New Aqueous Base Developable Photoresist for Lithographic Printing Plates Applications

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ABSTRACT: Negative photoresists are materials that become insoluble in developing solution when exposed to optical radiation. This work describes the production of simple negative-working resists, demonstrating aqueous development, for potential printing plate applications. The copolymers comprised glycidyl methacrylate (GMA) and acrylic acid (AA) via free-radical solution polymerization in methyl ethyl ketone as a solvent using azobisisobutyronitrile as initiator at 60°C. Characterization of the copolymers prepared was carried out via IR, ^{1}H-NMR, and thermal analysis techniques. The copolymers of GMA/AA were successfully prepared over a wide range of composition. It was found that the copolymer containing 15 mol % of AA unit in the feed was developed with NaOH on copper plate rather than zinc plate and crosslinked in the presence of photogenerated acid (PAG) caused by acid-initiated ring-opening polymerization of pendant epoxide groups. Exposure of the resist films to UV radiation at λ_{max} = 365 nm results in the generation of acid, and the subsequent baking process at 80°C for 1 min promotes the diffusion of the PAG, which initiates the cationic crosslinking of the epoxide rings. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1933–1942, 2010

Key words: water-soluble polymers; glycidyl methacrylate; photoresist; lithography; onium salt

INTRODUCTION

Over the past 30 years, chemists and engineers have been able to provide a wide variety of resists, both negative (insolubilize upon exposure to radiation) and positive (solubilize upon exposure to radiation) to answer the need of a growing industry. Negative resists currently comprise the largest sector of the photoresist market. The choice of whether to use a negative or a positive resist system depends upon the need of the specific applications such as resolution, ease of processing, and cost.[1]

In recent years, copolymers based on glycidyl methacrylate (GMA) have received increasing attention. The interest in these copolymers is largely due to the ability of pendant epoxide groups to enter into a large number of chemical reactions, thus offering the opportunity for chemical modifications. The high reactivity of the epoxide group is primarily due to the considerable strain in the three-membered ring. The reactivity of the ring is also affected by the presence of other polar groups and bulky substituents in the molecule, by the type of solvent used for preparation, and by temperature. The monomer and the homopolymer of GMA are both hydrophobic.[2–5]

Previous work on the synthesis of GMA copolymers with methacrylic acid found that the copolymer which contains 83 mol % GMA in the feed gave an aqueous base solubility by the aid of photogenerated acid (PAG). Also, the sensitivity was enhanced when divinyl ether monomer was added as a crosslinker.[4]

Other work by Hunter and Price[5] on copolymers made from GMA and *N*-vinyl pyrrolidinone (NVP) were prepared via free-radical solution polymerization in chloroform. The copolymer composition and the tacticity were measured via ^{1}H-NMR and ^{13}C-NMR.

Also, the work by Davidson et al.[6–8] using onium salts in the formulations of negative resist was found suitable for aqueous development. The copolymers used were GMA/NVP, GMA/*N*,*N*-dimethylacrylamide (DMAC), and GMA/2-hydroxy ethyl methacrylate. It was found that the copolymers of GMA/DMAC containing between 25 and 30 mol % of GMA in feed demonstrated an optimum development time of 3 min in water, and the performance of GMA/DMAC was much better than the GMA/NVP resist.

Progress in optical lithography in the last few years was achieved by decreasing the exposure wavelength from 436 to 157 nm nowadays. Research

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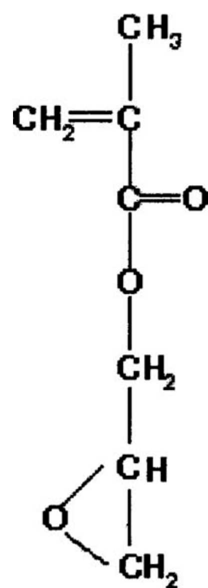


Figure 1 Structure of GMA monomer.

is in progress to push this boundary down to a few nanometers.[9–12]

In this work, the poly(GMA-*co*-AA) copolymers were prepared via solution polymerization in methyl ethyl ketone (MEK) and characterized by IR, ^{1}H-NMR, and thermal analysis techniques, and their evaluation as aqueous base developable photoresist were studied.

EXPERIMENTAL WORK

Materials

All materials used were commercially available from Aldrich Chemical Company (UK) except azobisisobutyronitrile (AIBN) from (Merck BDH, UK). GMA and acrylic acid (AA) were deinhibited by passage through a deinhibitor column (Aldrich, UK) and kept refrigerated.

Synthesis of photoacid generator

The photoacid generator (mixed arylsulfonium hexafluoro-antimonate) (MAS^+–SbF_6^-) was synthesized and characterized according to previously published works.[13–16]

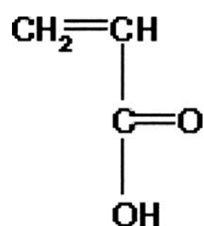


Figure 2 Structure of AA monomer.

