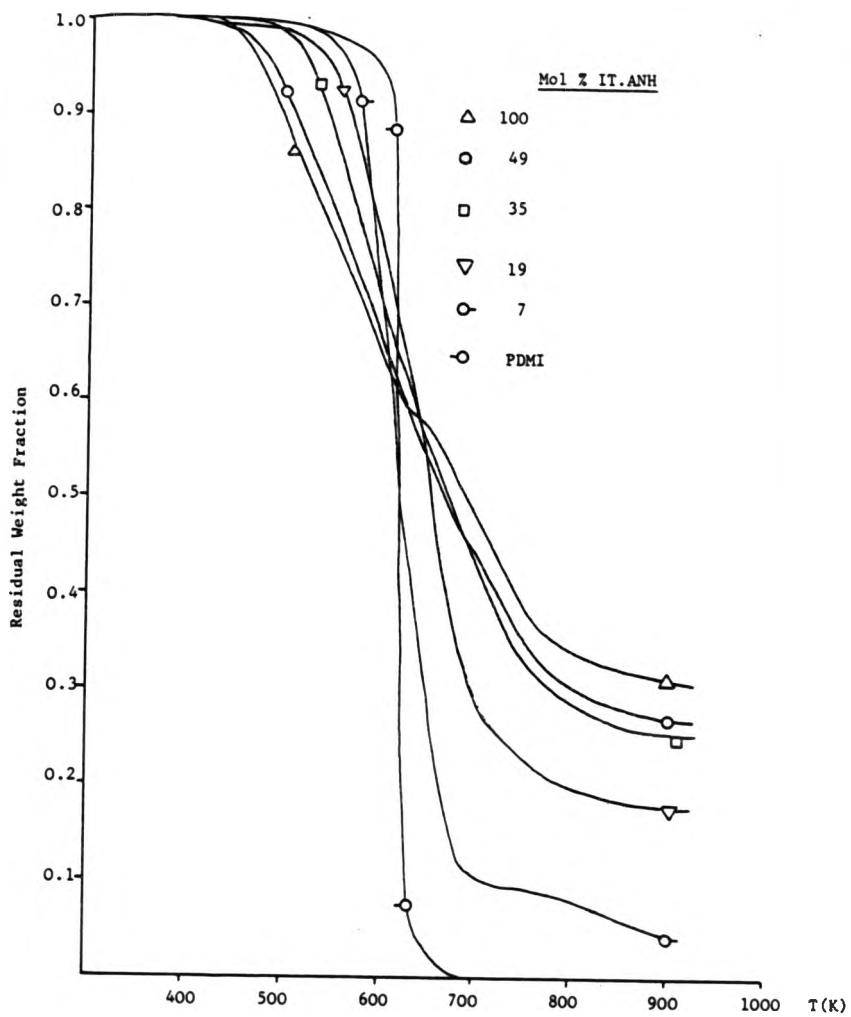
FIGURE 14   TGA Thermograms for IT.ANH-co-DMI Copolymers.
Heating Rate 20 $K.min^{-1}$. N_2 Atmosphere.
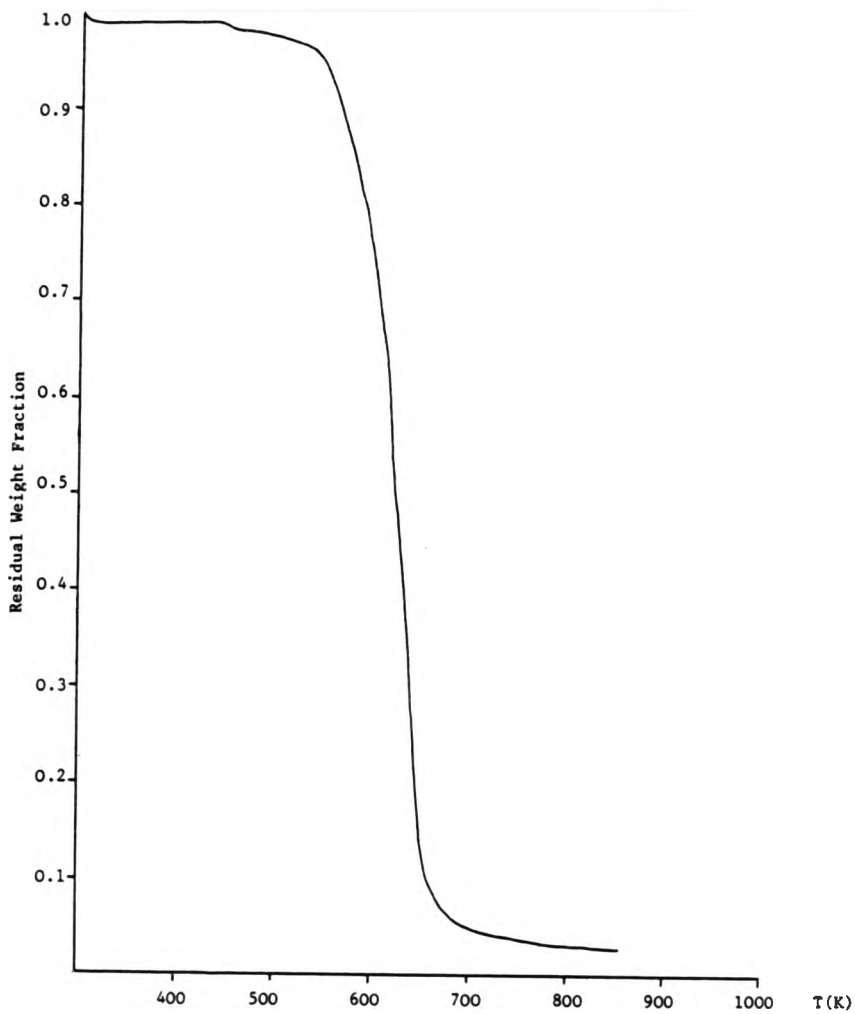
FIGURE 15   Thermogram 51 mol % (IT.ANH)-co-αMS.

Heating Rate 20 K.min^{-1}.   N$_2$ Atmosphere.

3.6.4 MMI-co-MMA

Copolymers of MMI-MMA were found to crosslink with heating above 393-413K (120-140°C). This behaviour has been observed previously for P(MMI) and for other poly(mono-n-alkyl itaconates) by Haq.[78]

Decompostition thermograms for P(MMI) (reproduced from ref 78), and for MMI-co-MMA copolymers are presented in figure 16. Copolymers of MMI-co-MMA can be seen to exhibit a complex behaviour with several inflexions in the thermogram. A relatively high residue (residual weight fraction ~0.45) is noted for P(MMI). Thermal stability would appear to decrease with increasing mol % MMI. For copolymers of 5 and 18 mol % (MMI) the onset of degradation occurs at 460-480K (187-207°C). This is reduced to ~423K (150°C) for the copolymer 35 mol % (MMI)-co-MMA.

3.6.5 ACMP-co-MMA

ACMP-co-MMA copolymers with copolymer compositions 9-36 mol % (ACMP)-co-MMA were found to crosslink when heated above ~403K (~130°C) and were insoluble after baking for one hour at 170°C. Because of crosslinking, glass transition temperatures for the uncrosslinked materials could not be determined by DSC.

Thermogravimetric Analysis

TGA thermograms for ACMP-co-MMA with copolymer compositions 9-36 mol % (ACMP) are presented in figure 17. Copolymer compositions of 9 and 15 mol % ACMP show a gradual weight loss beyond 400K (127°C), although samples retain approximately 0.85-0.90 residual weight fraction at 600K (327°C).
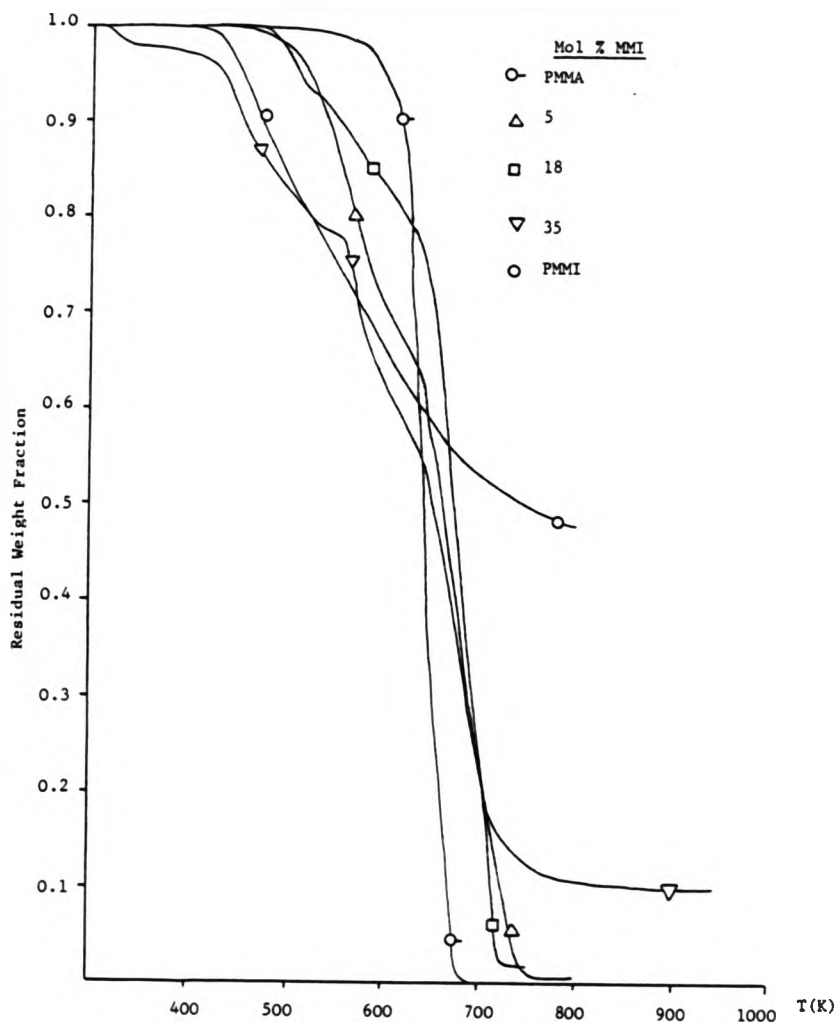
FIGURE 16   TGA Thermograms for MMI-co-MMA Copolymers.
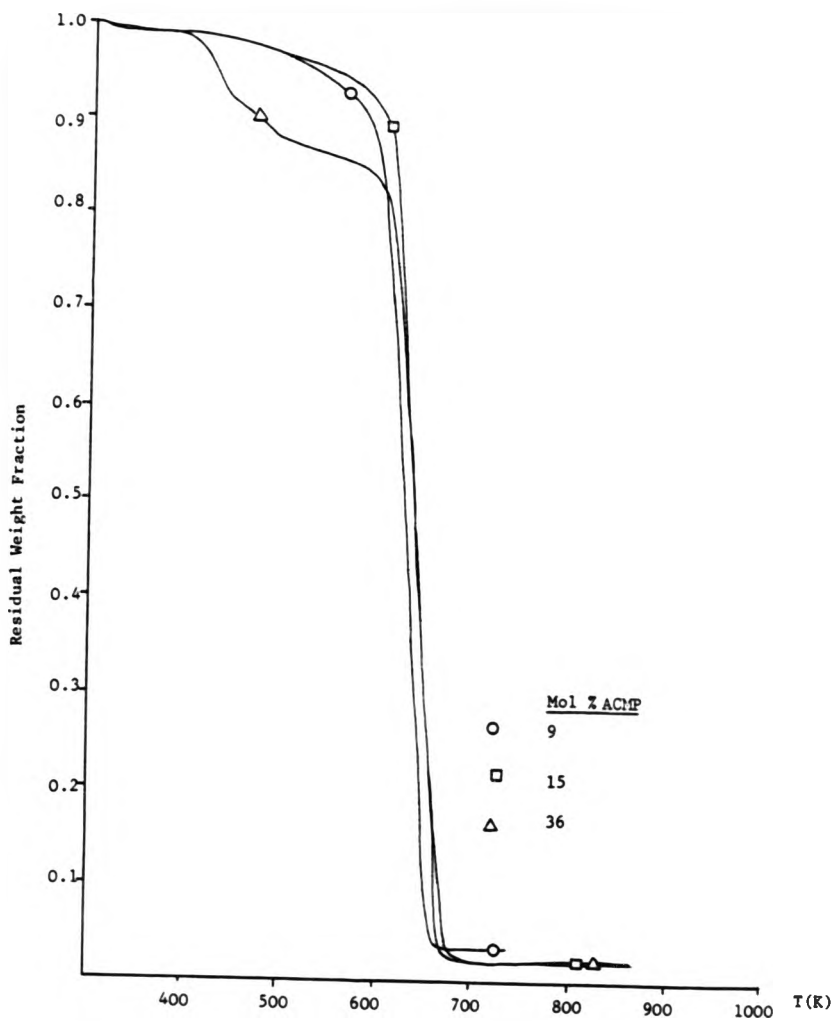Heating Rate 20 K.min^{-1}.   N$_2$ Atmosphere.

FIGURE 17   TGA Thermograms for ACMP-co-MMA Copolymers. Heating Rate 20 $K.min^{-1}$. N_2 Atmosphere.

Beyond 600K both samples show significantly increased weight loss with a small residue, 0.02-0.03, remaining at 670K (387°C).

A sample of 36 mol % (ACMP)-co-MMA appears to show a markedly different behaviour in the temperature range 400-600K (127-327°C). Significant weight loss is noted for this sample at ~400K (127°C).

3.7   Lithographic Assessment of Selected Materials
3.7.1 IT.ANH-co-MMA

Copolymers of IT.ANH-co-MMA were prepared as thin films by spin coating onto un-oxidised silicon wafers (section 2.3). Sample details are given in table 24.   Some initial difficulties in finding a suitable spinning solvent were overcome when it was found that good quality films were obtained using 2-methoxyethyl acetate. Following resist coating, all samples were pre-baked at 170°C for one hour.   The solubility of baked films was tested by immersing samples of each film in a known solvent for 3 days. Samples were then dried for one hour at 170°C.   The sol fraction is noted in table 24.

Table 24 Resist Films prepared from IT.ANH-co-MMA Copolymers

Comp mol % IT.ANH	Mn g.mol⁻¹	Spinning Solvent	Film Thickness micrometre	Sol Fraction
5		a	0.41	1.0(a)
10	227000	b	0.46	0.72(a) 0.74(g)
24	444200	b	0.59	0 .05(a)
33	154800	c	0.34	0(a) 0.32(g)
33	444200	d	0.64	0.02(a)
46	107900	a	1.41	1.0(f)
46	111200	a	0.60	0.17(a) 0.02(f)
46	117600	a	0.28	0.66(f)
46	145100	e	0.36	1.0(a) 1.0(g)
46	165900	a	0.17	0.18(a)
46	186300	a	0.17	1.0(f)
46	424300	a	0.18	0(f) 0.04(g)
46	530300	a	0.48	0.10(a) 0(f)
50		a	0.55	
67		a	0.52	

(a) = 2 methoxy ethyl acetate; (b) = mixture of chlorobenzene and 2-ethoxyethanol; (c) mixture of chlorobenzene, 2-ethoxy ethanol and methyl isobutyl ketone; (d) mixture of chlorobenzene, 2 ethoxy ethanol and methyl ethyl ketone; (e) mixture of 2 ethoxy ethyl acetate and methyl ethyl ketone; (f) cyclohexanone; (g) acetone.

Variation in Resist Performance with Copolymer Composition

Plots of normalised remaining thickness versus exposure dose for samples of 5-67 mol % (IT.ANH)-co-MMA are presented in figure 18. All samples were developed for 90 seconds plus 30 seconds in an 8:2 mixture of ethyl acetate:IPA, with 30 seconds IPA rinse. Samples were post-baked for 20 minutes at 100°C. Tabulated values of the minimum clearing dose 'Do' and resist contrast 'γ' are given in table 25, and are presented as a function of copolymer composition in figures 19 and 20.

Table 25 Minimum Clearing Dose and Resist Contrast for IT.ANH-co-MMA Copolymers as a Function of Copolymer Composition

Comp mol % IT.ANH	Mn g.mol^{-1}	Do $\mu C.cm^{-2}$	γ
5		8	
10	227000	24	1.8
24	444000	22	1.6
33	155000	32	2.4
33	444000	48	2.6
46	424000	67	3.2
50		122	~4.0
67		229	~5.0

It can be seen that both Do and γ tend to increase with increasing content of itaconic anhydride in the copolymer composition. The degree of thinning (measured as the loss in normalised remaining

FIGURE 18   Normalised Remaining Thickness versus Exposure Dose.

IT.ANH-co-MMA Copolymers.
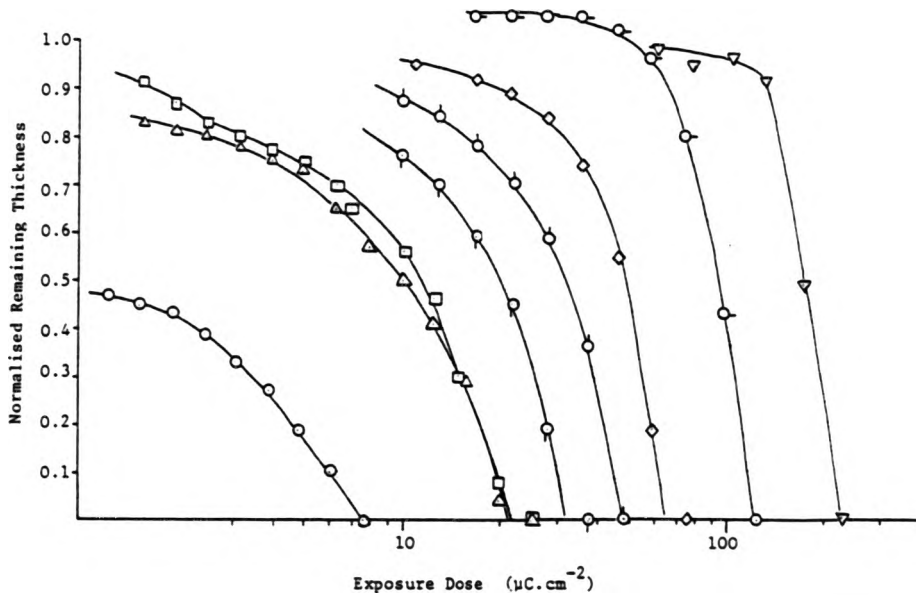
Key

○	5 mol % (IT.ANH)-co-MMA
△	10 mol % (IT.ANH)-co-MMA
□	24 mol % (IT.ANH(-co-MMA Mn 444000 g.mol^{-1}
○	33 mol % (IT.ANH)-co-MMA Mn 155000 g.mol^{-1}
○	33 mol % (IT.ANH)-co-MMA Mn 444000 g.mol^{-1}
◇	46 mol % (IT.ANH)-co-MMA Mn 424000 g.mol^{-1}
○	50 mol % (IT.ANH)-co-MMA
▽	67 mo- % (IT.ANH)-co-MMA
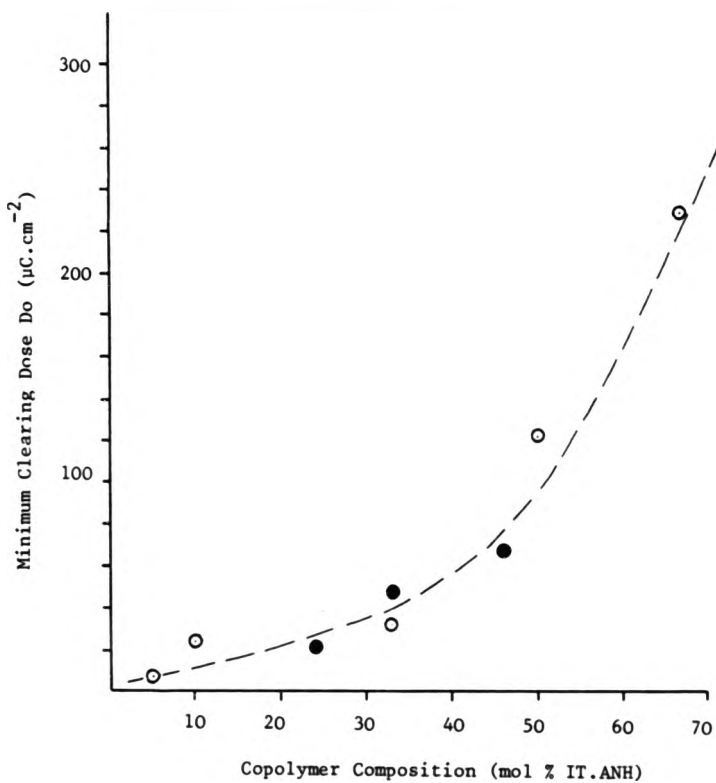
● Sample Mn   430000 g.mol^{-1}

FIGURE 19   Resist Sensitivity (Minimum Clearing Dose) versus Copolymer Composition for IT.ANH-co-MMA Copolymers.   Developed 90s + 30s 8:2 ethylacetate:isopropanol.