TABLE I
Composition and Some Physical Properties of the GMA/AA Copolymer

Polymer	Mole fraction of GMA in feed	Yield (%)
GMA/AA 90%/10%	90%	35%
GMA/AA 85%/15%	85%	40%
GMA/AA 80%/20%	80%	46%
GMA/AA 75%/25%	75%	48%
GMA/AA 70%/30%	70%	52%

General preparation of GMA/AA copolymers

GMA and AA comprising (10 g) mass in total were combined with MEK (50 mL) and AIBN (0.2 g) as initiator in a round-bottomed flask. The reaction was purged with nitrogen gas for 30 min before being stirred for further 4 h at ~ 60°C. The reaction was terminated by rapid cooling in ice. The polymer formed was precipitated by dropwise addition to cyclohexane or *n*-hexane as a nonsolvent before being washed and dried at room temperature under vacuum.

CHARACTERIZATION AND TESTING

Infrared spectra

The five copolymers of GMA/AA that have been prepared were examined as KBr disks using Perkin–Elmer 1430 ratio recording infrared spectrophotometer. However, the GMA and AA monomers have been examined as a neat liquid on NaCl plates.

Thermal analysis

Thermogravimetric analysis (TGA) measurements were performed using Perkin–Elmer, TGA-50 H analyzer. About 7–12 mg of the polymer sample were placed in a platinum pan and heated from 25 to

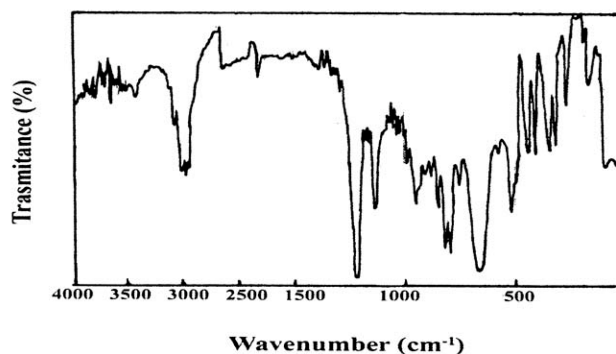


Figure 3 IR spectrum of the GMA monomer.

TABLE II
IR Band Assignments for GMA Monomer

Frequency (cm^{-1})	Assignment
3480 (w)	OH— band of absorbed water
2800 (m)	C—H stretching vibration
1720 (s)	C=O stretching vibration
1650 (m)	C=C stretching vibration
1200 (s)	Epoxy group of GMA
1020 (m)	
890 (m)	

w, weak; m, medium; s, strong.

TABLE III
IR Band Assignments for AA Monomer

Frequency (cm^{-1})	Band assignments
3200–3600 cm^{-1} (s)	OH of AA side chain
2800–3000 cm^{-1} (vs)	Aliphatic C—H stretching vibration
1720 cm^{-1} (vs)	C=O carbonyl stretching vibration
1550 cm^{-1} (s)	C=C backbone stretching vibration
1150–1300 cm^{-1} (m)	C—O stretching vibration
1400–1450 cm^{-1} (m)	C—O—H in-plane bending vibration
750–950 cm^{-1} (m)	O —H out of plane bending vibration

w, weak; m, medium; s, strong; vs, very strong.

450°C with a heating rate of 20°C/min under nitrogen atmosphere.

^{1}H-NMR analysis

500 MHz ^{1}H-nuclear magnetic resonance (NMR) spectra was recorded on a Jeol JNM–ECA–500 spectrometer. The solvent used was DMSO. Signals were recorded in ppm downfield from tetramethylsilane (TMS).

UV spectrum analysis

The PAG (MAS^+–SbF_6^-) was prepared, characterized by melting point, and UV absorption measurements on a Unicam 8700 series UV/vis spectrometer.

SPREADING OF FILMS, EXPOSURE, DEVELOPMENTS, AND EVALUATION

Zinc printing plates were prepared by gentle abrasion of their surfaces using a nylon pad (15% H_2SO_4), and also copper plates were used after cleaning their surfaces with CCl_4 solvent followed by acetone. Typically, 1 g of the polymer was dissolved in about 7 mL of 2-methoxy ethyl ether (diglyme) as a solvent along with 0.1 g of the photoacid generator (MAS^+–SbF_6^-). Crystal violet dye was added at 2 wt % to aid visualization. Also, perylene was added at 2 wt % to act as a sensitizer. Films were spread onto the prepared zinc and copper plates using a wire-wound drawdown bar to give films of approximately 8–10 μm thickness.

Exposure of the films were carried out using UV lamp (100 watt) with $\lambda_{max} = 365$ nm. Exposure times were typically 1 h. Development of the resist films was attempted in 10% tetramethyl ammonium hydroxide (TMAH), water, and 0.5*M* aqueous NaOH with little detergent. Image quality was assessed by eye, using a watch-maker's glass. Etching of zinc plates was carried out by immersion in 10% nitric acid and H_2O : HNO_3 (1 : 5 ratio) for etching copper plates.

RESULTS AND DISCUSSION

The GMA was chosen as the epoxide-containing monomer; the low cost and ready availability of this

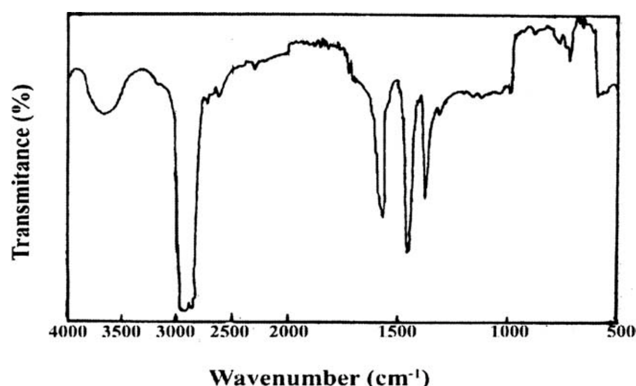


Figure 4 IR spectrum of the AA monomer.

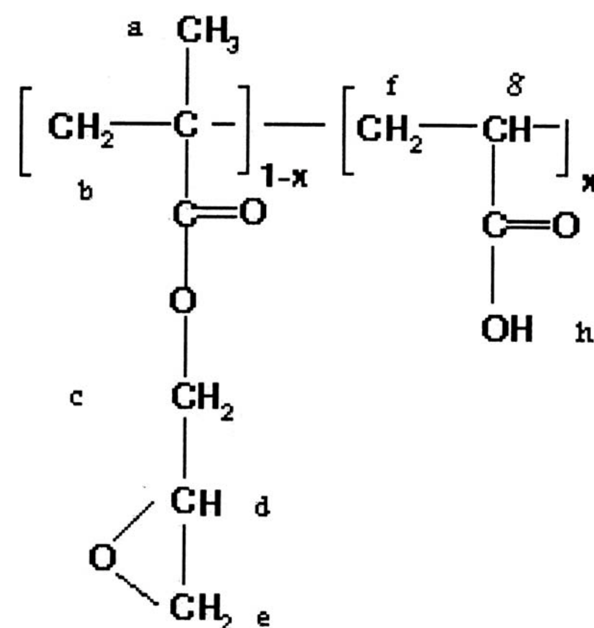


Figure 5 Structure of the GMA/AA copolymer.

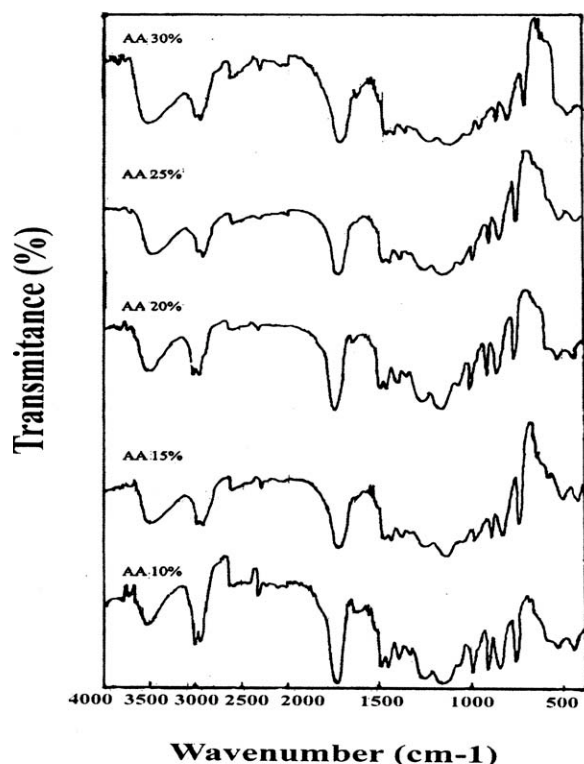


Figure 6 IR spectrum of the GMA/AA copolymer.

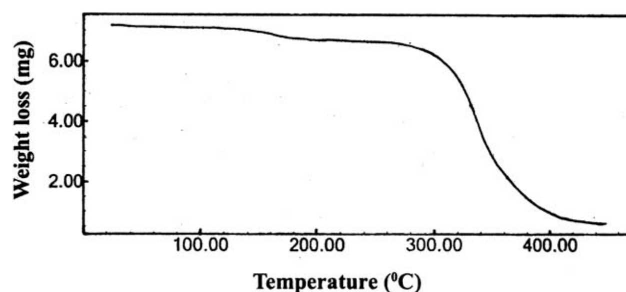


Figure 7 TGA curve of the GMA/AA copolymer with 10% of AA in feed.

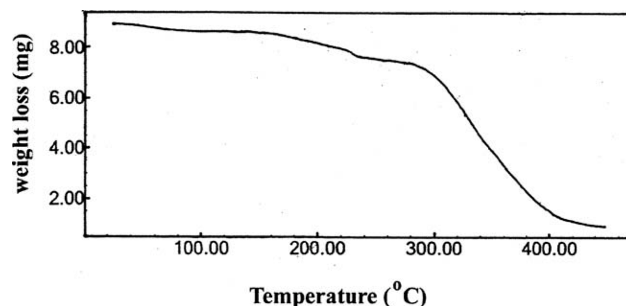


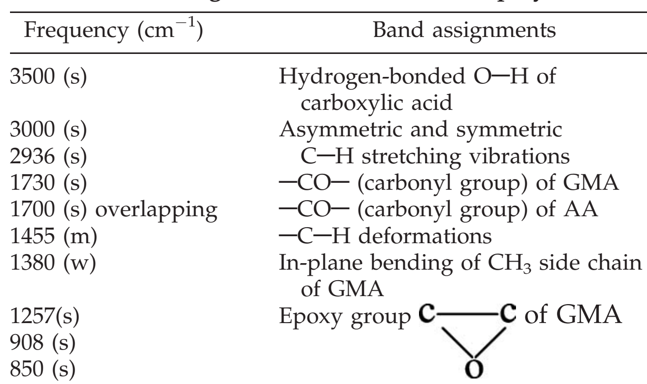
Figure 8 TGA curve of the GMA/AA copolymer with 15% of AA in feed.