FIGURE 20 Resist Contrast (γ) versus Copolymer Composition for IT.ANH-co-MMA

Copolymers.

Developed 90s + 30s 8:2 ethyl acetate:isopropanol

thickness at low exposure doses) decreases with increasing content of IT.ANH. Thinning is most pronounced for copolymers containing 5-10 mol % (IT.ANH)-co-MMA. Figure 18 also shows that some degree of swelling (normalised remaining thickness increasing beyond unity) is present for the copolymer of 50 mol % (IT.ANH)-co-MMA. 'Do' for 33 mol % (IT.ANH)-co-MMA samples appears to be dependent upon the primary molecular weight.

Figure 19 suggests a sharp increase in minimum clearing dose occurs for copolymer compositions of more than ~50 mol % (IT.ANH)-co-MMA. An optimum balance of resist sensitivity and contrast is obtained for copolymer compositions in the range 40-50 mol % IT.ANH.

Choice of Solvent Developer

Plots of normalised remaining thickness versus exposure dose for a copolymer of 33 mol % (IT.ANH)-co-MMA (Mn 155000 g.mol^{-1}) with development in various solvents are presented in figure 21. Developing time was maintained constant. Although significant thinning was not observed, resist sensitivity can be seen to vary over an order of magnitude with changes in the solvent developer used.

Comparison of the quality of resist images obtained with each type of developing solvent showed that results obtained with an 8.2 mixture of ethyl acetate:IPA compared favourably with other solvent systems investigated. This combination of solvent and non-solvent was selected purely by trial and error, and it is recognized that improved results may be possible with further experimentation. For copolymers of 46 mol % (IT.ANH)-co-MMA cyclohexanone was later

FIGURE 21   Normalised Remaining Thickness versus Exposure Dose for a
Copolymer of 33 mol % (IT.ANH)-co-MMA.   Various Developers.

adopted as the preferred solvent developer.

Measurement of gel fraction remaining at long times.

The variation in resist sensitivity obtained with different solvent developers suggested that plots of normalised remaining thickness versus exposure dose obtained in the usual way do not represent the breakdown of the pre-crosslinked network to the first-formed soluble polymer.

To test this hypothesis a sample of 46 mol % (IT.ANH)-co-MMA, Mn 111000 g.mol^{-1}, was exposed over the range 0.5-50 μC.cm^{-2} and the exposed resist immersed in 2-methoxyethyl acetate for a total of 72 hours. The sample was then re-baked for one hour at 170°C and the normalised remaining thickness determined for each exposure dose.

Examination of the residual film using optical microscopy showed that the surface contained a large number of irregularities (figure 22-23).

Normalised remaining thicknesses for two portions of the same film, (a) developed for 120s plus 120s in cyclohexanone, and (b), immersed for 72 hours in 2-methoxyethyl acetate, are presented in Figure 24. It can be seen that the minimum clearing dose 'Do' obtained for the sample immersed for 72 hours in 2-methoxy ethyl acetate is many times less than 'Do' observed with development for 120 seconds plus 120 seconds in cyclohexanone.

Variation in Resist Performance with Pre-bake Temperature.

Samples of 46 mol % (IT.ANH)-co-MMA, Mn 111000, and Mn 530000 g.mol^{-1}, were pre-baked at two different temperatures,
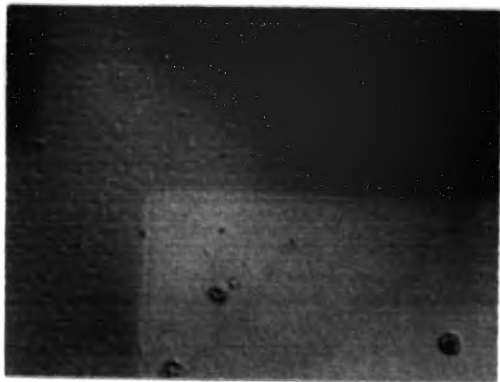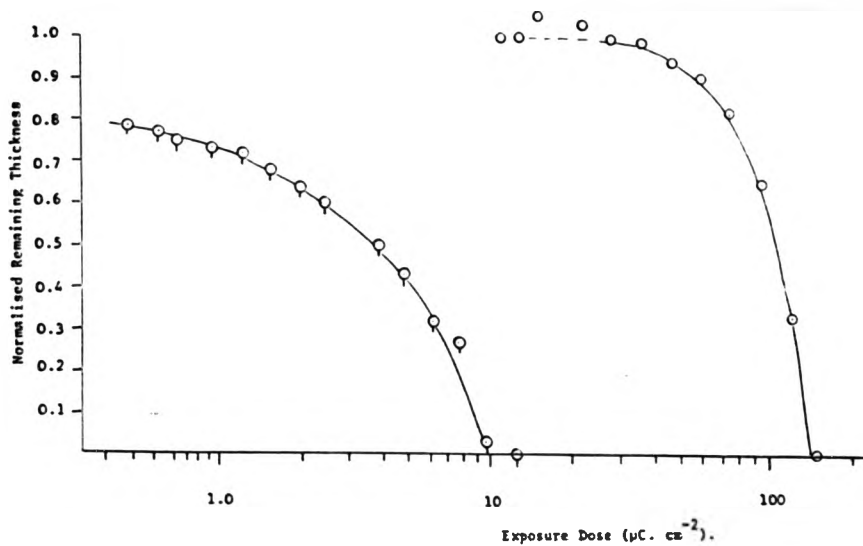
10 micrometre

FIGURE 22 Optical Micrograph showing Residual Film with Portion
of Lightly Exposed Rectangle.

10 micrometre

FIGURE 23 Optical Micrograph with Interference Contrast showing
Surface Relief in Heavily Exposed Rectangle.

FIGURE 24: Normalised Remaining Thickness versus Exposure Dose.

46 mol % (IT.ANH)-co-MMA. Mn µ₁000 g.mol⁻¹

105°C and 170°C for one hour, in order to determine the effect of pre-bake temperature upon resist performance. The samples were exposed in the normal way and then developed for 120s plus 120s in cyclohexanone. Plots of normalised remaining thickness versus exposure dose for the two samples, and for the two different pre-bake conditions, are shown in figure 25. Tabulated values of the minimum clearing dose 'Do' and γ are presented in table 26.

Following pre-baking, a portion of each sample was immersed for three days in 2-methoxyethyl acetate. Sol fractions for the samples pre-baked for one hour at 170°C are detailed in table 24. Samples pre-baked at 105° were completely soluble.

Comparison of the results obtained for the two pre-bake conditions (Figure 25, Table 26) show that both contrast and the minimum clearing dose are significantly increased for samples pre-baked at 170°C. It seems most likely that these effects can be directly attributed to crosslinking. Sensitivity and contrast for the two primary molecular weights can be seen to be different.

Table 26 Minimum Clearing Dose and Resist Contrast for 46 mol % (IT.ANH)-co-MMA Pre-baked at 105 and 170°C.

Mn g.mol^{-1}	Pre-bake Temp. °C	Do[a] $\mu C.cm^{-2}$	γ[a]
111000	105	75	2.6
111000	170	145	4.0
530000	105	82	2.1
530000	170	210	4.4

(a) developed 120s plus 120s cyclohexanone.
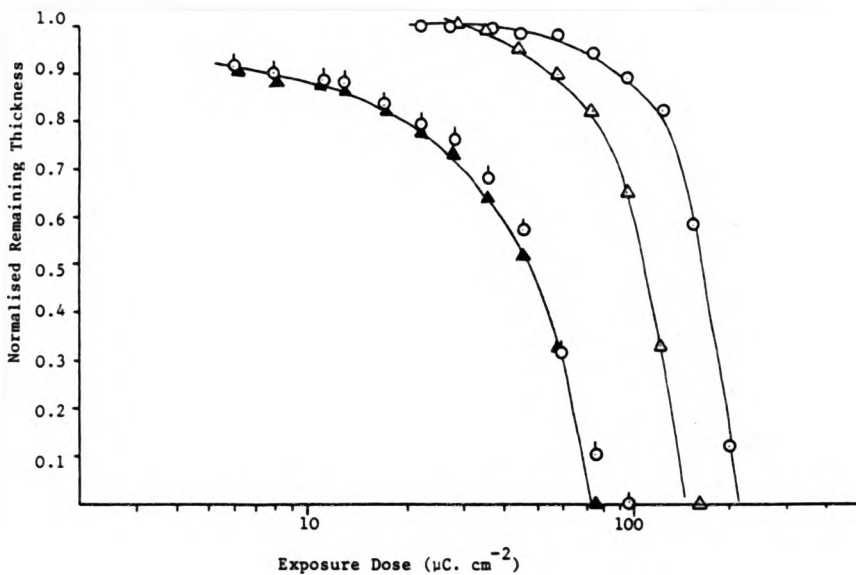
Key

○ 46 mol % (IT.ANH)-co-MMA.   Mn 530000 PB 170°C

△ 46 mol % (IT.ANH)-co-MMA.   Mn 111000 PB 170°C

◒ 46 mol % (IT.ANH)-co-MMA.   Mn 530000 PB 105°C

▲ 46 mol % (IT.ANH)-co-MMA.   Mn 111000 PB 105°C

FIGURE 25: Normalised Remaining Thickness versus Exposure Dose for Samples

of 46 % mol % (IT.ANH)-co-MMA pre-baked at 105°C amd 170°C.

Variation in Resist Performance with Primary Molecular Weight.

To investigate the variation in resist properties with primary molecular weight, samples of 46 mol % (IT.ANH)-co-MMA, Mn 111000, 166000, 424000 and 530000 g.mol^{-1} were exposed and developed in an identical manner. Normalised remaining thickness versus exposure dose for these samples with development for 120 seconds plus 120 seconds in cyclohexanone are presented in figure 26. Values of the minimum clearing dose 'Do' and resist contrast are presented in table 27.

These results show a strong variation in minimum clearing dose with primary molecular weight. The variation in Do does not appear to be attributable to any variation in sol fraction following pre-baking (table 24), and would appear to show a minimum in resist sensitivity at Mn 166000 g.mol^{-1}.

Table 27 Minimum Clearing Dose and Resist Contrast for 46 mol % (IT.ANH)-co-MMA as a Function of Primary Molecular Weight.

Mn g.mol^{-1}	Do[a] μC.cm^{-2}	γ[a]
111000	145	4.0
166000	66	3.4
424000	156	4.5
530000	210	4.4

(a) developed 120s plus 120s cyclohexanone.
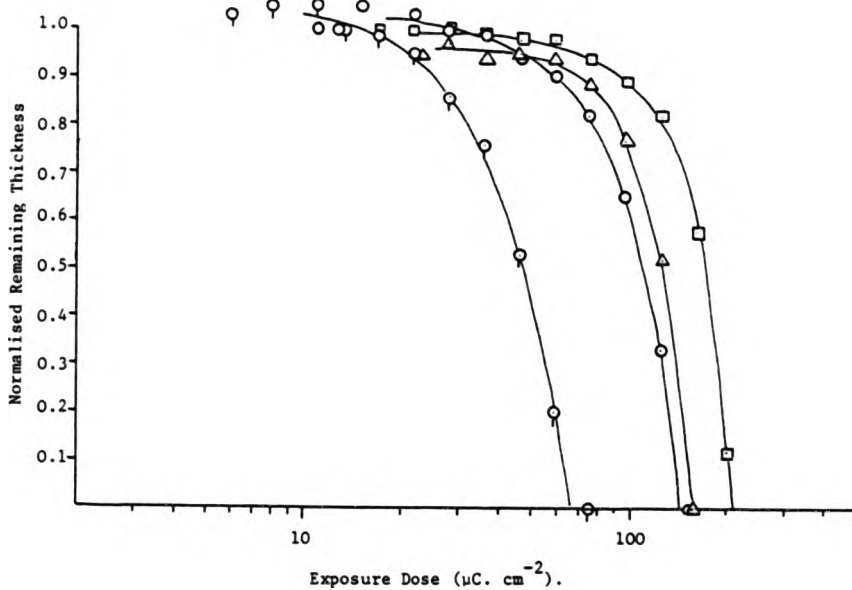
Key
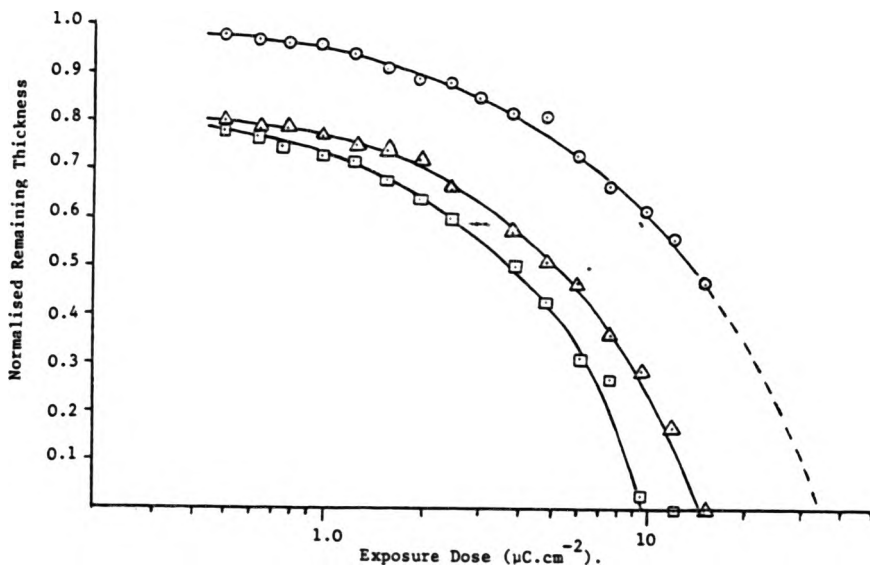
○   Mn 111000

◔   Mn 166000

△   Mn 424000

▢   Mn 530000

FIGURE 26:   Normalised Remaining Thickness versus Exposure Dose for 46 mol %

(IT.ANH)-co-MMA.   Various Molecular Weights.

Results presented in Figure 27 show values of normalised remaining thickness for samples of primary molecular weight Mn 111000, 166000, 424000 $g.mol^{-1}$ after samples were exposed and soluble portions removed by soaking portions of the exposed wafers in 2-methoxy ethyl acetate for a total of ~96 hours. It can be seen that the minimum clearing dose is greatest for the sample Mn 424000 $g.mol^{-1}$ and decreases in the order 424000 $g.mol^{-1}$ > 166000 $g.mol^{-1}$ > 111000 $g.mol^{-1}$. The minimum clearing dose can in each case be seen to be very much less than that observed with development in cyclohexanone for 120s plus 120s. The values of the minimum clearing dose (for the gel fraction) presented in Figure 27 do not show the minima found for samples developed in cyclohexanone.

Resolution.

Resist patterns prepared using 24, 33 and 46 mol % (IT.ANH)-MMA copolymers were examined by scanning electron microscopy, and the optimum resolution appeared to be obtained for a sample of 46 mol % (IT.ANH)-MMA, Mn 530000 $g.mol^{-1}$. Scanning electron micrographs of resist features prepared in this material using cyclohexanone as the developing solvent are presented in figures 28-30. The microscope stage was tilted at 70-80° to provide an indication of the profile of the resist features. Individual captions are provided.

FIGURE 27: Normalised Remaining Thickness versus Exposure Dose.

46 mol Z (IT.ANH)-co-MMA (see text).

FIGURE 28 Nominal 250 nm 1:1 Lines and Spaces. 46 mol % IT.ANH-co-MMA. 530000 g.mol^{-1}. Exposure Dose 200 µC.cm^{-2}.

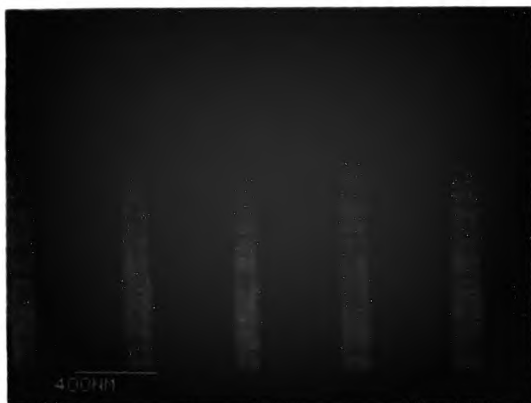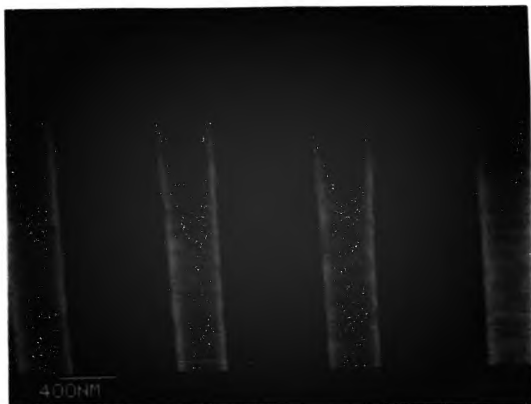FIGURE 29 Nominal 500 nm 1:1 Lines and Spaces. 46 mol % IT.ANH-co-MMA. Mn 530000 g.mol^{-1}. Exposure Dose 200 µC.cm^{-2}.
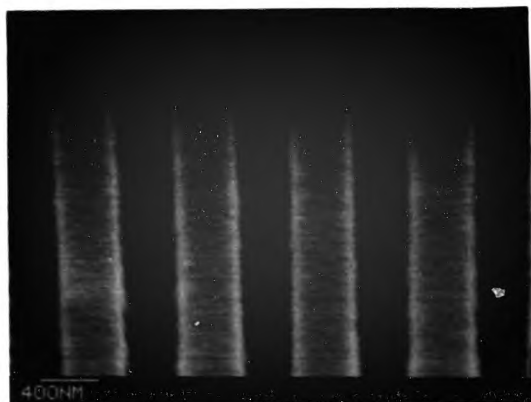
FIGURE 30 Nominal 250 nm 1:2 Lines and Spaces.   46 mol % IT.ANH-co-MMA.
Mn 530000 g.mol^{-1}.   Exposure Dose 200 μC.cm^{-2}.

Plasma Etch Resistance.

Copolymer samples were subjected to plasma etching as
described in section 2.8, and the results are presented in table 28.
For these conditions the etch resistance of these materials can be
seen to be marginally improved over that of P(MMA).

Table 28 Oxygen Plasma Etch Rates of IT.ANH-co-MMA Copolymers.

Comp. mol % IT.ANH	Etch Rate nm. min^{-1}
10	140
24	140
33	120
46	120
50	140
67	110
P(MMA) Ref	150

3.7.2 IT.ANH-co-MMA , HEMA-co-MMA Copolymer Mixtures.

Mixtures of IT.ANH-co-MMA and HEMA-co-MMA detailed in
table 29 were found to form good quality films, with no evidence of
phase separation, when spun from solution in 2-ethoxy ethyl acetate.
No evidence of phase separation was observed with baking for one
hour at 170-225°C.

Table 29 IT.ANH-co-MMA, HEMA-co-MMA Copolymer Mixtures.

Mixture Composition	Code	Film Thickness micrometre
1:1 5 mol % (IT.ANH)-co-MMA: 5mol % (HEMA)-co-MMA	A	0.50
1:1 15 mol % (IT.ANH)-co-MMA: 5 mol % (HEMA) co-MMA	B	0.41

Samples of the copolymer mixture 'A' were pre-baked for one hour at 170, 195 and 225°C. Portions of each film were immersed for seven days in 2-ethoxyethyl acetate to determine the sol fraction following pre-baking. Details are given in table 30. These measurements would suggest that for this mixture, crosslinking does not take place with pre-baking for one hour at 170°C, but that an increasing gel fraction is formed with pre-baking at 195 and 225°C respectively.

Samples of mixture 'B' were found to give an insoluble film with baking at 170°C for one hour. Due to an oversight, the insoluble fraction was not determined in this case.

Table 30 Sol Fraction Following Pre-baking IT.ANH-co-MMA, HEMA-co-MMA Copolymer Mixture A.