monomer are other factors that increase the attractiveness of this material. Also, the poly(GMA) has found a great deal of applications in the photoresist chemistry as an e-beam resist.[4,5]

The copolymerization reaction of GMA with AA was carried out in MEK as a solvent for 5 h under nitrogen gas at 70°C. In the first experiment, the molar feed ratio of AA was 50% and the polymerization resulted in intractable crosslinked material. This was due to thermal crosslinking reaction between the pendant epoxide group of GMA and poly-AA pendant carboxylic groups.

So, it was decided to carry out the polymerization reaction for 4 h with maximum molar feed ratio of AA 30%, and the temperature was controlled and did not exceed 60°C.

TABLE IV
IR Band Assignments for GMA/AA Copolymers



Frequency (cm^{-1})	Band assignments
3500 (s)	Hydrogen-bonded O—H of carboxylic acid
3000 (s)	Asymmetric and symmetric
2936 (s)	C—H stretching vibrations
1730 (s)	—CO— (carbonyl group) of GMA
1700 (s) overlapping	—CO— (carbonyl group) of AA
1455 (m)	—C—H deformations
1380 (w)	In-plane bending of CH_3 side chain of GMA
1257(s)	Epoxy group C—C(—O—) of GMA
908 (s)	
850 (s)	

IR spectroscopy

The structures of the GMA and AA monomers are shown in Figures 1 and 2, respectively. Also, Table I gives some composition and physical properties of the GMA/AA copolymers. It can be seen in Table I that as the mole fraction of GMA in the feed decreases, the yield % of the polymer product increases.

The structure of the GMA monomer (Fig. 1) was confirmed by IR spectroscopy as shown in Figure 3.

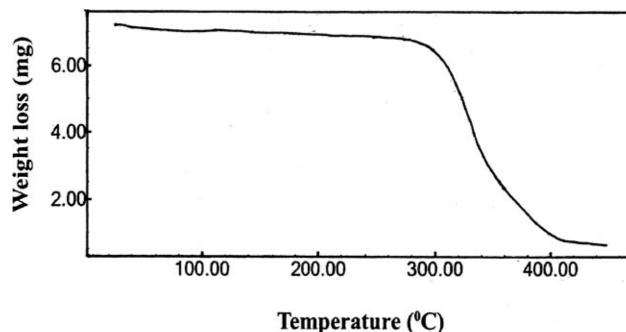


Figure 9 TGA curve of GMA/AA copolymer with 25% of AA in feed.

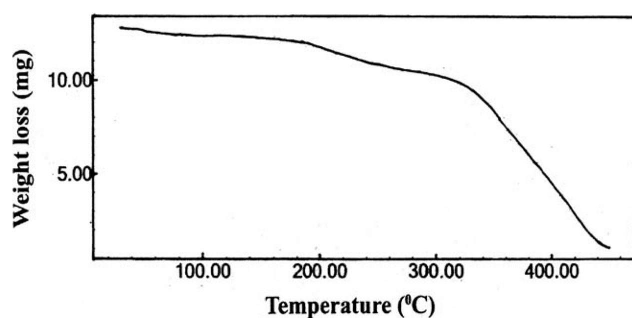


Figure 10 TGA curve of the GMA/AA copolymer with 20% of AA in feed.

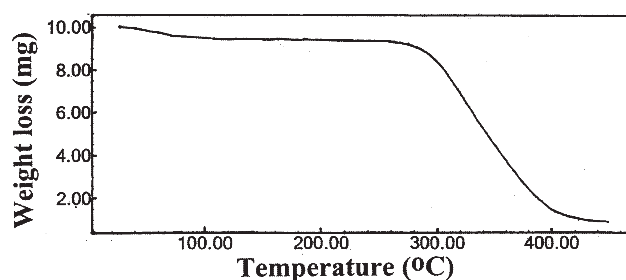


Figure 11 TGA curve of the GMA/AA copolymer with 30% of AA in feed.

Also, Table II shows the IR band assignments for this monomer.[17,18] The structure of the AA monomer (Fig. 2) was confirmed by IR spectroscopy as shown in Figure 4. Also, Table III shows the IR band assignments for this monomer. The structure of the GMA/AA copolymer (Fig. 5) was confirmed by IR spectroscopy as in Figure 6. Also, Table IV shows the IR band assignments for these copolymers.