Pre-bake Temp. ^oC	sol fraction
170	1.0
195	0.32
225	0.12

Exposure and Solvent Development.

Plots of normalised remaining thickness versus exposure dose for mixture compositions A and B, with development in various solvents are given in Figures 31-33. Tabulated values of the minimum clearing dose and resist contrast are presented in Table 31.
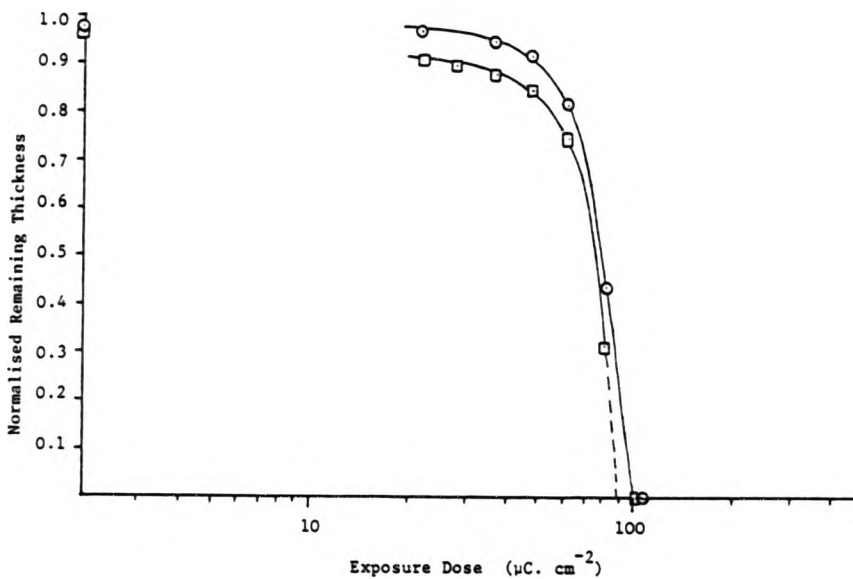
FIGURE 31: Normalised Remaining Thickness versus Exposure Dose.
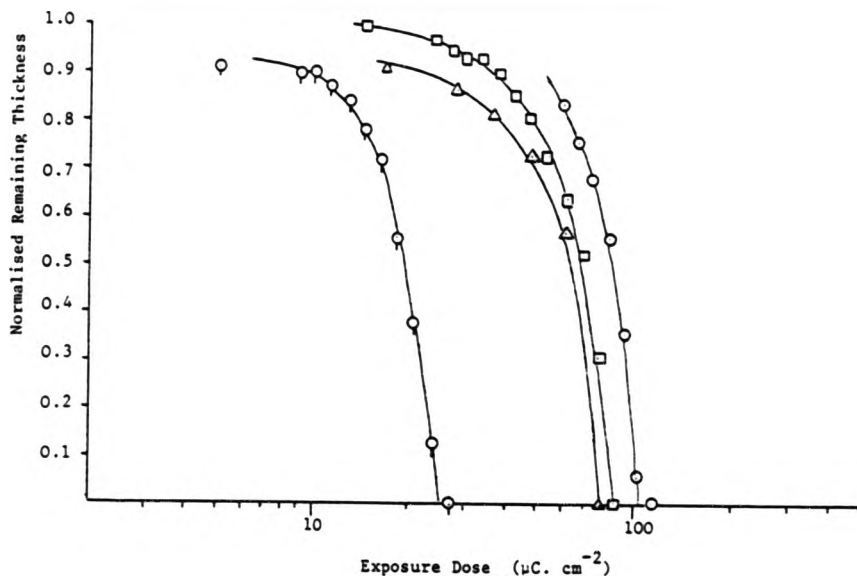IT.ANH-co-MMA, HEMA-co-MMA Mixture A.   Pre-baked 170°C.

Key
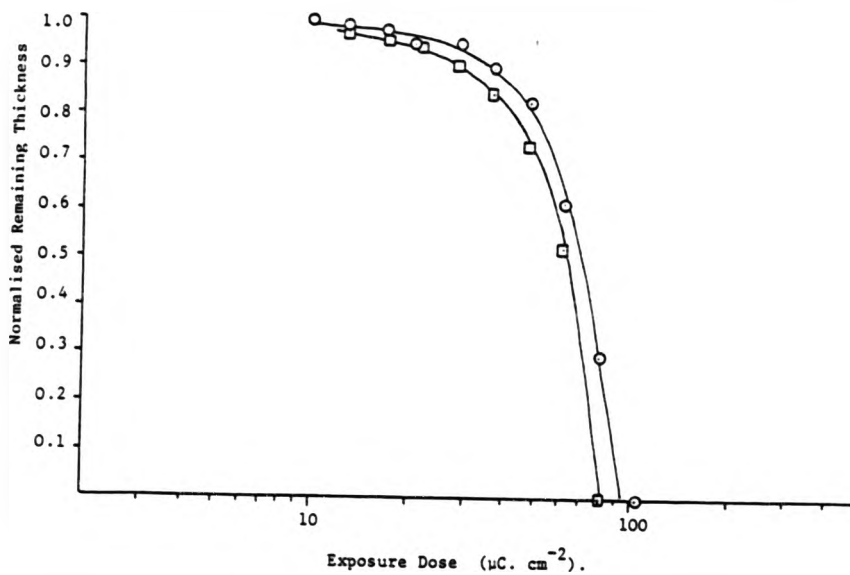
○   90s + 30s 8:2 mixture butyl acetate:hexyl acetate

□   120s + 120s cyclohexanone

FIGURE 32: Normalised Remaining Thickness versus Exposure Dose.

IT.ANH-co-MMA, HEMA-co-MMA Mixture A.   Pre-baked 225°C.

Key

♀ 90s + 30s 8:2 mixture ethyl acetate:isopropanol

△ 90s + 30s p-dioxane

□ 90s + 30s methyl isobutyl ketone

○ 120s + 120s cyclohexanone

FIGURE 33: Normalised Remaining Thickness versus Exposure Dose.
IT.ANH-co-MMA, HEMA-co-MMA Mixture B. Pre-baked 170°C.
Various Developers.

Table 31 Minimum Clearing Dose and Resist Contrast for IT.ANH-
co-MMA, HEMA-co-MMA Copolymer Mixtures.

Blend Comp.	Pre-bake Temp. °C	Developer	D_o $\mu C.cm^{-2}$	γ
A	170	(a)	94	3.9
A	170	(b)	82	4.3
A	225	(a)	100	5.0
A	225	(b)	86	
B	170	(b)	105	5.6
B	170	(c)	88	4.5
B	170	(d)	80	5.3
B	170	(e)	26	4.7

(a) 60s 8:2 butyl acetate:n-hexyl acetate.

(b) 120s + 120s cyclohexanone.

(c) 90s + 30s methyl isobutyl ketone.

(d) 90s + 30s p-dioxane.

(e) 90s + 30s 8:2 ethyl acetate:IPA

Comparison of the values presented in table 31 suggests that the mixture B generally exhibits higher values of resist contrast, although the minimum clearing dose 'Do' can be seen to vary over a relatively wide range. Differences in Do for mixture A pre-baked at 170°C and 225°C are probably not significant. Resist contrast appears higher for samples pre-baked at 225°C.

Resolution.

All samples were examined using optical microscopy. For mixture A there appeared to be little difference in resolution for samples pre-baked at 170°C, 195°C and 225°C. The resolution of the mixture B was significantly better than that of mixture A. Resist performance for the mixture B is superior to that of IT.ANH-co-MMA copolymers of similar composition in the absence of HEMA-co-MMA. Scanning electron micrographs of resist patterns prepared in mixture B, with development in cyclohexanone are presented in Figures 34 and 35. Individual captions are provided.

3.7.3 IT.ANH-HEMA-MMA Terpolymers

IT.ANH, HEMA, MMA terpolymers were found to show a large change in their solubility characteristics with increasing proportion of IT.ANH and HEMA in the feed composition. Terpolymers with feed compositions 5:5:90 and 10:10:80 (IT.ANH:HEMA:MMA) were soluble in 2-ethoxy ethyl acetate and could be spun to form thin, even films. Terpolymers of feed compositions 20:20:60 and 35:35:30 could not be dissolved in a suitable spinning solvent and so work was not continued with these materials. Samples of 5:5:90 and 10:10:80 feed composition were pre-baked at 170°C. Following pre-baking, the materials were found to be insoluble in both 2-ethoxyethyl acetate and acetone. Sol fractions were 0.52 and 0.16 respectively. (Original film thickness = 0.49 and 0.43 micrometre).

Exposure and Solvent Development.

A limited evaluation of the lithographic properties of these materials was made. Plots of normalised remaining thickness
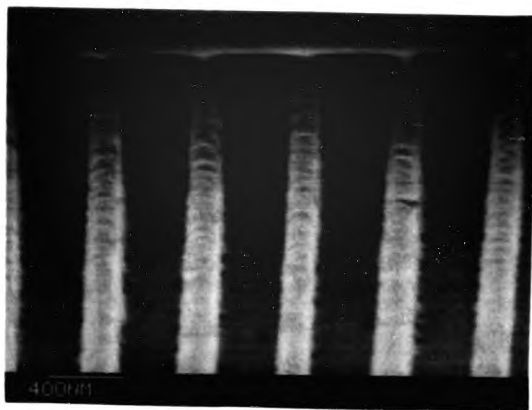
FIGURE 34   Nominal 250 nm Lines and Spaces (Mixture B) 1:1 Blend (15 mol %)
IT.ANH-co-MMA : (5 mol %)HEMA-co-MMA.   Esposure Dose 175 μC.cm^{-2}.
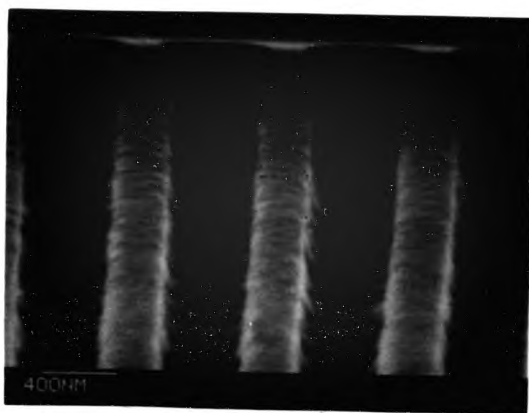

FIGURE 35   Nominal 375 nm Lines and Spaces (Mixture B) 1:1 Blend (15 mol %)
IT.ANH-co-MMA : (5 mol %) HEMA-co-MMA.   Exposure Dose 158 μC.cm^{-2}.

versus exposure dose for terpolymers of feed composition 5:5:90 and 10:10:80 IT.ANH:HEMA:MMA with development in cyclohexanone are presented in Figure 36. Anomalous behaviour is noted for the terpolymer of feed composition10:10:80 IT.ANH: HEMA: MMA. The resolution of this material was also found to be relatively poor.

Resolution.

Resist patterns prepared in the terpolymer of feed composition 5:5:90 are shown in figures 37-38. Optimum resolution appeared to be obtained with development in cyclohexanone or 80:20 butyl acetate:hexyl acetate mixture. Some slight barrelling of resist features, where the dimensions of exposed lines reduce near their ends, was noted for samples developed in 80:20 butyl acetate:hexyl acetate, although in general, resist images were found to be realtively sharp.

3.7.4 IT.ANH-co-DMI.

Thin films of IT.ANH-co-DMI copolymers and P(DMI) homopolymers were spun from 20 w/v % solution in 2-methyoxy ethyl acetate. Sample details are given in table 32. Following resist coating all samples were pre-baked at 170°C for one hour.

The solubility of the pre-baked films was tested by immersing samples of each film in 2-methoxy ethyl acetate for seven days. Only in the case of 35 mol % (IT.ANH)-co-DMI was a significant gel fraction noted. Further comment on this observation is provided in section 4.3.
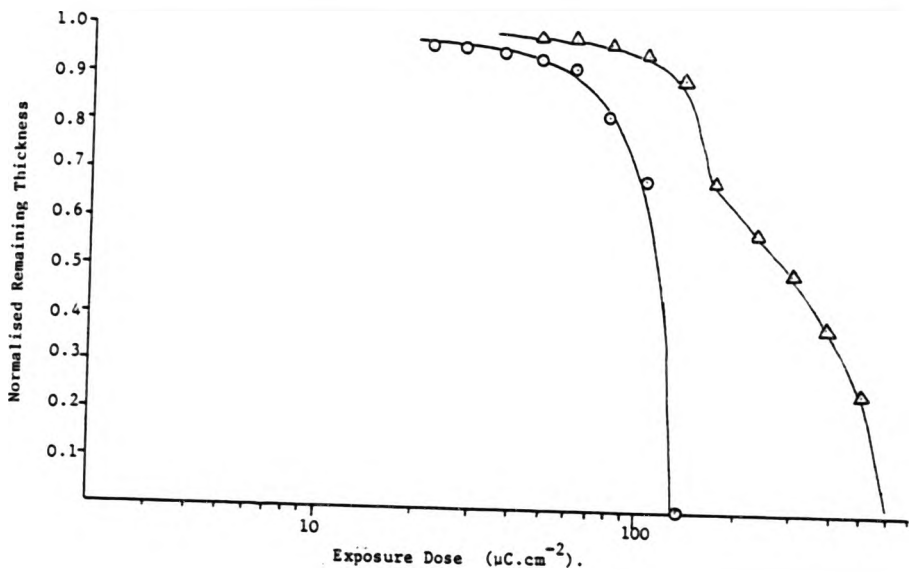
Key

○   5:5:90 Feed.   IT.ANH:HEMA:MMA

△   10:10:80 Feed.   IT.ANH:HEMA:MMA

FIGURE 36:   Normalised Remaining Thickness versus Exposure Dose. IT.ANH-HEMA-MMA Terpolymers.   Pre-baked 170°C. Developed 120s + 120s cyclohexanone.
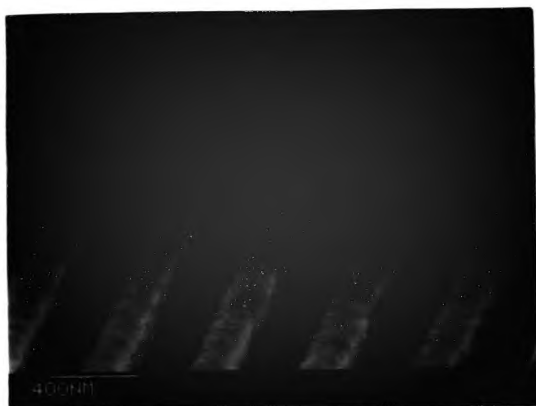
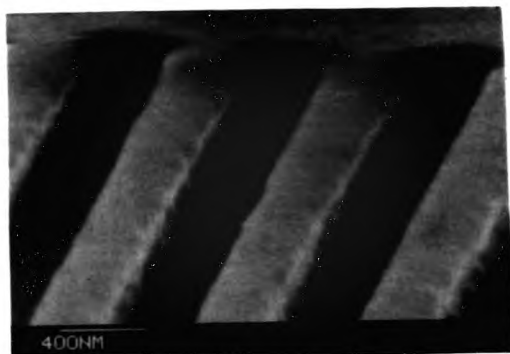FIGURE 37   Nominal 250 nm 1:1 Lines and Spaces IT.ANH:HEMA:MMA Terpolymer. Exposure Dose 365 µC.cm^{-2}.

FIGURE 38   Nominal 375 nm 1:1 Lines and Spaces IT.ANH:HEMA:MMA Terpolymer.   Exposure Dose 365 µC.cm^{-2}.

Table 32 Resist Films Prepared from IT.ANH-co-DMI Copolymers.

| Comp. mol % IT.ANH	Film thickness micrometre	Sol fraction
P(DMI)	0.81	1.0
7	0.61	1.0
18	0.72	1.0
25	0.76	1.0
35	0.93	0.77
49	0.74	1.0

Variation in Resist Performance with Copolymer Composition.

Plots of normalised remaining thickness versus exposure dose for samples of copolymer compositions 7-25 mol % (IT.ANH)-co-DMI , with development for 120 seconds plus 120 seconds in cyclohexanone, are presented in Figure 39. Also shown are results for P(DMI) developed in the same manner. Copolymers of 35 mol % and 49 mol % (IT.ANH)-co-DMI did not show clearing doses below 500 $\mu C.cm^{-2}$ with development in cyclohexanone.

Results for copolymers of 7 and 18 mol % (IT.ANH)-co-DMI, with development in a 1:2 mixture of 2-methoxy ethyl acetate:n-hexyl acetate and methyl isobutyl ketone (120 seconds plus 120 seconds and 180 seconds plus 180 seconds respectively) are shown in Figure 40.

Tabulated values of minimum clearing dose Do and resist contrast are given in table 33 and are presented as a function of copolymer composition in Figures 41 and 42. Results are shown on

Key
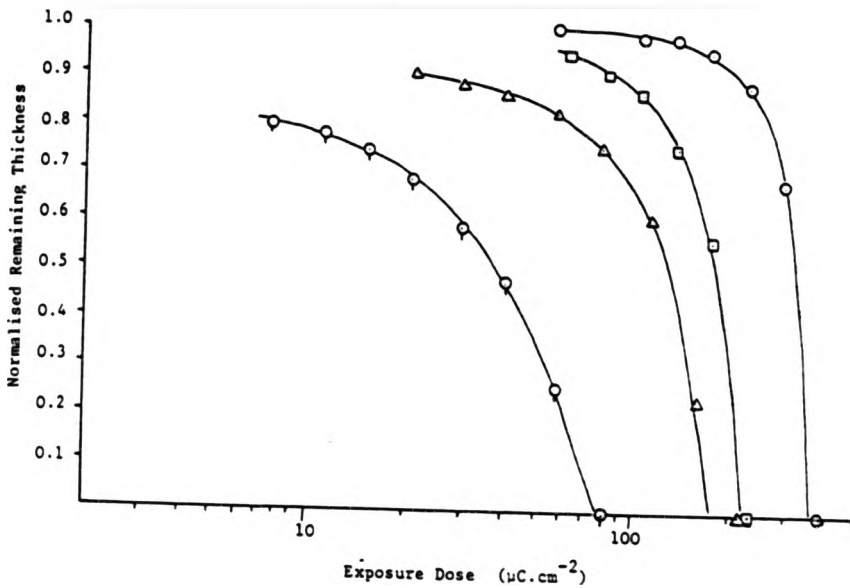
○   PDMI

φ   7 mol % (IT.ANH)-co-DMI

△   18 mol % (IT.ANH)-co-DMI

□   25 mol % (IT.ANH)-co-DMI

FIGURE 39:   Normalised Remaining Thickness versus Exposure Dose.

IT.ANH-co-DMI Copolymers.   Developed 120s + 120s cyclohexanone.
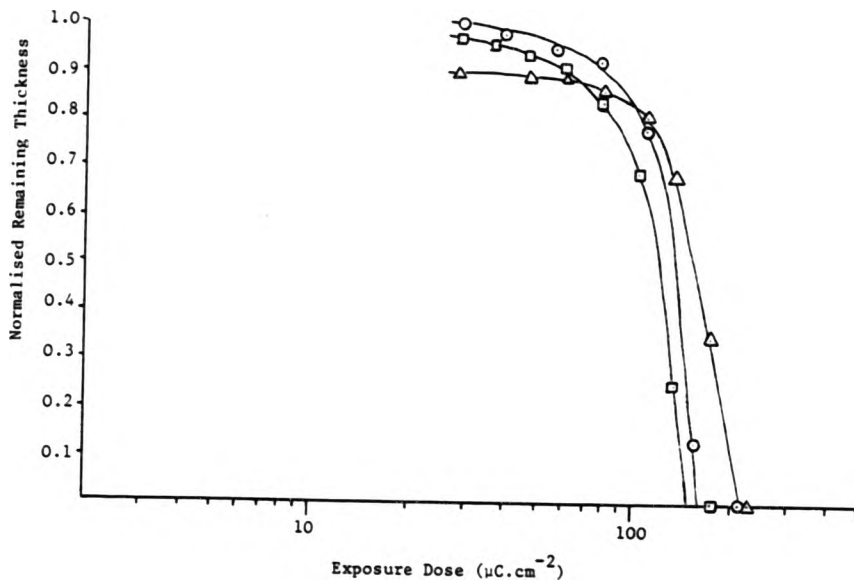
Key

◻   PDMI[a]

◯   7 mol % (IT.ANH)-co-DMI[b]

△   18 mol % (IT.ANH)-co-DMI[c]

FIGURE 40:   Normalised Remaining Thickness versus Exposure Dose.

IT.ANH-co-DMI Copolymers.

a   developed 120s + 120s Mixture 2:1 2-methoxy ethyl acetate:n-hexyl acetate

b   developed 120s + 120s Mixture 1:2 2-methoxy ethyl acetate:n-hexyl acetate

c   developed 180s + 180s methyl isobutyl ketone.

FIGURE 41: Resist Sensitivity (Minimum Clearing Dose) versus Copolymer
Composition IT.ANH-co-DMI Copolymers.

Legend:
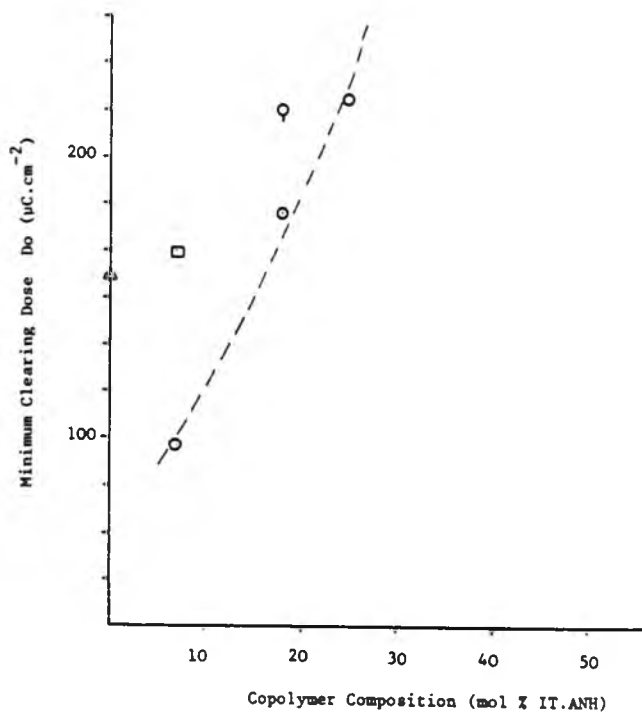
O   120s + 120s cyclohexanone

△   90s + 30s Mixture 2:1 2-methoxyethylacetate:n-hexyl acetate

□   90s + 30s Mixture 1:2 2-methoxyethylacetate : n-hexyl acetate

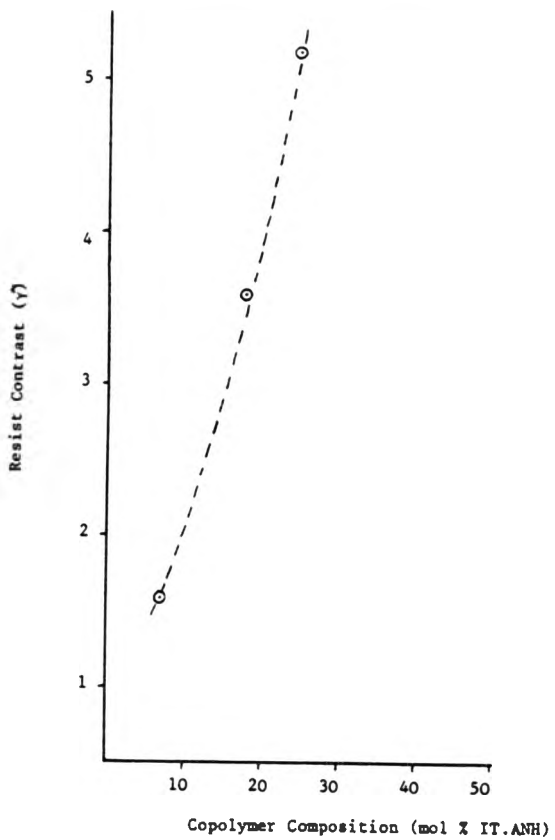⌀   90s + 30s Mixture methyl isobutyl ketone

FIGURE 42:   Resist Contrast (γ) versus Copolymer Composition.

IT.ANH-co-DMI.   Developed 120s + 120s cyclohexanone.

the same scale to those given in section 3.7.1 (Figures 19 and 20) with which they may be compared.

Table 33 Minimum Clearing Dose and Resist Contrast for IT.ANH-co-DMI Copolymers.

Comp mol % IT.ANH	Developer	Do $\mu C.cm^{-2}$	γ
P(DMI)	(a)	365	~9
	(b)	145	~6
7	(a)	78	1.6
	(c)	160	7
18	(a)	177	3.6
	(c)	>500	
	(d)	220	3.2
25	(a)	225	5.2
35	(a)	>500	
49	(a)	>500	

(a) 120s + 120s cyclohexanone; (b) 120s + 120s 2:1 2-methoxyethyl acetate:n-hexyl acetate; (c) 1:2 2-methoxyethyl acetate:n-hexyl acetate; (d) 180s + 180s methyl isobutyl ketone.

Examination of developed resist patterns by optical and scanning electron microscopy showed that although measured values of resist contrast are relatively high, the resolution of IT.ANH-co-DMI copolymers is generally poor. With the exception of 7 mol %

(IT.ANH)-co-DMI, all other materials did not show resolution capabilities better than ~0.75 micrometre.   Many samples also showed pronounced proximity effects.

Figures 41 and 42 show that the minimum clearing dose, and resist contrast, increase sharply with increasing content of IT.ANH in the copolymer composition.   Unlike the copolymers of IT.ANH-co-MMA investigated previously, resist resolution was not found to improve with increasing mol % IT.ANH.   Optimum resolution was noted for copolymers of 7 mol % (IT.ANH)-co-DMI with development in a 1:2 mixture of 2-methoxy ethyl acetate:n-hexyl acetate. Scanning electron micrographs of resist patterns produced in this material are shown in Figures 43-45.   Figure 44 shows the resist pattern following de-scumming where the substrate and resist are given a light plasma etch treatment.   Figures have individual captions.

3.7.5 IT.ANH-co-αMS.

The copolymer 51 mol % (IT.ANH)-co-αMS (Mn 93000 g.mol^{-1}), was dissolved at room temperature in 2-methoxy ethyl acetate. Heating the solution of the copolymer in the solvent caused precipitation of the polymer, suggesting the presence of a lower critical solution temperature.

A thin film of the copolymer sample was prepared by spin coating in the normal manner.   Samples were pre-baked for one hour at 170°C and 200°C.   Samples pre-baked at 200°C were allowed to cool slowly from the baking temperature.   All samples were found to be completely soluble.

A limited assessment of the lithographic properties of this copolymer was made.   A plot of normalised remaining thickness

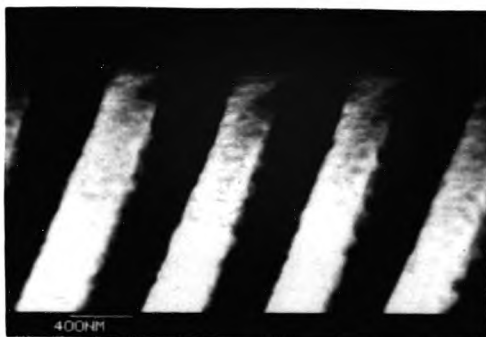FIGURE 43   Nominal 375 nm 1:1 Lines and Spaces   7 mol % (IT.ANH)-co-DMI. Exposure Dose 300 $\mu C.cm^{-2}$.
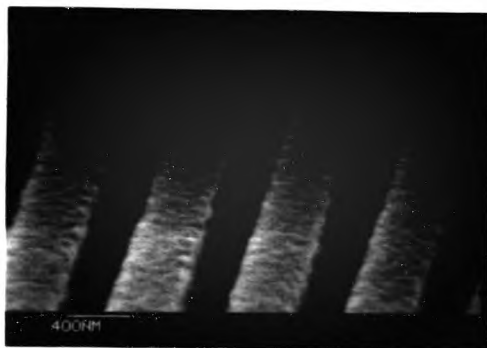

FIGURE 44   Following De-scum.

FIGURE 45   Nominal 250 nm 1:2 Lines and Spaces   7 mol % (IT.ANH)-co-DMI.
Exposure Dose 300 μC.cm^{-2}.

versus exposure dose for the sample pre-baked at 170°C for one hour
and developed for 120 seconds plus 120 seconds in methyl isobutyl
ketone is presented in figure 46.   Extensive cracking of the resist
film following resist development was noted.,   This problem was
later overcome by slow cooling following pre-baking at 200°C, and
with the adoption of 1:1 cyclohexanone:IPA as the preferred
developer.   Scanning electron micrographs of resist patterns
produced in this sample pre-baked for one hour at 200°C with
development in 1:1 cyclohexanone:IPA are presented in Figure 47-48.

Plasma Etch Resistance.

       The etch rate in oxygen plasma under the conditions
described in section 2.8 was 115 nm.min^{-1}.   Under the same
conditions P(MMA) was etched at 150 nm.min^{-1}.

3.7.6 MMI-co-MMA.

       MMI-co-MMA copolymers were spun from solution in 2-
methoxy ethyl acetate or 2-ethoxy ethanol.   Sample details are
given in table 34.   All films were pre-baked for one hour at 170°C.
The solubility of the pre-baked films was tested by immersing
samples of each film in the respective casting solvent for seven
days.   The samples were then re-baked for one hour at 170°C.
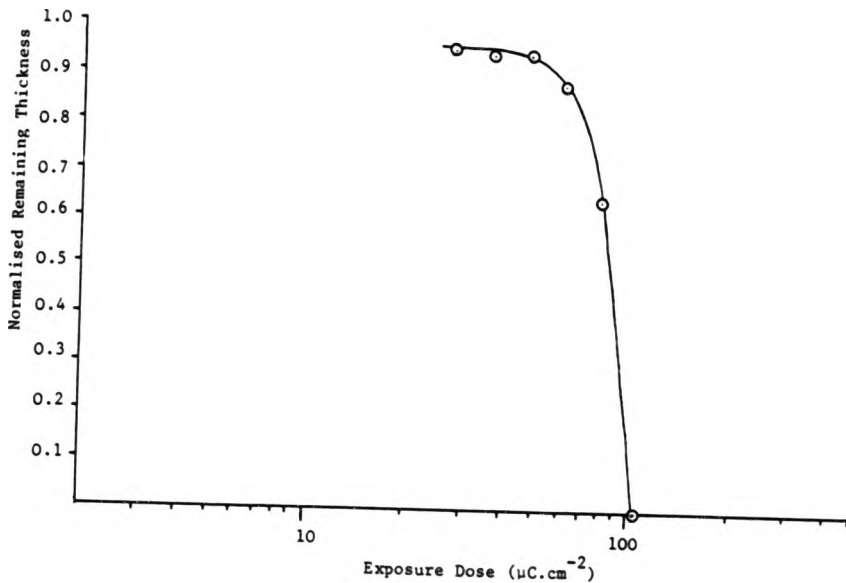The sol fraction for each sample is noted in table 34.

FIGURE 46:   Normalised Remaining Thickness versus Exposure Dose.

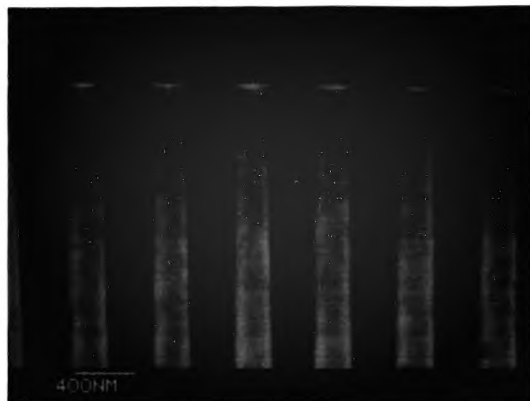51 mol % (IT.ANH)-co-αMS.   Developed 120s + 120s methyl isobutylketone.

FIGURE 47   Nominal 250 nm 1:1 Lines and Spaces   IT.ANH-co-αMS

Exposure Dose 385 μC.cm^{-2}.

FIGURE 48   Nominal 375 nm 1:1 Lines and Spaces   IT.ANH-co-αMS

Exposure Dose 385 μC.cm^{-2}.

Table 34 Resist Films Prepared from MMI-co-MMA Copolymers.

| Comp mol % MMI	Spinning Solvent	Film Thickness micrometre	Sol Fraction	
5	(a)	0.47	1.0	(a)
10	(a)	0.58	0.59	(a)
20	(a)	0.44	0.21	(a)
35	(a)	0.40	0.27	(a)
54	(b)	0.63	0.05	(b)

(a)   2-methoxy ethyl acetate   (b)   2-ethoxy ethanol.

Variation in Resist Performance with Copolymer Composition.

Plots of normalised remaining thickness versus exposure dose for samples of copolymer composition 5-54 mol % (MMI)-co-MMA with development for 90 seconds plus 30 seconds in 7:3 methyl isobutyl ketone:IPA are presented in Figure 49.   Quantitative values of the minimum clearing dose and resist contrast cannot be given with any certainty because of the limited experimental data.   The relationship between copolymer composition and resist sensitivity and contrast was not pursued because although a number of different solvent developers were tried, the resolution of MMI-co-MMA copolymers with increasing mol % MMI was generally poor.   Optimum results appeared to be obtained with a copolymer of (10 mol %) MMI-co-MMA with development in 4:1:1 n-butyl acetate:n-hexyl acetate:2-methoxy ethyl acetate or 8:2 n-butyl acetate:n-hexyl
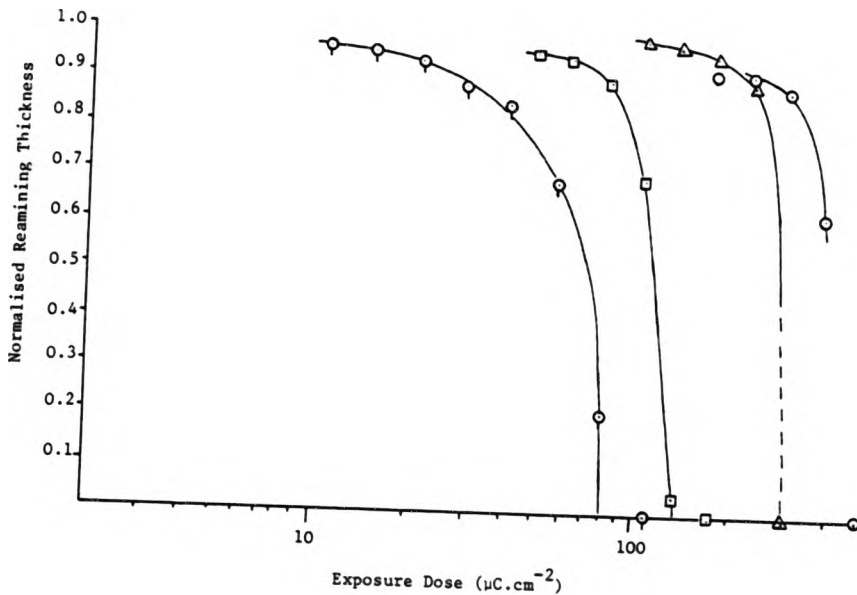
Key

⚲	5 mol % (MMI)-co-MMA
☐	20 mol % (MMI)-co-MMA
△	35 mol % (MMI)-co-MMA
◯	54 mol % (MMI)-co-MMA

FIGURE 49: Normalised Remianing Thickness versus Exposure Dose.
MMI-co-MMA Copolymers.   Developed 90s + 30s mixture
7:3 methyl isobutyl ketone : isopropanol.

acetate mixtures.   Plots of normalised remaining thickness versus exposure dose for 10 mol % (MMI)-co-MMA with development in various solvents are given in Figure 50.   Tabulated values of the minimum clearing dose 'Do' and resist contrast are presented in Table 35.

Table 35 Minimum Clearing Dose and Resist Contrast for 10 mol % (MMI)-co-MMA.   Various Developers.

Developer	Do $\mu C.cm^{-2}$	γ
2-methoxyethyl acetate	40	1.7
4:1:1 acetate mix (a)	79	5.3
8:2 acetate mix (b)	79	~9
Cyclohexanone	100	1.1

(a)   4:1:1 n-butyl:n-hexyl:2-methoxy ethyl acetate mixture

(b)   8:2 n-butyl:n-hexyl acetate mixture.

Resolution.

Scanning electron micrographs of resist patterns produced in 10 mol % (MMI)-co-MMA with development in 4:1:1 n-butyl acetate:n-hexyl acetate:2-methoxy ethyl acetate and 8:2 n-butyl acetate:n-hexyl acetate are shown in figures 51-53 and 54-57 respectively. Individual captions are provided.
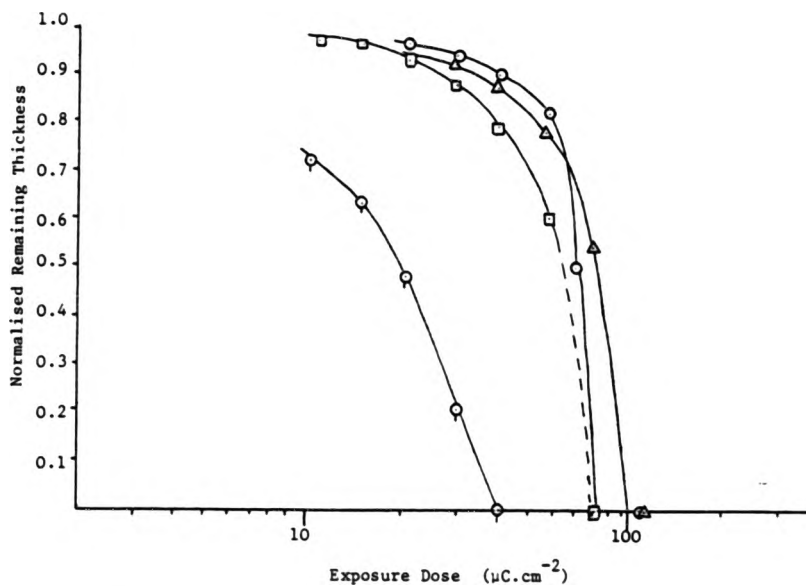
FIGURE 50: Normalised Remaining Thickness versus Exposure Dose.
10 mol % (MMI)-co-MMA. Various Developers.
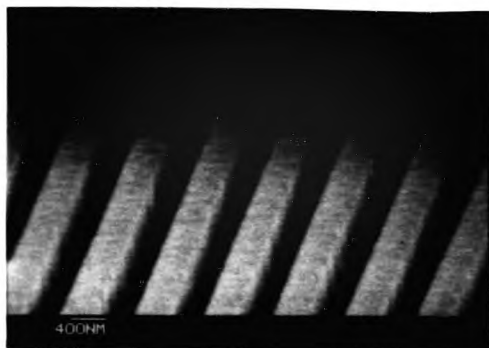
FIGURE 51   Nominal **250 nm 1:2 Lines** and Spaces 10 mol % (MMI)-co-MMA.
Exposure **Dose** 154 μC.cm^{-2}.   4:1:1 Acetate Mix.
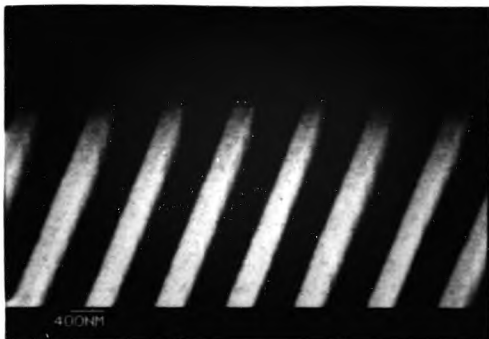
FIGURE 52   Nominal 375 nm 1:1 Lines and Spaces   10 mol % (MMI)-co-MMA.
Exposure Dose 154 μC.cm^{-2} 4:1:1 Acetate Mix.
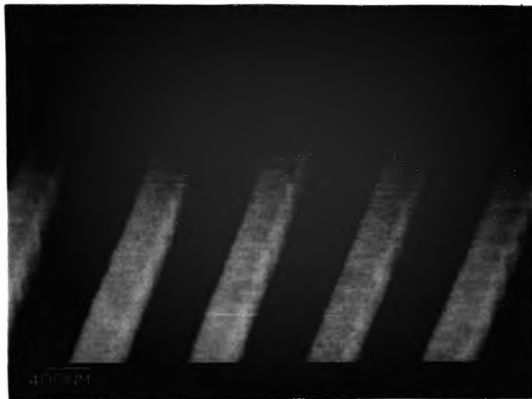
FIGURE 53   Nominal 500 nm 1:1 Lines and Spaces   10 mol % (MMI)-co-MMA.
Exposure Dose 154 µC.cm^{-2}.   4:1:1 Acetate Mix.