Thermogravimetric analysis

The TGA curves for the five copolymers prepared are shown in Figures 7–11, and their assignments are summarized in Table V. The first stage that occurs in the temperature ranges 33–76, 43–82, 30–66, and 34–79°C with a corresponding weight loss 2.4, 2.1, 1.83, and 4%, respectively, for copolymers that contain 85 mol % of GMA up to 70 mol % in feed may be due to the loss of retained solvent molecules. However, the first stage of decomposition (129–191°C) of the copolymer that contains 90% of GMA in the feed with 4.5% weight loss may be due to the degradation in the side chain of the copolymer.[19]

The second stage of decomposition was observed at 270–436, 146–226, 140–190, 273–414, and 267–425°C with a corresponding weight loss of 82.9, 8.1, 3.2, 83.9, and 81.5%, respectively, for copolymers which contain 90 mol % of GMA up to 70 mol % in feed. The degradation at 146–226 and 140–190°C may be due to the decomposition in the side chain of the copolymer, whereas degradation at higher temperatures (270–436, 273–414, and 267–425°C) may be attributed to a random main-chain scission of the copolymer.[20]

The third stage of decomposition was represented at 226–236°C and 189–255°C with weight loss of 2.7% and 9.2%, which were observed only for the two polymers that contain 85 and 80 mol % of GMA in feed.

The fourth stage of decomposition was represented at 274–419°C and 255–446°C with weight loss of 70% and 75.3%, which were observed only for the two polymers that contain 85 and 80 mol % of GMA in feed. The decomposition in the third and fourth stages may also be due to a random main-chain scission of the copolymer.[21]

^{1}H-NMR of (GMA/AA) copolymers

The structure of prepared (GMA/AA) copolymers in Figure 5 was confirmed by the ^{1}H-NMR spectrum as shown in Figure 12 [and the enlarged sections 12(a–d)] and its assignments in Table VI.

TABLE V
TGA Results of GMA/AA Copolymers

	Copolymers				
	GMA/ AA 90%/10%	GMA/ AA 85%/15%	GMA/ AA 80%/20%	GMA/ AA 75%/25%	GMA/ AA70%/30%
First-stage weight loss (%)	4.55	2.4	2.1	1.83	4
Temperature (range) (°C)	129–191	33–76	43–82	30–66	34–79
Second-stage weight loss (%)	82.9	8.1	3.2	83.9	81.5
Temperature (range) (°C)	270–436	146–226	140–190	273–414	267–425
Third-stage weight loss (%)		2.7	9.2		
Temperature (range) (°C)	–	226–236	190–255	–	–
Fourth-stage weight loss (%)		70	75.3		
Temperature (range) (°C)	–	274–419	255–446	–	–
Total weight loss (%)	87.4	83.2	89.8	85.73	85.5