FIGURE 54   Nominal 250 nm 1:1 Lines and Spaces   10 mol % (MMI)-co-MMA.
Exposure Dose 154 µC.cm^{-2}.   8:2 n-Butyl Acetate: n-Hexyl
Acetate Mix.

FIGURE 55   Nominal 250 nm 1:2 Lines and Spaces   10 mol % (MMI)-co-MMA.
Exposure Dose 215 μC.cm^{-2} 8:2 n-Butyl Acetate : n-Hexyl
Acetate Mix.

FIGURE 56   Nominal 375 nm 1:1 Lines and Spaces   10 mol % (MMI)-co-MMA.
Exposure Dose 154 μC.cm^{-2} 8:2 n-Butyl Acetate : n Hexyl
Acetate Mix.
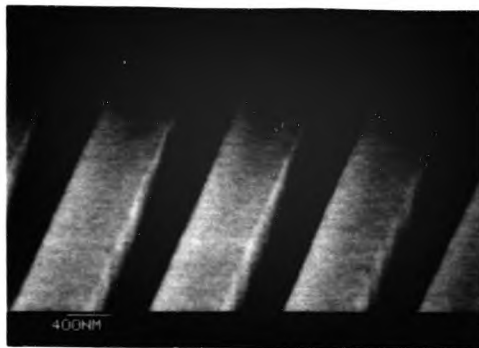
FIGURE 57   Nominal 375 nm   1:2 Lines and Spaces   10 mol% (MMI)-co-MMA.
Exposure Dose 215 μC.cm^{-2}.   8:2 n-Butyl Acetate : n-Hexyl
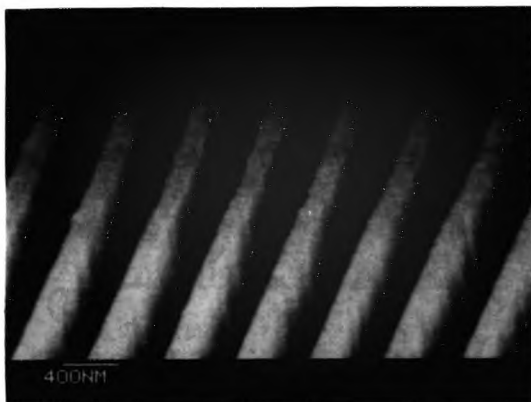Acetate Mix.

3.7.7 ACMP-co-MMA

Copolymers of ACMP-co-MMA were spun from solution in 2-ethoxyethyl acetate. Solutions of 10 w/v% concentration were of relatively low viscosity, and so reduced spin speeds (1000-1800 rpm) were used to obtain the required film thickness. Samples were pre-baked at 170°C for one hour. Sol fractions following pre-baking were determined by immersing a portion of each film in 2-ethoxy ethyl acetate for four days. The soluble fraction is noted for each sample in Table 36.

Table 36 Resist Films Prepared from ACMP-co-MMA Copolymers.

Comp mol % ACMP	Mn g.mol^{-1}	Film Thickness micrometre	Sol Fraction
5		0.45	0
9		0.37	0.5
14	155000	0.23	0 (swollen)
15	210000	0.55	0 (swollen)
36		0.38	0

Variation in Resist Performance with Copolymer Composition.

Plots of normalised remaining thickness versus exposure dose for samples of copolymer composition 5-36 mol % (ACMP)-co-MMA with development for 120 seconds plus 120 seconds in cyclohexanone are shown in Figure 58. Approximate values of the minimum clearing dose Do and resist contrast are given in table 37.
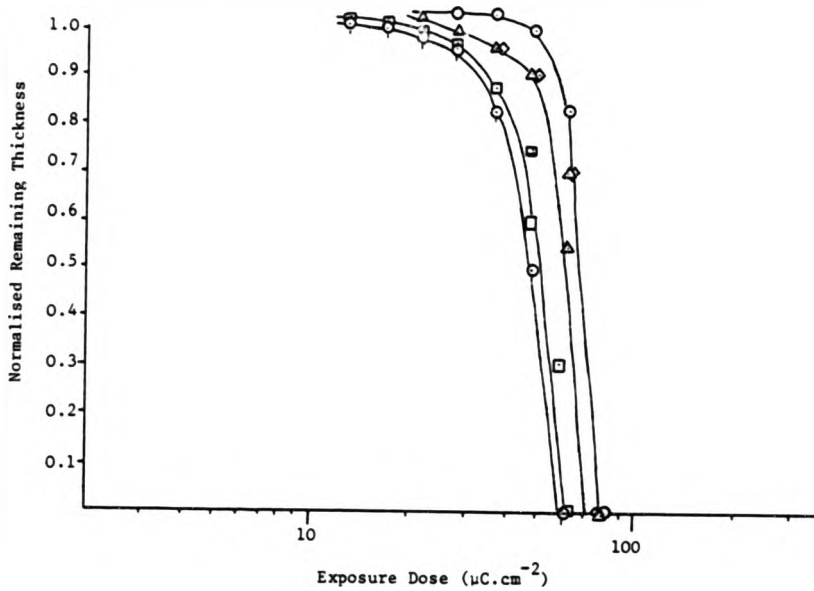
FIGURE 58: Normalised Remaining Thickness versus Exposure Dose.
ACMP-co-MMA Copolymers.

It is not possible to be more precise over the presentation of these values due to the limited number of experimental points on the lower positions of the curve.

Table 37 Minimum Clearing Dose and Resist Contrast for ACMP-co-MMA Copolymers.

Comp. mol % ACMP	Mn g.mol^{-1}	Do $\mu C.cm^{-2}$	γ
5		~59	~5
9		62	6
14	155000	72	7
15	210000	80	7
36		80	6

Comparison of these results to those given previously (sections 3.7.1, 3.7.4, and 3.7.6), show that copolymers of ACMP-co-MMA show smaller variations in minimum clearing dose with variation in copolymer composition than those noted previously. Results for the copolymer of 36 mol % (ACMP)-co-MMA appear to deviate from the general variation in minimum clearing dose and resist contrast with copolymer composition. It was noted that this composition also showed reduced thermal stability (section 3.6.5).

Resolution.

Optimum resolution was obtained for a copolymer of 15 mol % (ACMP)-co-MMA. Scanning electron micrographs of resist

patterns produced in this material with development for 120 seconds plus 120 seconds in cyclohexanone are shown in Figures 59-60.

3.7.8 MAA-co-MMA, MAM-co-MMA Copolymer Mixtures.

Mixtures of MAA-co-MMA and MAM-co-MMA copolymers, detailed in table 38, showed no evidence of phase separation when spun from solution in 2-ethoxy ethanol. Film quality, which was otherwise good, was affected by filaments of the polymer solution being re-deposited on the surface of the wafer during spinning. Samples of each copolymer mixture were pre-baked at 170, 205 and 225°C for one hour. Samples were completely soluble following pre-baking.

Table 3 8 MAA-co-MMA, MAM-co-MMA Copolymer Mixtures.

Mixture Composition	Code	Film Thickness micrometre
1:1 3 mol % (MAA)-co-MMA: 4 mol % (MAM)-co-MMA	A	0.31
1:1 8 mol % (MAA)-co-MMA: 7 mol % (MAM)-co-MMA	B	0.33

Exposure and Solvent Development.

Plots of normalised remaining thickness versus exposure dose for mixtures A and B pre-baked for one hour at 205°C and developed in various solvents are given in Figure 61. Resist resolution was generally observed to be poor. Marked undercutting
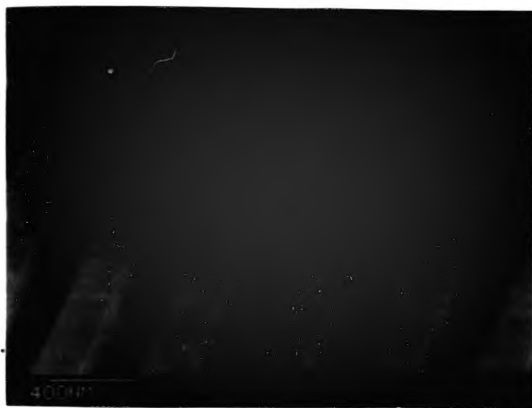
FIGURE 59 Nominal 250 nm 1:1 Lines and Spaces 15 mol % (ACMP)-co-MMA.
Exposure Dose 137 μC.cm^{-2}.

FIGURE 60 Nominal 250 nm 1:2 Lines and Spaces 15 mol % (ACMP)-co-MMA.
Exposure Dose 155 μC.cm^{-2}.
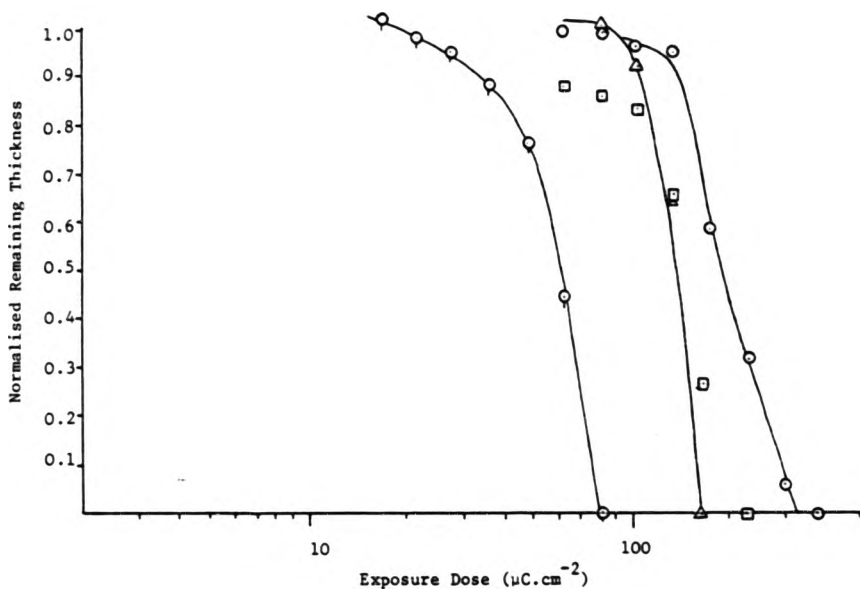
Key

○—   Blend A.   90s + 30s 2-ethoxy ethanol

○   Blend A.   90s + 30s ethanol

△   Blend A.   90s + 30s 2-butoxy ethanol

□   Blend B.   90s + 30s mixture 8:2 ethanol:2-butoxy ethanol

        (points only)

FIGURE 61:   Normalised Remaining Thickness versus Exposure Dose.

                  MAA-co-MMA, MAM-co-MMA Copolymer Mixtures.   Various Developers.

was noted for a number of different solvent developers, and the optimum resolution was approximately 0.75-1.0 micrometre.

3.7.9 General Observations.

For two materials, 15 mol % (ACMP)-co-MMA and 7 mol % (IT.ANH)-co-DMI, it was noted that the ability to define 1:1 lines and spaces appeared to be limited by mechanical instability of the resist features.   Scanning electron micrographs showing this behaviour are presented in Figures 62 and 63.   This limitation to resist resolution would appear quite different from problems of snake-like distortion or resist stringing which can be attributed to resist swelling.

3.7.10   Miscellaneous Materials.

A brief description is given below of various materials which have not been included in the main body of the results section because initial results were discouraging, or where materials were only partially characterised.

Monomethyl itaconyl chloride copolymer mixtures.

Mixtures of monomethyl itaconyl chloride (MMICl)-co-MMA, with composition 4-19 mol % (MMICl), Mn 16800-63000 $g.mol^{-1}$, and MMI-co-MMA (Mn 95000-184000 $g.mol^{-1}$) were found to form good quality films with no evidence of phase separation when spun from solution in 2-methoxy ethyl acetate.   Two of five mixture compositions investigated were found to form insoluble films with pre-baking for one hour at $170^{o}C$.   Values of the minimum clearing dose Do were 30-120 $\mu C.cm^{-2}$ for samples developed using methyl isobutyl ketone or cyclohexanone.   Results obtained did not suggest any significant
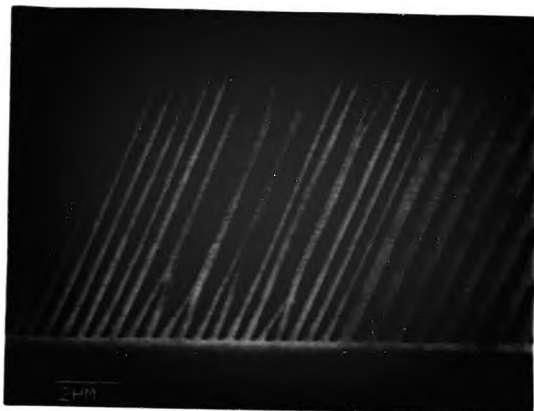
FIGURE 62   15 mol % (ACMP)-co-MMA.

FIGURE 63   7 mol % (IT.ANH)-co-DMI.

improvement over those reported for MAA-co-MMA:MACl-co-MMA blends[13,14] and so work was not continued on this system.

Methyl, 2 Hydroxyl ethyl itaconate - MMA Copolymer.

Methyl, 2-hydroxyl ethyl itaconate monomer was prepared using the method described by Ferguson[79]. An estimated 20% of the isomer methyl, 2-hydroxy ethyl citraconate was also believed to have been present in the material prepared.

A copolymer of feed composition 20 mol % (MHEI)-co-MMA was investigated for use as a conventional positive resist. Values of the minimum clearing dose and resist contrast with development in various solvents are given in Table 39. Insufficient material was available for blending studies with IT.ANH-co-MMA copolymers.

Table 3 9 Minimum Clearing Dose and Resist Contrast for MHEI-co-MMA Copolymers.

Developer	Do $\mu C.cm^{-2}$	γ
1 min 2:1 2-ethoxyethanol:IPA	105	4.5
1 min 2:1 p-dioxane:IPA	58	2.6
1 min p-dioxane	47	2.3

(1-Acetoxy carboxy, 4 methyl, 2 methylene butanedioate)-co-MMA.

A copolymer of MMA with 1-acetoxy carboxy, 4 methyl, 2 methylene butanedioate (VII), 10% feed, was prepared and evaluated. Monomer VII can be considered to be structurally analogous to the

monomer ACMP.

$$
\begin{array}{c}
COOCH_3 \\
| \\
CH_2 \\
| \\
C=CH_2 \\
| \\
CO.O.CO.CH_3
\end{array}
$$
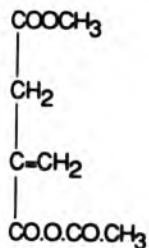
VII

Resist sensitivity and contrast was found to be similar to that found for ACMP-co-MMA copolymers with similar high resolution capabilities.

Mixtures of MMI-co-MMA with low molecular weight crosslinking agents.

Mixtures of a copolymer of 7 mol % (MMI)-co-MMA with malonic acid, malonyl dichloride or dimethyl malonic acid were dissolved together in 2-methoxyethyl acetate. The solution of the copolymer plus the crosslinking agent were then dispensed onto the surface of a silicon wafer and spun to give a thin film. The coated wafers were then pre-baked for one hour at 170°C. No evidence of crosslinking was noted and so the experiment was abandoned.

Polymers Containing Glycidyl Methacrylate.

Copolymers of glycidyl methacrylate (GMA)-co-MMA and terpolymers of GMA-HEMA-MMA and GMA-MAA-MMA were found to form insoluble films with pre-baking at 170°C for one hour.

Positive resist images were produced in these materials with development in 7:3 methyl ethyl ketone:IPA mixtures, and p-dioxane, but resolution was generally observed to be poor.

MAA-MAM-MMA Terpolymers.

Terpolymers of MAA:MAM:MMA were found to show large differences in their solubility characteristics with increase in the proportion of MAA and MAM in the feed.   A terpolymer prepared with feed composition in the proportion 10:10:80 (MAA:MAM:MMA) was found to be soluble lin 2-ethoxyethanol and could be spun to give a thin, even film.   Pre-baking for one hour at 205°C was found to give an insoluble film, where the sol fraction ~0.25.   Relatively poor resolution was observed for samples developed in cyclohexanone or 2-ethoxyethanol, although improved results were noted for mixtures containing THF or dimethylsulphoxide (DMSO).   Relatively high sensitivities (Do ~30-50 μC.cm^{-2}) were found.

IT.ANH-co-Methyl-α-Chloroacrylate.

Two copolymers of feed composition 10 and 19 mol % (IT.ANH)-co-methyl-α-chloroacrylate were prepared by copolymerisation in bulk at 60°C.   Copolymer composition was found to be ~8 and 11 mol % (IT.ANH) respectively.   Copolymer samples were soluble in acetonitrile, nitromethane, dichloromethane and p-dioxane and were insoluble in chloroform, methanol, MEK, THF, chlorobenzene, 2-methoxyethyl acetate, 1,4-dichlorobutane, and chloroacetaldehyde.   Attempts to prepare thin films by spin coating from solution in a 6:4 mixture of dichloromethane:1,4 dichlorobutane were unsuccessful.

CHAPTER FOUR

DISCUSSION OF RESULTS

4.1 Crosslinking of Linear Chains

The crosslinking of long chain molecules can be considered to pass through the following main stages:

(1) Increases in average molecular weight and polydispersity of the primary chains;

(2) The formation of an incipient gel or insoluble fraction at the gel point;

(3) Increases in the proportion of insoluble material or gel;

(4) Increases in the density of crosslinks and in the elastic properties of the gel.

Changes in the various parameters have been described by Flory[61, 80] and Stockmayer.[81] Both authors used the following major assumptions:

(1) That crosslinking is entirely random, all functionalities are assumed to have an equal probability of reaction;

(2) All finite molecules are "tree-like", ie there are no intramolecular cyclisation reactions.

The most notable violations of these assumptions are likely where significant intramolecular reactions take place, or where the structure of the network is very inhomogeneous (section 4.2).

For a statistical copolymer of arbitrary molecular weight distribution, Stockmayer[81] gives the following expressions for changes in the number average and weight average degrees of polymerisation below the gel point:

$$Pn = \frac{\lambda n}{(1 - \gamma/2)} \qquad (10)$$

$$Pw = \frac{\lambda w}{(1 - \gamma/\gamma c)} \tag{11}$$

where

Pn = number average degree of polymerisation

Pw = weight average degree of polymerisation

λn = primary number average degree of polymerisation

λw = primary weight average degree of polymerisation

γ = number of crosslinked units per primary molecule of number average molecular weight

$$\gamma c = \frac{\lambda n}{\lambda w}$$

For a random copolymer:

$$\gamma = \alpha.p.\lambda n$$

where

α = fraction of total functional groups involved in crosslinking

p = fraction of copolymer units bearing reactive functional groups (~copolymer mol. fraction).

These expressions describe diverging values of Pn and Pw. Prior to the gel point, all molecules remain of finite length and are capable of being dissolved in a suitable solvent. Due to an increased probability of branching taking place along their length, a small

proportion of molecules of relatively high molecular weight will tend to increase their molecular weight at a higher rate than other molecules. One of these molecules will later constitute the gel, notionally a molecule of the same size as the external dimensions of the polymer. The critical condition for gel formation is given by Stockmayer[81] as:

$$\alpha_c = \frac{1}{p(\lambda \bar{w} - 1)} \qquad (12)$$

ie gel formation is dependent upon the primary weight average degree of polymerisation but not upon the original MWD. It was recognised by Flory,[80] that changes in the sol and gel fractions beyond the gel point are more critically dependent upon the original MWD. In general, the development of the gel fraction is more rapid for molecules of an originally monodisperse MWD.

Beyond the gel point, the average molecular weights and MWD of remaining soluble molecules undergo reversal of the trends followed prior to the gel point. This arises as a result of the same probabalistic argument that longer molecules will have an increased probability of reaction occurring along their length. The removal of high molecular weight material by preferential attachment to the gel therefore causes a reduction in average molecular weight and a narrowing in MWD of the remaining soluble fraction. With increasing reaction the density of crosslinking within the gel fraction will increase, causing an increase in moduli and reducing the equilibrium swelling ratio in a given solvent. Changes in the various parameters are represented schematically in figure 64.
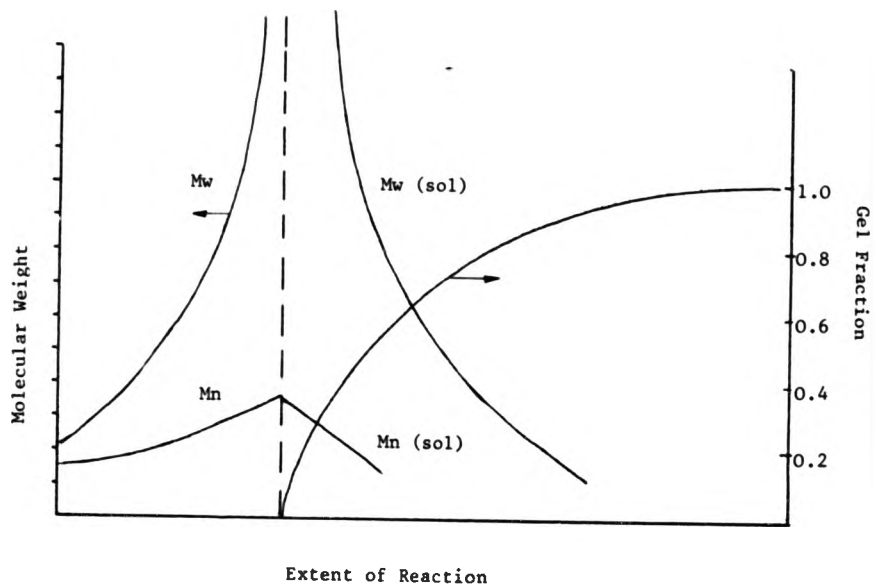
FIGURE 64: Schematic Representation of the Changes in Average Molecular
Weight and Gel Fraction during Crosslinking of Primary Chains.

4.2 Intramolecular Cyclisation and Network Inhomogenieties

Intramolecular cyclisation reactions and network inhomogeneities are likely to provide the most significant violations of the gelation theory as presented by Flory and Stockmayer. Intramolecular reactions reduce the number of functional groups present without increasing the molecular weight of the species involved, and can also lead to the formation of cyclised structures. This in turn can reduce the accessibility of certain groups, violating the requirement that all groups should have equal reactivity, and making it more likely that the final gel will be inhomogeneous. These effects are primarily of importance below the gel point but they can also affect the properties of the gel that is formed and can influence the extent of reaction to which a system must proceed for the gel point to be reached.

The importance of intramolecular cyclisation and network inhomogeneities can be different for each of the main types of reaction used to prepare crosslinked polymers, viz stepwise polycondensation, the crosslinking of linear chains, and chain polymerisation of poly-unsaturated monomers. For the crosslinking of linear molecules, Dusek[82] has suggested that the proportion of groups involved in intramolecular reactions may be of the order of 5-50%, and that this value does not change significantly during the course of the crosslinking reaction.

4.3   Crosslinking of IT.ANH Copolymers

The thermal crosslinking of IT.ANH-co-MMA copolymers was not originally anticipated, but was discovered accidentally during routine drying of the first batch of copolymers that were prepared. Results presented in table 24 show that the soluble fraction present following controlled pre-baking does not vary directly with copolymer composition or primary number average molecular weight. Similar, although more pronounced, irregularities were noted for copolymers of IT.ANH-co-DMI (table 32).

Expression (12) shows that the critical condition for gel formation is expected to depend upon copolymer composition and the primary weight average degree of polymerisation.   Some dependence upon copolymer composition is noted for copolymers of IT.ANH-co-MMA, although this can be seen not to be the only factor.   In the absence of weight average molecular weight measurements it would be difficult to provide further comment on these results.   Although only speculative, it is possible from the previous considerations to suggest that irregularities in the degree of crosslinking observed might arise from a variation in the weight average degree of polymerisation, or in the MWD prior to thermal crosslinking. Differing levels of intramolecular cyclisation might also have to be considered with different copolymer samples.

Investigation of the infrared spectra of IT.ANH-co-MMA copolymers pre-baked at 170°C revealed no obvious differences before and after pre-baking.   Although care was taken to avoid the exposure of monomer or copolymer materials to moisture, it remains possible that prior to the crosslinking operation, some degree of hydrolysis might have taken place and that the hydrolysed units may

be important to the crosslinking reaction(s) observed. Variation in the degree of hydrolysis between individual samples may also have contributed to the irregularities in the gel fraction present following pre-baking noted previously.

A further measure of crosslinking in IT.ANH-co-MMA copolymers was obtained with changes in the glass transition temperature after pre-baking various copolymers for one hour at 170°C (table 22). The variation in the glass transition temperature shows a general dependence upon copolymer composition (mol % IT.ANH), but would seem to be a less sensitive measure of the degree of crosslinking compared to measurement of the sol fraction.

Changes in glass transition temperature with crosslinking have been reviewed by Miller,[60] and Boyer.[64] In the absence of chemical modifications, this has been attributed to a reduction in free volume and an associated increase in the restriction to molecular motion.

Insoluble material was not noted for a copolymer of IT.ANH-co-αMS, although only a limited investigation of this material was made.

4.4 Crosslinking of IT.ANH-co-MMA, HEMA-co-MMA Mixtures

Although no direct analytical investigation of these mixtures was made, support for crosslinking occurring via the general scheme shown in figure 65 was found for IT.ANH-HEMA-MMA terpolymers by comparing changes in infrared spectra following pre-baking at 170°C for one hour. Following pre-baking, an additional peak, centred at 3265 cm^{-1}, was noted; the new peak was identified by

its broad absorption pattern to be due to COOH formation, supporting the general scheme proposed. It should be noted that two types of crosslink are possible according to the site of attack of the ROH group.

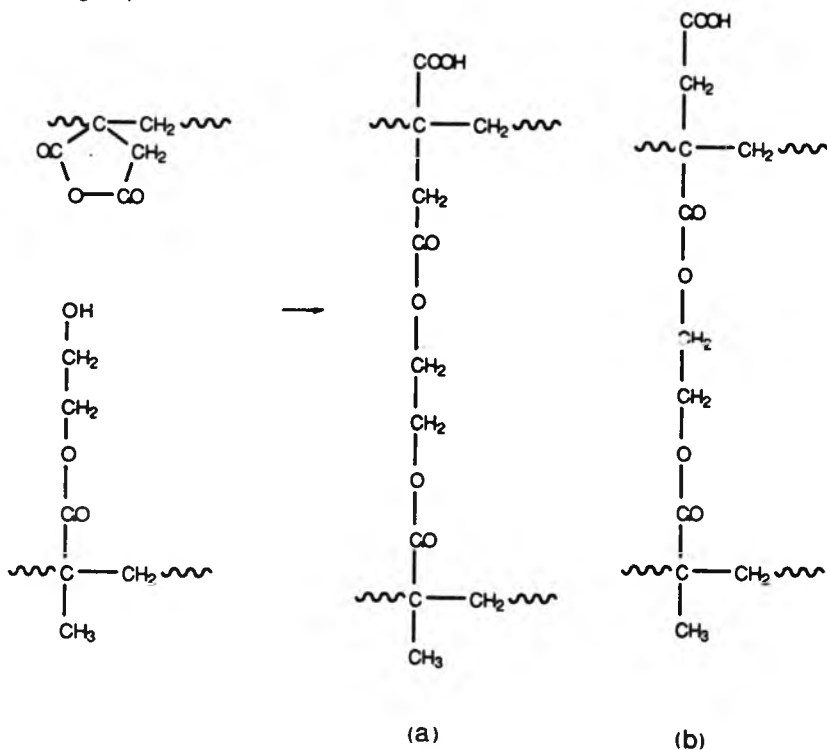(a)　　　　　　　　(b)

Figure 65 Proposed Scheme for Crosslinking between IT.ANH and HEMA Repeat Units.

4.5　Crosslinking of MMI-co-MMA Copolymers

The crosslinking of MMI-co-MMA copolymers was largely anticipated following the previous work of Anderson[50] and Haq.[78] Analytical studies of P(MMI) homopolymer were made by Haq, who reported that baking the homopolymer at 180°C yielded methanol and

water as volatile products in approximately equal proportions. Haq also reported the appearance of infrared absorptions at 1855 cm^{-1} and 1780 cm^{-1} which were attributed to the formation of anhydride structures. At least two types of condensation reaction were postulated in order to explain the different volatile products observed.

During this present work it was found that the insoluble fractions formed during baking tend to increase with increasing mol % (MMI) present in the copolymer. Examination of the infrared spectra of copolymer samples following pre-baking for one hour at $170^{o}C$ showed new absorptions at 1861 cm^{-1} and 1785 cm^{-1}, the peak at 1785 cm^{-1} being more intense in each case. These absorptions would be in accordance with those expected from the presence of a five membered ring, eg from the intramolecular cyclisation of a single MMI unit with the evolution of methanol (figure 66a). However, such a scheme could not explain the evolution of water found by Haq, nor could this, on its own, explain the formation of crosslinked material. Some proportion of additional reactions such as those shown in figures 66b,c,d, or some further reaction of the five membered ring must therefore take place.

4.6   Crosslinking of ACMP-co-MMA

No experimental evidence has been obtained which might allow an understanding of the thermal crosslinking of ACMP-co-MMA copolymers.
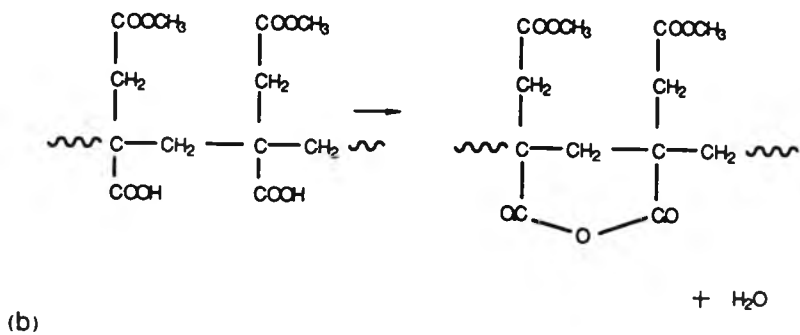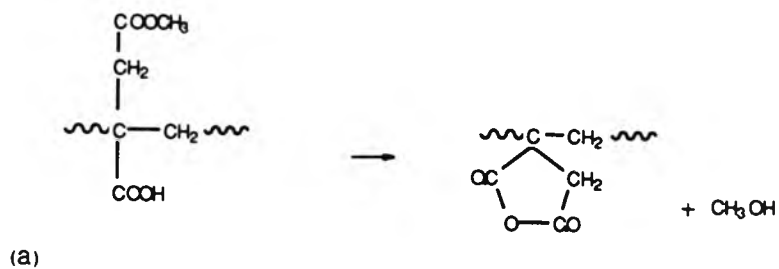
(a)

(b)

Figure 66   Possible Schemes for the Crosslinking of MMI-co-MMA
Copolymers

(c)

(d)
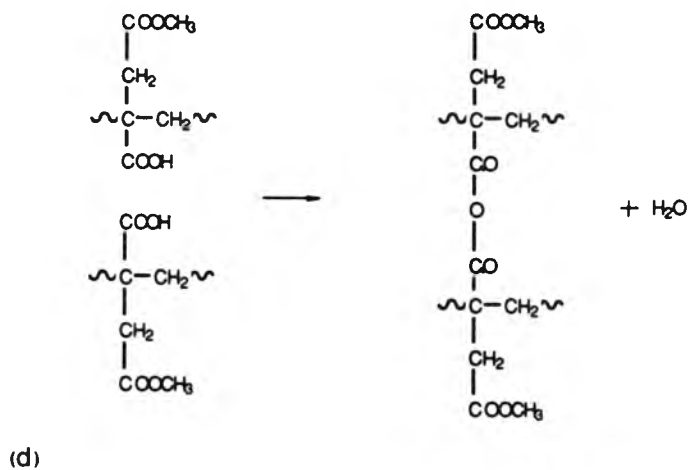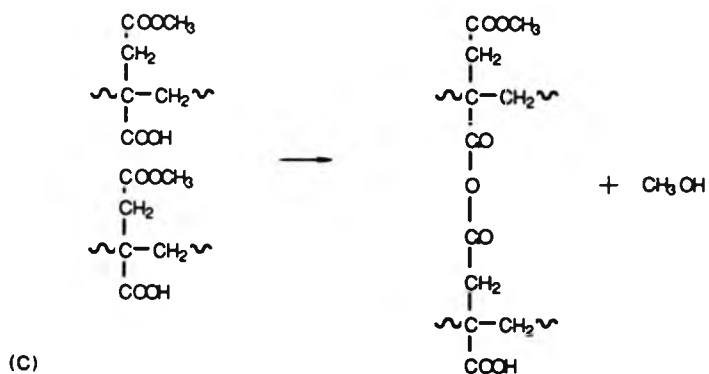
Figure 66 (cont)   Possible Schemes for the Crosslinking of
MMI-co-MMA Copolymers

4.7   Discussion of the Lithographic Results

4.7.1 Variation in Minimum Clearing Dose with Copolymer Composition

Results presented in chapter 3 have shown that for a number of copolymer systems, eg IT.ANH-co-MMA, MMI-co-MMA, ACMP-co-MMA, the minimum clearing dose increases with increasing incorporation of the repeat unit responsible for crosslinking (figure 67).   For the system IT.ANH-co-DMI a similar trend to that shown in figure 67 is observed (see figure 41) although in this case it would seem unlikely that these results can be related to the effects of crosslinking, since no systematic variation in the sol fraction present following pre-baking is observed.   The slight reduction in minimum clearing dose for the sample 36 mol % (ACMP)-co-MMA may be due to thermal degradation of the sample during pre-baking (see section 3.6.5).

The apparent dependence on copolymer composition may be due to one or more of the following effects:

(1)   An increase in the degree of crosslinking due to increased incorporation of reactive functional groups;

(2)   Differences in the radiation sensitivity of individual copolymer compositions;

(3)   Differences in solubility or dissolution rate behaviour with copolymer composition.

Quite pronounced changes in solubility for copolymers of different compositions have been noted throughout the course of this work, and are therefore likely to be a contributory factor in these results.   Such an effect could account for the results found for copolymers of IT.ANH-co-DMI without the need to consider changes
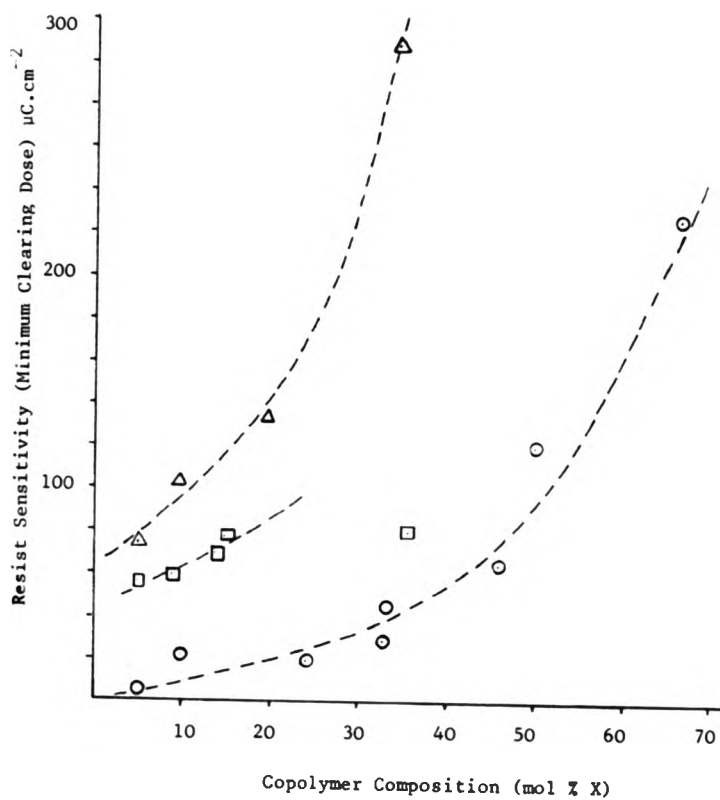
FIGURE 67: Collected Data: Variation in Minimum Clearing Dose with Copolymer Composition.

due to crosslinking. For the copolymers IT.ANH-co-MMA, ACMP-co-MMA, and MMI-co-MMA, variation in resist properties due to crosslinking represent an additional factor.

Variations in the minimum clearing dose with the degree of crosslinking alone can be isolated by considering the variation in minimum clearing dose with pre-bake temperature. This has been investigated in most detail by Roberts[21,83] who has shown that this can be related to the proportion of soluble material present following pre-baking. Interestingly, Roberts also found a maximum in the relationship between minimum clearing dose and pre-bake temperature, and that at temperatures $\geq 200^{\circ}C$, the minimum clearing dose and insoluble fraction of resist can reduce.[14,21] This was attributed by Roberts to thermal degradation of the crosslinked structure. Since the proportion of insoluble material introduced during crosslinking can be varied in more than one way it should be concluded that the minimum clearing dose may depend upon both copolymer composition, (the proportion of reactive groups available for crosslinking) and the extent of reaction (pre-bake temperature).

Differences in the radiation sensitivity (radiation chemical yields for main chain scission) for one of the materials investigated in this work, (MMI-co-MMA), have been reported by Anderson,[50] who found that G(s) for MMI-co-MMA copolymers increased from G(s) = 1.7 for a copolymer containing 19 mol % (MMI)-co-MMA, to G(s) = 2.1 for a copolymer of 39 mol % (MMI)-co-MMA. Comparison of these results with the observed variation in minimum clearing dose for the pre-crosslinked resist shows that these results are counter to the observed trend. It can be seen that for this system at least, the variation in G(s) with copolymer composition cannot explain the results observed.

4.7.2 Variation in Minimum Clearing Dose with Solvent Developer

Results presented in chapter 3 (figures 21, 33, 49, 61) have shown that experimentally determined values of the minimum clearing dose vary significantly with the use of different solvents. Where mixtures of a solvent and a non-solvent have been used, (eg figure 21), the minimum clearing dose is reduced as the quantity of non-solvent is lowered. Further correlation, eg between the minimum clearing dose, and properties of the solvent such as solvent solubility parameters, or solvent molar volume, do not appear straightforward. These are, in any case, likely to be complicated by the unknown weightings which should be given to thermodynamic and kinetic factors.

Experimentally determined values of resist sensitivity represent non-equilibrium measurements of normalised remaining thickness versus exposure dose. Thus it should be recognised that measured sensitivity values will also be dependent on development time. Results presented in figures 24 and 27 have suggested that values obtained using relatively short developing times do not represent the initial solubilisation of the pre-crosslinked network.

4.7.3 Variation in Resist Properties with Primary Molecular Weight

A dependence of resist sensitivity upon primary molecular weight has been noted for samples of 33 and 46 mol % (IT.ANH)-co-MMA, and for samples of 14-15 mol % (ACMP)-co-MMA. Two types

of result can be distinguished:

(1)   A molecular weight dependence of results obtained for a
        given solvent at short development times;

(2)   (Solvent and time independent) measurements of the gel
        fractions remaining at long times for samples of different
primary average molecular weight.

The most detailed results available in this present work are for the
copolymer 46 mol % (IT.ANH)-co-MMA with primary molecular
weights between 111000 and 530000 $g.mol^{-1}$.   For this material,
development for 120s + 120s in cyclohexanone resulted in a
variation in the minimum clearing dose between 66 and 210 $\mu C.cm^{-2}$
for samples of different primary molecular weight.   An apparent
mimimum in resist sensitivity was noted for Mn 166000 $g.mol^{-1}$.
This variation cannot be satisfactorily explained by differences in
the sol fraction present prior to exposure, or by differences in the
original film thickness.

        Available data for the gel fractions remaining at long times
for samples of different primary molecular weight (figure 27)
appear to show that the gel clearing dose increases with increasing
primary average molecular weight.

        Very little further experimental data is available in the

literature.   Roberts[83] found no clear dependence of minimum clearing dose upon primary weight average molecular weight for samples prepared from a mixture of styrene-co-MAA and styrene-co-MACl with Mw in the range 80000-180000 g.mol^{-1}.   For this particular system however, the results may be complicated by a tendency for these materials to radiation crosslink at high values of Mw.

In the only theoretical treatment of pre-crosslinked resists, Suzuki[37] suggested that the highest attainable sensitivity (equivalent to the gel fraction remaining at long times) would be inversely proportional to the primary weight average molecular weight.   However, this was not supported by clear experimental evidence.

4.8   Discussion of the Model of Suzuki

The model of Suzuki was introduced in section 1.6. According to the formula obtained, a low value of δ (the number of crosslinked units per weight average molecule), a high value of G(s), and a high value of Mw, are required for high resist sensitivity. Quantitative comparison of the values obtained in this present work with values predicted using the formula cannot unfortunately be made since the weight average molecular weights of samples prepared in this work have not been determined.   However, merely as a qualitative assessment, the general improvement in resist sensitivity with increasing primary molecular weight predicted by the formula has not been found.