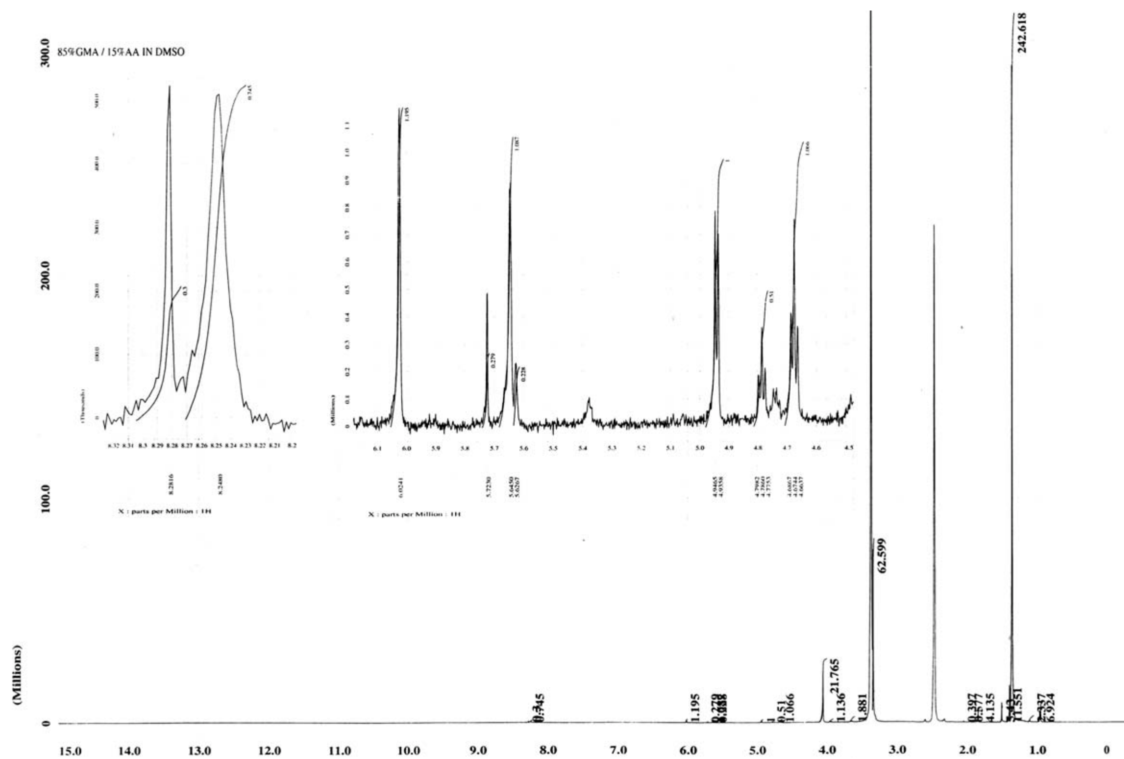
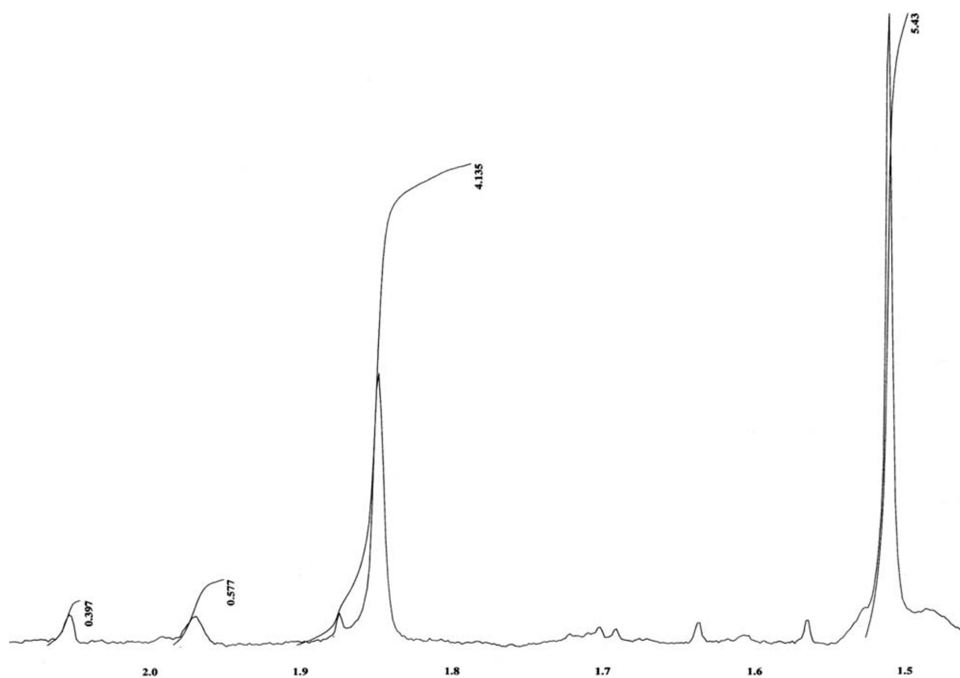
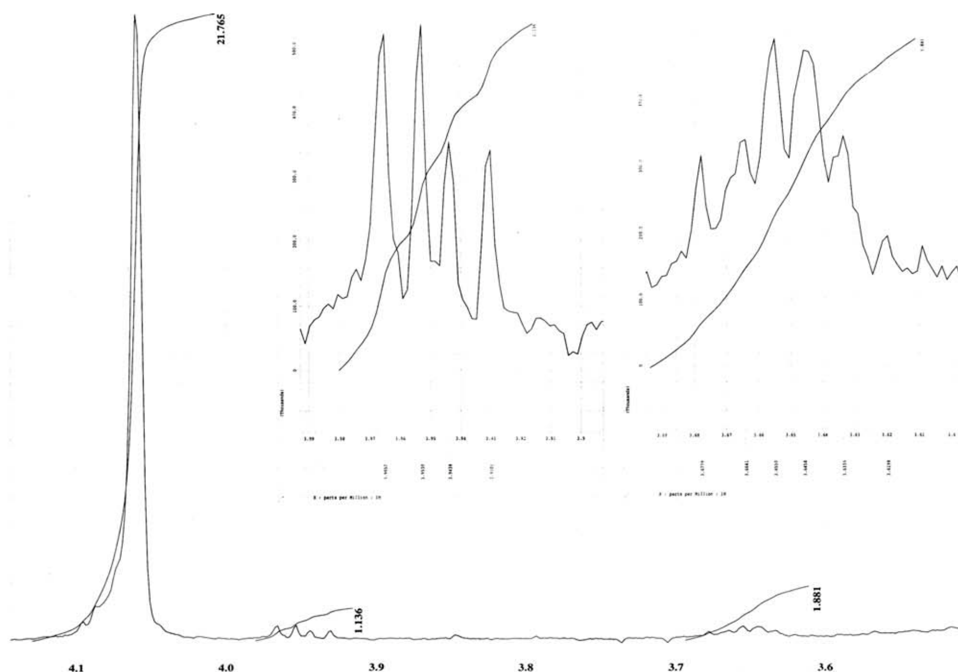


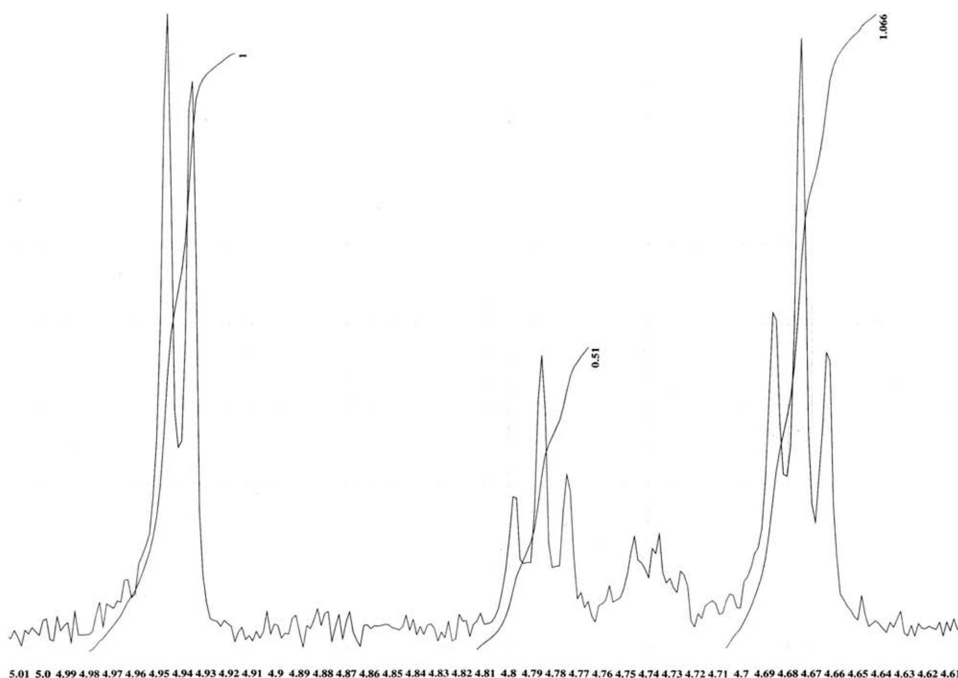
Figure 12 ^{1}H-NMR of poly(GMA-*co*-AA) with 85 mol % of GMA in feed in DMSO solvent. (a–d) The enlarged sections of the spectrum.



(a) Enlarge section from Figure 12.



(b) Enlarge section from Figure 12.

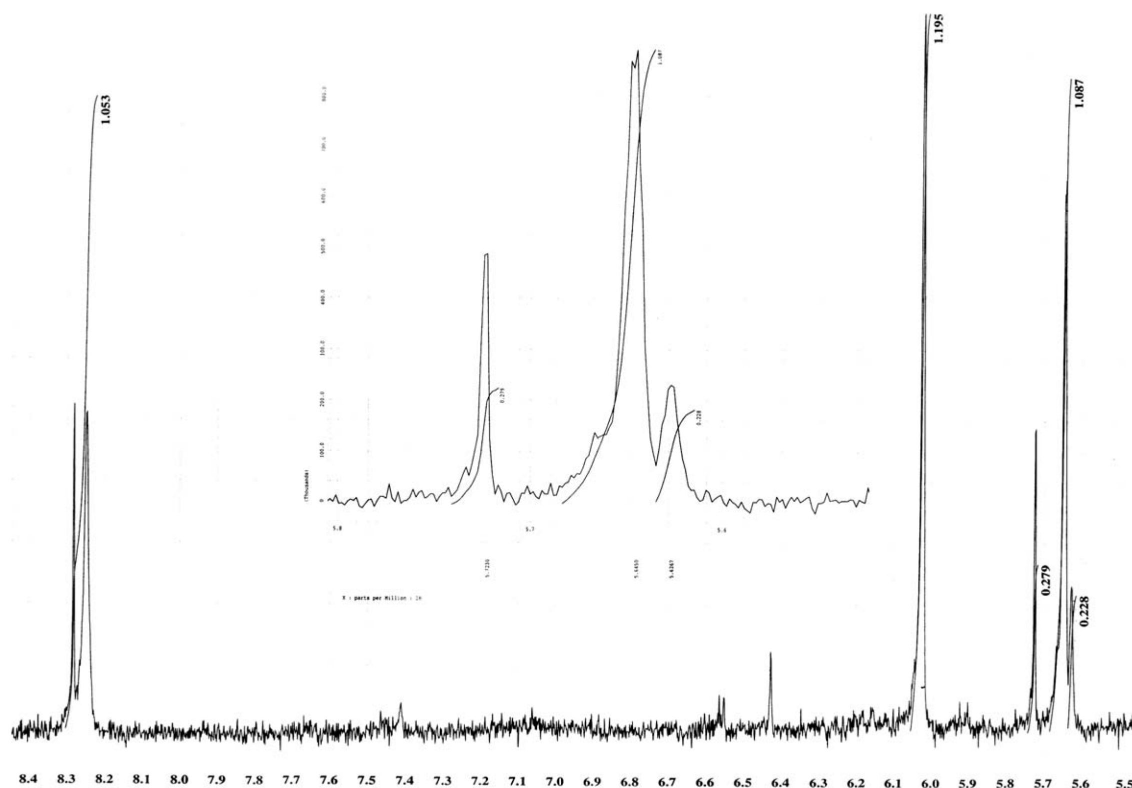


(c) Enlarge section from Figure 12.