The major conceptual assumption in the approach presented by Suzuki was that by analogy to linear positive resist materials,

the weight average molecular weight following electron exposure is immediately reduced. This concept is most notably at odds with experimental measurements made following the solubilisation of model poly(styrene) networks, and also of wood lignin, in which a pattern of initially increasing average molecular weight and molecular weight distribution is found.[84,85] These results will be discussed in more detail in the following section.

Suzuki found that the formula proposed gave values in fairly good agreement with experiment, with the exception of results obtained using a mixture of a polymer and 2,6-di-(4' azido benzal) cyclohexanone (DABC) as a photo-initiated crosslinking agent. This formulation probably represents an extreme example of a case where the crosslinking group could be expected to show a very low electron sensitivity. Comparison between the results predicted by the theoretical formula and mixture compositions containing more than 1-2% DABC show very poor agreement (table 2).

4.9 Network Degradation as the Reverse of Network Formation

Szabo[85] has been credited with first proposing that random network degradation can be conceptually treated as the reverse process of random network formation. This proposition was originally made following studies of degraded sol fractions of the natural gel, lignin, in which it was noted that the average molecular weight of the extractable fractions increased with increasing degree of solubilisation. This was recognised to follow the pattern of behaviour expected if random gel degradation were to follow the statistical theories of Flory and Stockmayer, except applied in

reverse. This has been demonstrated experimentally by Argyropoulos.[84,86-89] To illustrate the results obtained, experimental measurements of Argyropoulos[85,88] for the random degradation of a model tri-functional network, and for networks formed by the random crosslinking of monodisperse poly(styrene) chains are reproduced in appendix A. It can be seen that the increases in average molecular weight(s) are at odds with the straightforward reduction in average molecular weight proposed by Suzuki,[37] but would be in accordance with the changes in average molecular weight and MWD for the sol fraction present during network formation, except applied in reverse (figure 64).

There seems little reason to suspect that the degradation of pre-crosslinked resists by electron beam exposure should be grossly different from the general trends presented by Argyropoulos. It is therefore believed that an improved model for the degradation of pre-crosslinked resists can be constructed based on the premise that network degradation can be conceptually treated as the reverse of network formation. It will be shown in the following section that such a model can provide a reasonable rationalisation for the experimental results obtained in this work.

To explain fully the behaviour of the resist over a wide range of exposure doses an extension of this theory is required. For the relatively simple model proposed here, the major assumptions required are:

(1) Network scission is entirely random;

(2) (from (1)), Higher molecular weight fragments will have an increased probability of scission occurring along their length, and will therefore be preferentially degraded;

(3)   Continued scission of the degraded network fragments will
        result in fragments having a most probable molecular weight
        distribution.

This extension involves only a direct continuation of the concept
proposed by Szabo[89], and utilises the qualitative changes in average
molecular weight and MWD predicted by Flory,[80] and Stockmayer[81]
for the early stages of network formation, except again, applied in
reverse.   The assumption that random scission of the degraded
resist will result in material having a most probable distribution of
molecular weights is made by analogy to changes in MWD for
originally linear chains.[3]   It seems reasonable that this assumption
should be made in the first instance.

        Qualitative changes in the gel fraction and in the molecular
parameters of the degraded (sol) fractions according to this model
are shown schematically in figure 68.

        Within this general model it may be necessary to make
corrections to allow for the fact that the degree of crosslinking in
pre-crosslinked resists is likely to be low.   In particular, it may be
necessary to allow for two factors:

(1)   The presence of a relatively large sol fraction;

(2)   Network imperfections such as free chain ends.

        Molecules constituting the sol fraction are most likely to be
either linear, or only lightly branched species, and will degrade
directly with a net reduction in average molecular weight and only
minor changes in MWD (for linear molecules $Mw/Mn \longrightarrow 2$ whatever
the initial MWD).   It should therefore be recognised that it is only
the portion of molecules constituting the gel fraction that will
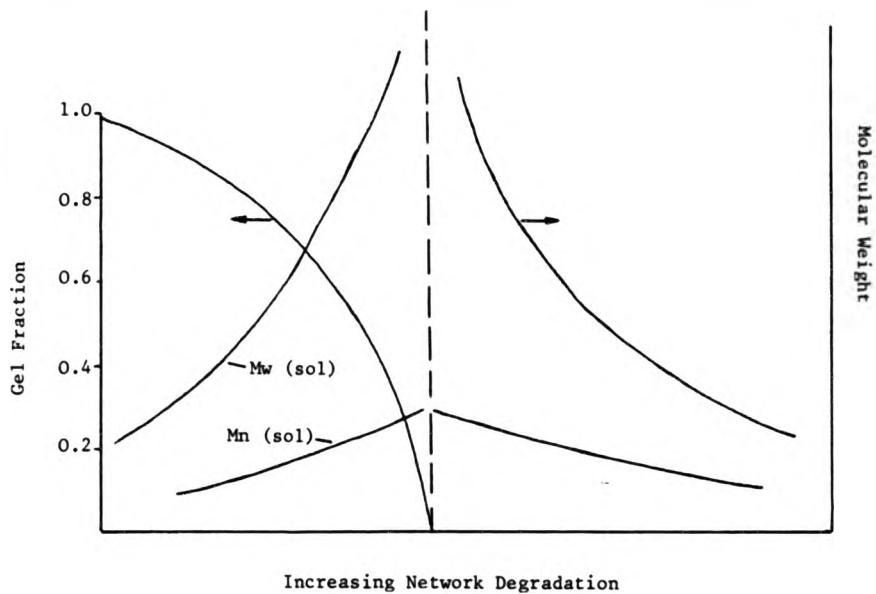degrade with an initial increase in average molecular weight and

FIGURE 68 Schematic Representation of the Changes in Average Molecular
Weight and Gel Fraction Proposed to occur during the Degradation
of Pre-crosslinked Resist.

broadening of MWD.

Correction for the proportion of a network present as free chain ends was first proposed by Flory.[61]   It was recognised by Flory that network structures formed by the crosslinking of originally linear molecules will contain free chain ends, and that the proportion of these species will be greatest at low densities of crosslinking.

The importance of these species to this present work cannot readily be proved, although in the first instance it should be recognised that direct scission of these portions of the network will not contribute to increases in average molecular weight expected for scission of internal network chains.   Some form of correction, although weighted for the proportion of free chain ends released by direct scission, compared to the proportion of free chain ends released as part of larger network fragments, should probably be considered.

Flory[61] calculated that the proportion of free chain ends is given by:

$$S_f = \frac{2Mc}{M + Mc} \tag{13}$$

where: S_f = weight fraction of network chain ends

Mc = average molecular weight between crosslinks

M = primary (number) average molecular weight.

It can be seen that S_f will reduce in proportion to the network as a whole as the molecular weight of the primary chains is increased.

4.10 Comparison of Model to Experimental Results
General Characteristics

On the basis of the previous discussion, the general dependence of the minimum clearing dose upon the gel fraction introduced prior to exposure noted in section 4.7.1 can be attributed to two main factors:

(1)   A proportionality between the electron exposure dose required to degrade the gel and the quantity of gel present;

(2)   A complementary effect whereby a smaller gel fraction leads to a reduction in the weight of material contributing to the increases in molecular weight and the broadening of the MWD which occurs when the gel is degraded.

Of the two factors above, the relationship between the quantity of gel and the electron exposure dose required to degrade the gel is most straightforward.   An important factor in this relationship is likely to be the G(s) value for (network) chain scission (main chain + crosslinks).

Comparison of tables A2 and A3, given in the appendix, suggest that for originally monodisperse samples, the increases in average molecular weight and the broadening of the MWD are in proportion to the degree of crosslinking present prior to electron exposure.   However, where the degree of crosslinking is low, it might be equally important to consider the average number of crosslinked units per primary molecule.

The characterisation of the gel by the average number of

crosslinked units per primary molecule was first considered by Flory[80] and Charlesby.[12]   The average number of crosslinked units per primary molecule would be expected to be directly related to the primary degree of polymerisation.   The number of crosslinked units per primary molecule is not uniquely related to the gel fraction but is also dependent upon the original MWD.[12]

It can therefore be seen that this approach would involve consideration of a number of other factors.   It may be significant to note that the relationship between the degree of polymerisation and the average number of crosslinked units per molecule (due to molecules of higher molecular weight having a higher probability of a crosslink forming along their length), would give rise to dependence of resist sensitivity on primary molecular weight in accordance with results discussed in section 4.7.3.   However, elucidation of the important factors would clearly require further experimental work.

Development of the Resist

With reference to figure 68, the experimental observation that network solubilisation takes place at a much lower exposure dose than that required for the definition of high resolution resist images can be rationalised in terms of an additional level of exposure required to reduce the average molecular weight, and to narrow the MWD from that at the point where the network is first solubilised.

The experimental observation that a wide range of resist sensitivities is found with variation in the solvent developer can be understood as being due to the varying abilities of the developing

solvents to remove the degraded resist at different levels of electron exposure, and therefore at different values of average molecular weight.   This ability will obviously also be time dependent.

As a general point, two possibilities can be seen to arise:

(1)   The solvent is capable of dissolving all tree-like molecules;

(2)   The solvent is capable of dissolving all molecules up to a particular limiting molecular weight or degree of branching.

It can be seen that solvents of the general type (2) will have both thermodynamic and kinetic limitations to their ability to remove the degraded resist.

Molecular Weight Dependence

Although only a limited amount of experimental data are available, preliminary results discussed in section 4.7.3 have suggested that the minimum clearing dose has a pronounced dependence upon primary molecular weight.   Within the general framework of the model described here, two effects have been discussed which may account for this behaviour:

(1)   A molecular weight dependence of the number of crosslinked repeat units per primary molecule;

(2)   A variation in the weight fraction of free chain ends with primary average molecular weight.

In the first instance these may be tentatively put forward as a possible explanation for the observed results.   An interesting corollary of (2), that the weight fraction of internal network chains is increased as the primary average molecular weight is increased, is that solvent swelling should be reduced, and therefore that resist resolution should be improved, for samples of high primary

molecular weight.   Again, this can only be put forward as a hypothesis to which future results can be compared.

4.11   Resist   Contrast

Resist contrast, as defined in section 2.5, is commonly used as a characteristic parameter of a resist material.   The underlying usefulness of this measurement is that it provides a measure of the response of the resist, in terms of normalised thickness remaining, to changes in exposure dose.   The measurement itself is recognised to have a number of limitations including a dependence upon how it is measured, and the fact that it is not a unique characteristic, varying (like sensitivity) with type of developer, developing time, and temperature.   The inter-relationship of resist contrast and sensitivity for negative acting resists has been discussed by Griffiths.[90]

For conventional positive resists, contrast can be related to the change in solubility or dissolution rate with exposure dose. Since in most cases the change in MWD can be expected to be small, this can probably be related directly to the reduction in average molecular weight during irradiation.[6]

The contrast of pre-crosslinked resists can be expected to depend upon similar factors.   From the preceeding discussion, however, important distinctions to be made are that: (1) changes in solubility or dissolution rate behaviour relate to changes in solubility or dissolution rate of what are probably tree-like molecules;   (2) the change in molecular weight distribution is likely to be more significant.   It is possible to hypothesise that the generally high values of resist contrast noted for pre-crosslinked

resists arise from these two factors.

Values of resist contrast presented in chapter 3 for the resist materials investigated in this work have shown several general trends:

(1)   A general increase in contrast with increasing incorporation of the crosslinkable monomer or with pre-bake temperature;

(2)   Materials exhibiting high sensitivity generally show poor contrast;

(3)   There is no clear relationship between contrast values greater than 1.5-2.5, with resolution.

These points are provided as general observations only.

Experimental measurements showing dissolution rate as a function of exposure dose for a pre-crosslinked resist have been made by Farrah.[65]   A summary figure, illustrating the general trends observed is reproduced in appendix B.   It can be seen from this figure that all samples show an increase in dissolution rate with electron exposure.   Samples pre-baked at a higher pre-bake temperature clearly exhibit greater changes in dissolution rate with exposure dose and this would seem the most likely explanation for the improved contrast values obtained for pre-crosslinked resists.

CHAPTER FIVE

GENERAL CONCLUSIONS

5.0   General Conclusions

Statistical copolymers have been found to show a general variation in lithographic properties with copolymer composition. This variation has been suggested to depend upon three main factors:

(1)   An increase in crosslink density due to the increased incorporation of reactive functional groups;

(2)   Differences in the radiation sensitivity of copolymers of varying compositions;

(3)   Differences in the equilibrium solubility or in dissolution rate behaviour for samples of different copolymer composition.

Variations in the minimum clearing dose with crosslinking alone have been isolated by variation in the pre-bake temperature used. This has been illustrated most fully by the previously published results of Roberts[21,83] and Farrah.[65]   Where further information has been available, published values for the variation in G(s) for · main chain scission for copolymers of different composition have been found to be counter to the observed trend in minimum clearing dose, and have been discounted.   A number of the copolymer samples prepared have shown significant changes in their room temperature solubility with copolymer composition, and so it must be concluded that this factor is likely to be important.

The results obtained in this work have shown that the minimum clearing dose, and resist contrast can vary significantly with the use of different solvent developers.   Minimum clearing dose and resist contrast have also been shown to be dependent upon solvent development time.

By exposing representative samples over a suitable exposure range and then immersing the exposed resist in a solvent for periods

of up to seven days it has been shown that the exposure dose required to first solubilise the pre-crosslinked resist is very much less than the exposure dose required for the preparation of high resolution resist patterns. Both the minimum clearing dose for the gel fraction remaining at long developing times, and the minimum clearing dose observed for the development of high resolution resist patterns, appear to show a dependence upon the primary average molecular weight.

The major results of this work are believed to be best explained with reference to an earlier published theory in which random network degradation is conceptually treated as the reverse of network formation. A formula for the sensitivity of pre-crosslinked resists presented by Suzuki,[37] has been found to be at odds with the results contained in this present work, and elsewhere.

According to the new model, as the gel fraction present prior to electron exposure is degraded, the average molecular weight(s) and MWD of the fragments released from the gel initially increase. The average molecular weight and MWD obtain maximum values at the point at which the network is first made fully soluble. Beyond this point the average molecular weight is proposed to reduce, and the MWD to narrow, such that with increased exposure dose the MWD of the degraded fragments will tend towards the most probable distribution with $Mw/Mn = 2$. Molecules originally forming part of the sol fraction are assumed to degrade with a reduction in average molecular weight and changes in MWD towards $Mw/Mn = 2$.

A number of promising resist materials have been identified in this work. Statistical copolymers of IT.ANH-co-MMA and MMI-co-MMA have been shown to be capable of defining sub 500 nm wide

lines and spaces with sharp resist profiles. A gradual change in resolution capabilities was found for IT.ANH-co-MMA copolymers with optimum resolution being noted at a composition of ~46 mol % (IT.ANH)-co-MMA with Mn ~500000 g.mol^{-1}. For MMI-co-MMA, optimum resolution was noted for 10 mol % (MMI)-co-MMA with no further improvement found for samples of increasing mol % (MMI). Favourable results were also found for a copolymer of 15 mol % (ACMP)-co-MMA, although side wall definition was in this case a little less sharp. It should be recognised that in all of these materials further improvements are likely with increasing attention to the solvent developers used. A copolymer of 51 mol % (IT.ANH)-co-αMS showed high resolution capabilities although thermal crosslinking was not observed.

Mixtures of the two copolymers IT.ANH-co-MMA and HEMA-co-MMA have shown improved results compared to each of the copolymers used on their own. This has been attributed to enhanced crosslinking of the copolymer mixture. The results for this material suggest optimum results for copolymer compositions of ≥5-10 mol % (IT.ANH/HEMA)-co-MMA. Terpolymers of IT.ANH-HEMA-MMA have been demonstrated to operate as resist materials, although exhibiting relatively poor sensitivities.

Investigations of terpolymers and copolymer mixtures of MAA-MAM-MMA have suggested that high sensitivities may be obtained for these materials provided a suitable developer could be found, although in this present work the resolution was observed to be generally poor.

Suggestions for further work

Experimental verification of the model for resist degradation presented in chapter four would require the measurement of the number and weight average molecular weights of the soluble fractions extracted from the network, and also the measurement of the equilibrium gel fraction as a function of exposure dose. Measurement of the number and weight average molecular weights of the soluble fractions extracted from the network is likely to be complicated by the small quantities of material which can be collected from irradiated samples, and problems of determining the molecular weight of branched molecules. An additional factor might be the presence of microgel particles. These problems might be overcome using the technique of gel permeation chromatography (GPC) coupled with concentration, viscosity, and light scattering detectors. This technique has been demonstrated to be capable of determining the average molecular weights, and also the branching index (g) of branched molecules. In the case where measurements are to be made using light scattering apparatus an assumption for the refractive index increment (dn/dc), would have to be made for the distribution of copolymer compositions present.

For the system IT.ANH-co-MMA, the minimum clearing dose has been shown to depend upon the primary average molecular weight. A recommendation for future work would be to investigate this dependence in other thermally crosslinkable resist materials.

APPENDICES

Appendix A
Experimental Results of D S Argyropoulos and H I Bolker showing changes in Average Molecular Weight and MWD during Random Degradation of Model Networks.

Table 1   Degradation of Model Trifunctional Network.

Degradation time min	wt % sol isolated	Mw g.mol^{-1}	Mn g.mol^{-1}	$\dfrac{Mw}{Mn}$
2.5	1.5	1400	1070	1.3
2.0	2.9	1990	1070	2.2
4.0	3.8	1940	1280	1.5
6.0	5.6	1940	970	2.0
7.0	7.1	1000	858	1.2
7.5	10.6	3100	1650	1.9
11.0	13.5	4800	1620	3.0
9.0	17.5	4200	2600	1.6
14.5	20.2	8900	6300	1.4
15.0	55.5	10000	6400	1.6
13.5	67.3	9230	6500	1.4
16.5	88.6	49500	8700	5.7

Tables A2/A3 Degradation of Model Networks formed by Random Crosslinking of originally Monodisperse Primary Chains.

A2: With Average Degree of Crosslinking = 0.15.

Degradation time min	wt % sol	Mw g.mol^{-1}	Mn g.mol^{-1}	$\dfrac{Mw}{Mn}$
0.25	0.40	5700	4000	1.4
0.50	0.49	6000	3600	1.7
1.50	0.57	7500	4400	1.7
2.5	0.72	14000	8300	1.7

A3: With Average Degree of Crosslinking = 0.40.

Degradation time min	wt % sol	Mw g.mol^{-1}	Mn g.mol^{-1}	$\dfrac{Mw}{Mn}$
0.5	0.03	3800	3100	1.2
1.0	0.10	4500	3600	1.2
1.5	0.19	5900	4900	1.2
2.0	0.41	8800	6300	1.4
2.75	0.94	26000	10000	2.6

Reproduced from original work by D S Argyropoulos and H I Bolker.[84]
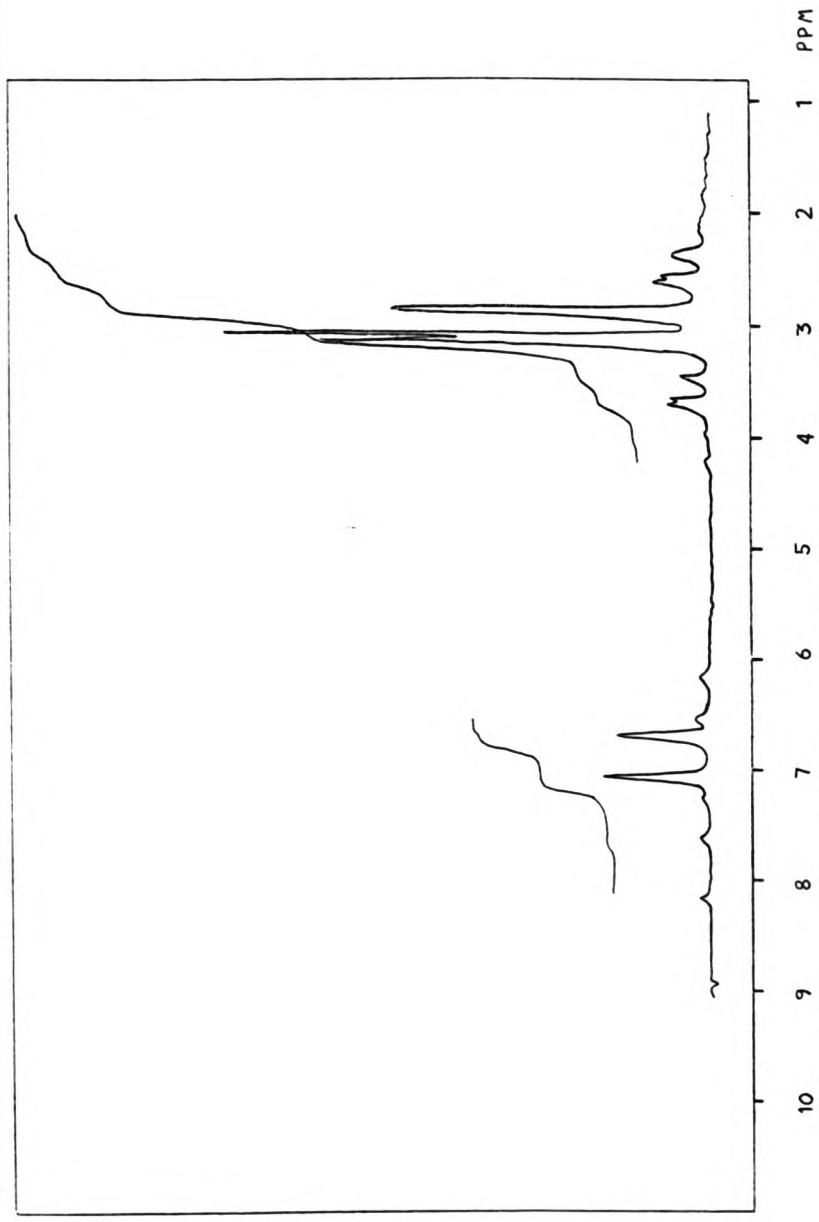
Appendix B   Summary Figure showing Dissolution Rate versus
Dose in Pre-crosslinked Resist baked at Various
Temperatures.   Reproduced from Original Work by
N R Farrah and G Owen.[65]
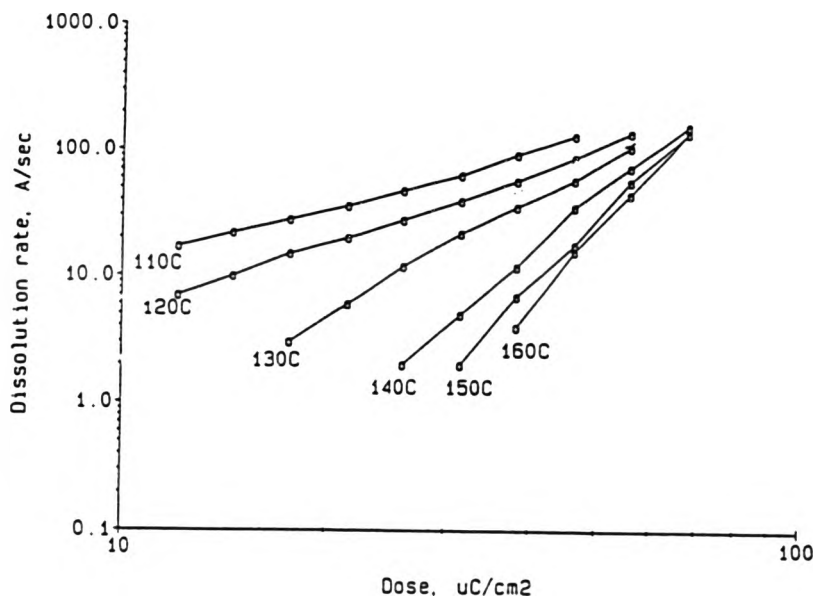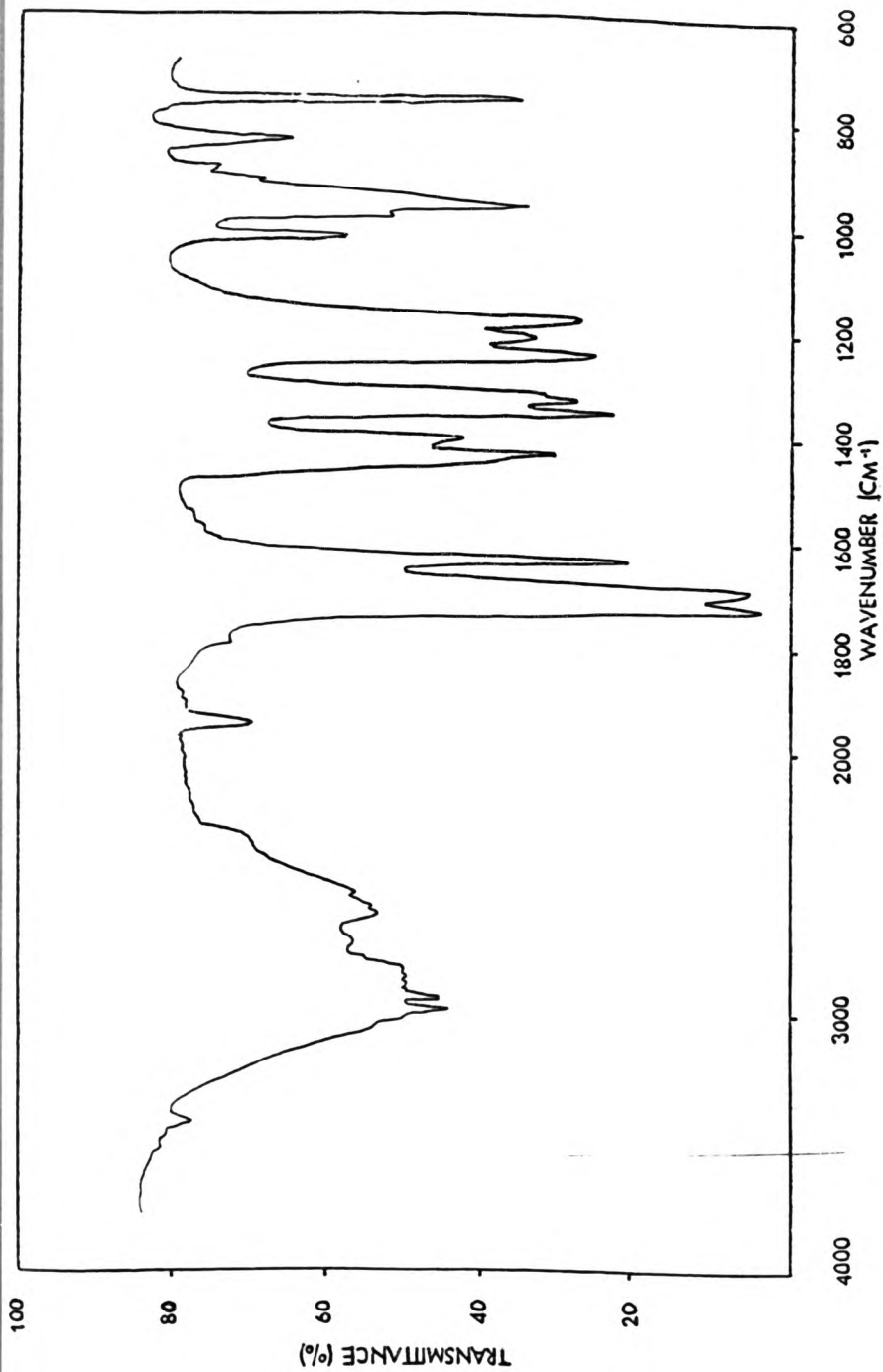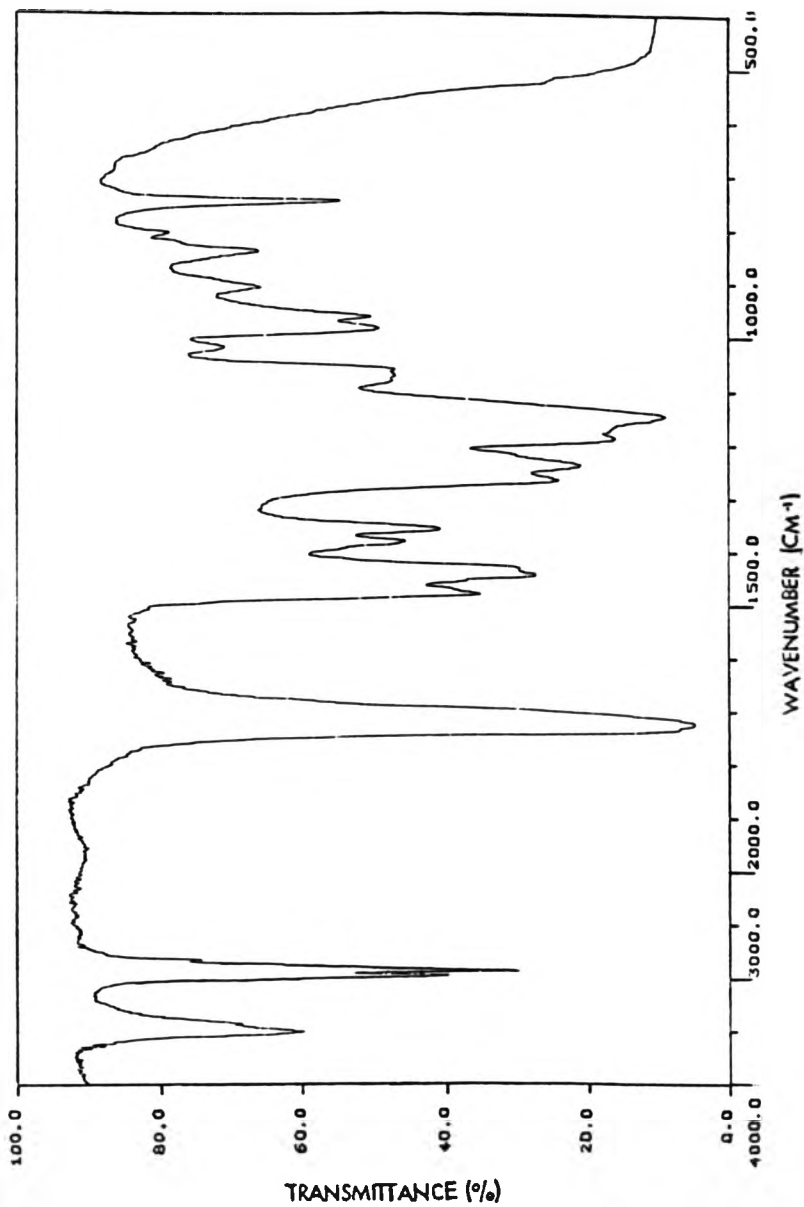
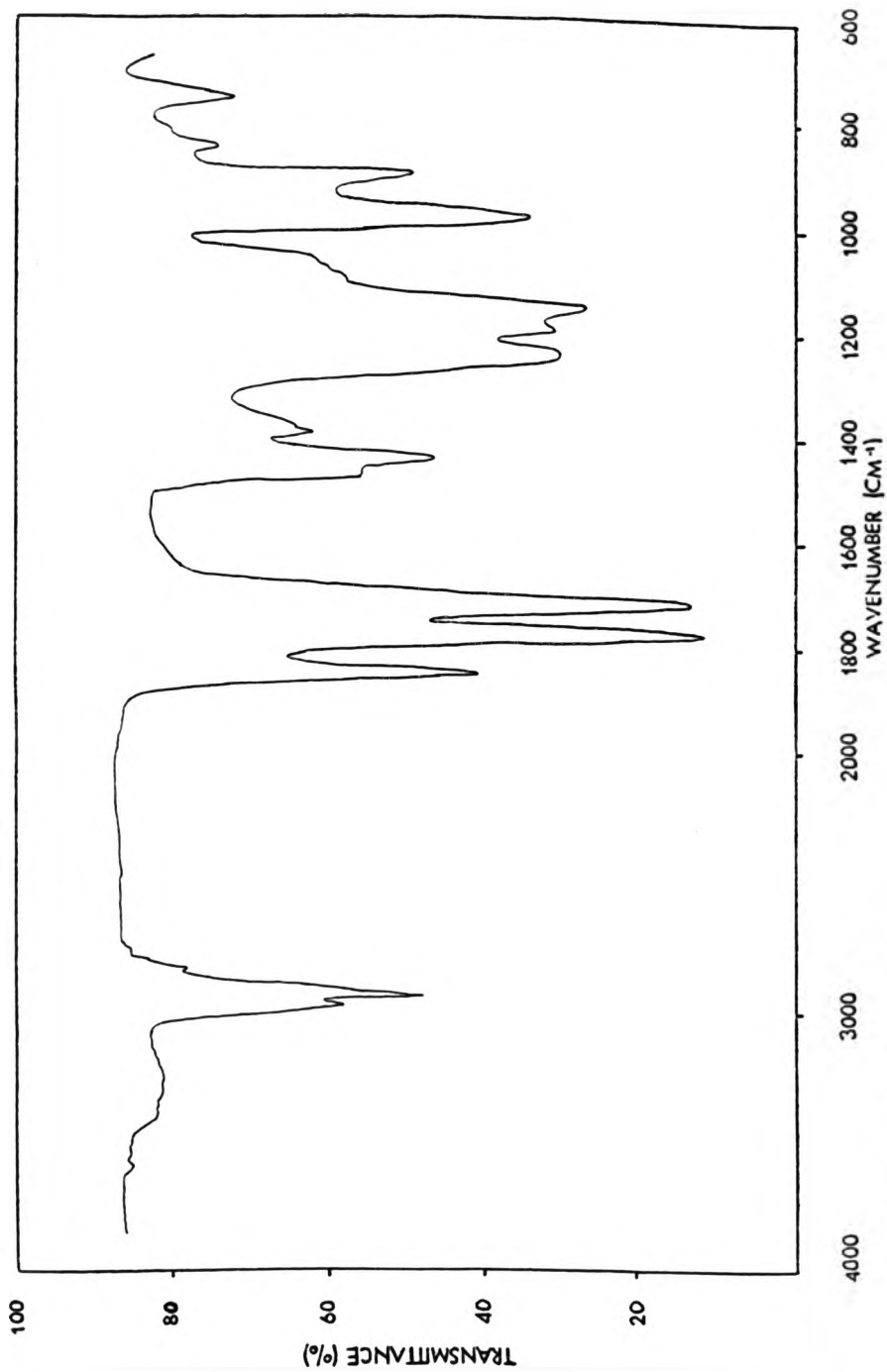**Appendix C**   Proton nmr and Infrared Spectroscopy

WITH D₂O
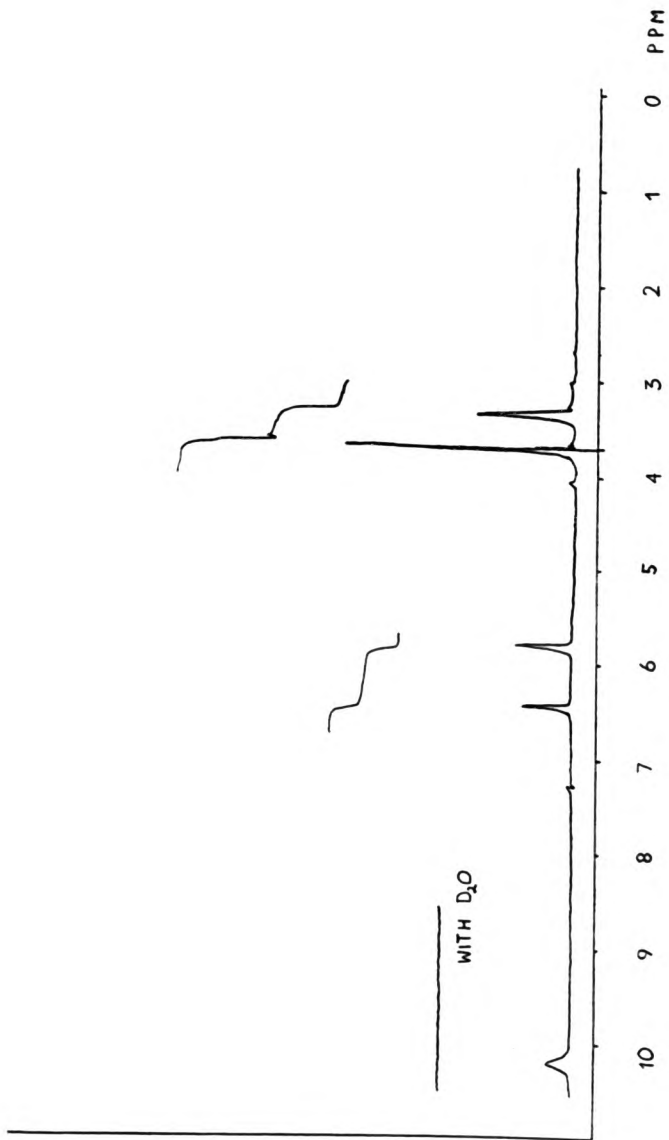
nmr MMI monomer

nmr ACMP monomer
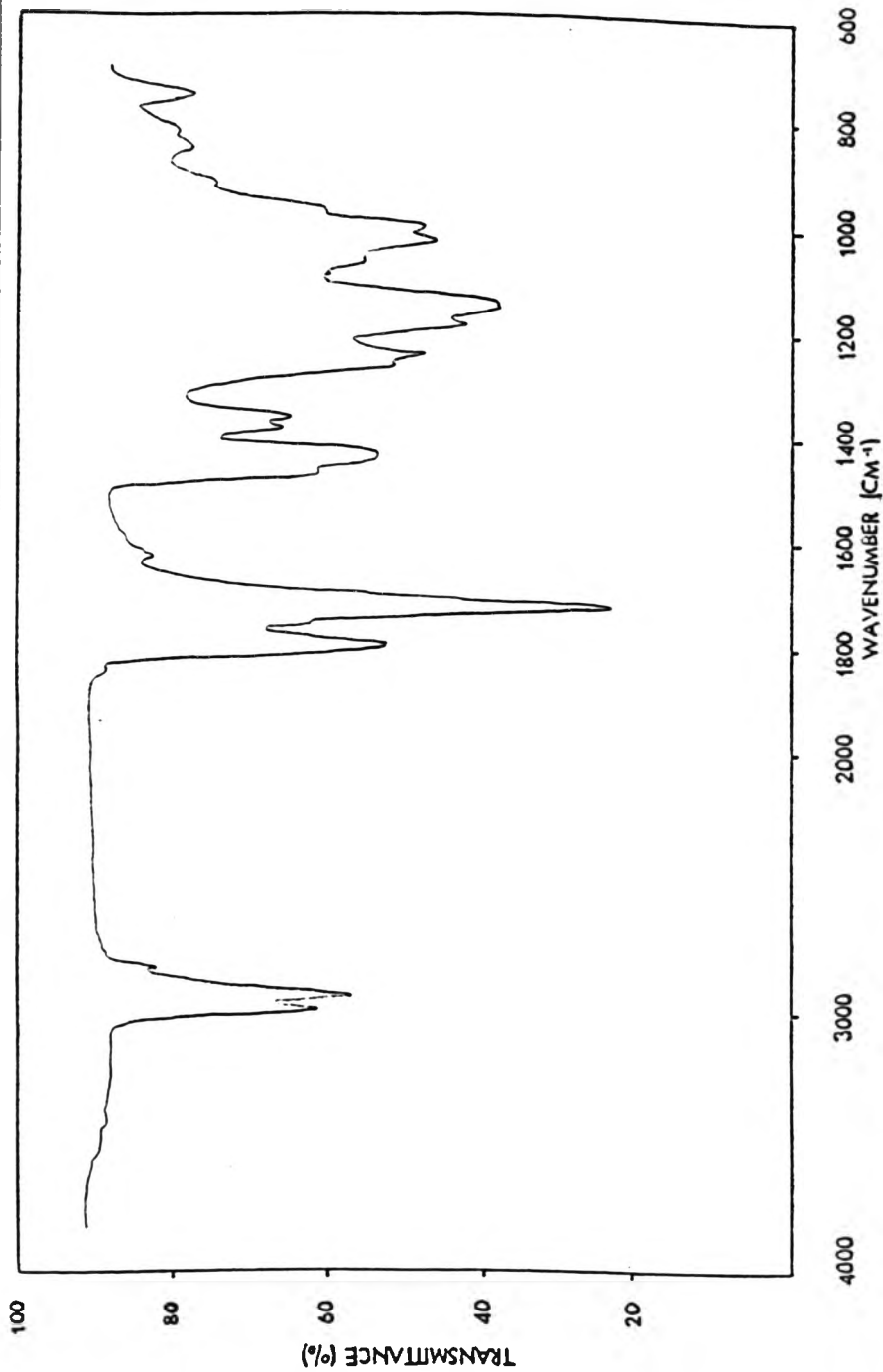
MMI monomer

WAVENUMBER (Cm⁻¹)

TRANSMITTANCE (%)

15 mol % (HEMA)-CO-MMA

46 mol % (IT.ANH)-co-MMA

10 mol % (ACMP)-co-MMA

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