Figure 12 (*Continued from previous page*)

Characterization of photoacid generator (MAS^{+}–SbF_6^{-})

The photoacid generator (MAS^{+}–SbF_6^{-}) was synthesized and characterized according to a previously published method.[6–8,22] As stated earlier, onium salt photoinitiators have found considerable use in photoresist chemistry for a wide range of applications. The (MAS^{+}–SbF_6^{-}) salt was made in a good yield as a white powder. The characterization data for this material is shown in Table VII. The salt is easily seen to be a mixture on examination of the melting



(d) Enlarge section from Figure 12.

Figure 12 (*Continued from previous page*)

TABLE VI
Assignments of ^{1}H-NMR Spectrum of GMA/AA Copolymer

Chemical shift (δ) relative to TMS in ppm	Multiplicity	Symbol	Number of protons	Peak
1.34	Singlet	(a)	3	CH_3 group of the side chain of GMA
2.5				DMSO-d^5 H
3.6–3.9				Water in DMSO
3.34–3.37	Doublet	(e)	2	Methylene group of side chain of GMA ring
4.66–4.75	Penta	(d)	1	Methine group of side chain of GMA ring
4.77–4.79	Triplet	(g)	1	Methine group of AA backbone
4.9	Doublet	(c)	2	Methylene group of GMA side chain
5.7–6.2	Doublet	(f)	2	Methylene group of AA backbone
6.4	Singlet	(b)	2	Methylene group of GMA backbone
8.2	Doublet	(h)	1	OH group of AA side chain (the splitting is due to spin–spin coupling)

TABLE VII
Characterization Data for (MAS^+–SbF_6^-) Salt

PAG	Yield (%)	Melting point (°C)	Melting point (°C)[a]	λ_{max} (nm)	λ_{max} (nm)[b]
(MAS^+–SbF_6^-)	Quantitative	95–106	98–107	300[c]	296[c]

[a] From Ref. 6.
[b] From Refs. 7 and 8.
[c] In methanol.

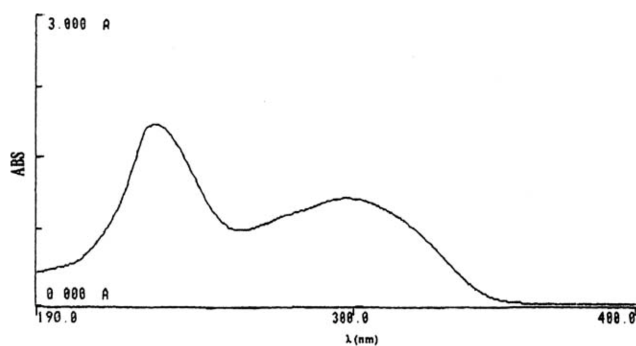


Figure 13 The UV spectrum of photoacid generator.

point measurement as it shows a wider range. The UV spectrum of this salt is shown in Figure 13. It can be seen from the spectrum that the absorption is broad and stretching beyond 300 nm.

Exposure, development, etching, and evaluation of the resist solution

Resist solutions were prepared as detailed in the "Experimental Work" section and spread onto both zinc and copper plates using K-bar only. Crystal violet dye was added for the aid of visualization. Perylene was also added as a sensitizing agent, which is known to be an efficient sensitizer for onium salts. The plates (Zn and Cu) have been exposed to UV radiation for 60 min followed by postexposure baking (PEB) for 1 min at 80°C. Good

Plate 1 Imaged Cu plate using poly(GMA-*co*-AA) resist with 15 mol % AA after exposure to UV light and before development.

Plate 2 Imaged Cu plate using poly(GMA-*co*-AA) resist with 25 mol % AA after exposure to UV light and before development.

image could be seen clearly after exposure and before development only for the resist polymer, which contains between 15 and 25 mol % of AA in the feed with copper plate rather than with zinc plate as in Plates 1 and 2.

When the polymer resists are exposed to UV radiation, a strong acid is generated in the exposed regions as a result of the photochemistry of the photoacid generator (MAS^{+}–SbF_6^{-}). Upon PEB, the acid generated catalyzed the crosslinking of the resist polymer via an electrophilic attack of the pendant epoxide groups, thus rendering the exposed areas insoluble[6–8,22] as shown in Scheme 1.

Development of the resist films was attempted via the immersion in 10% tetramethyl ammonium hydroxide (TMAH), pure water, and also in 0.5*M* aqueous NaOH for few minutes. It was found that the resist films of the polymer with 15 mol % of AA in feed demonstrated good development in 0.5*M* NaOH for 5 min especially with copper plates rather

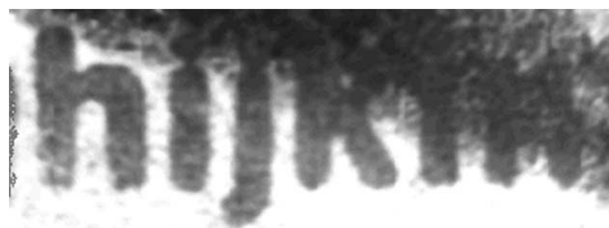
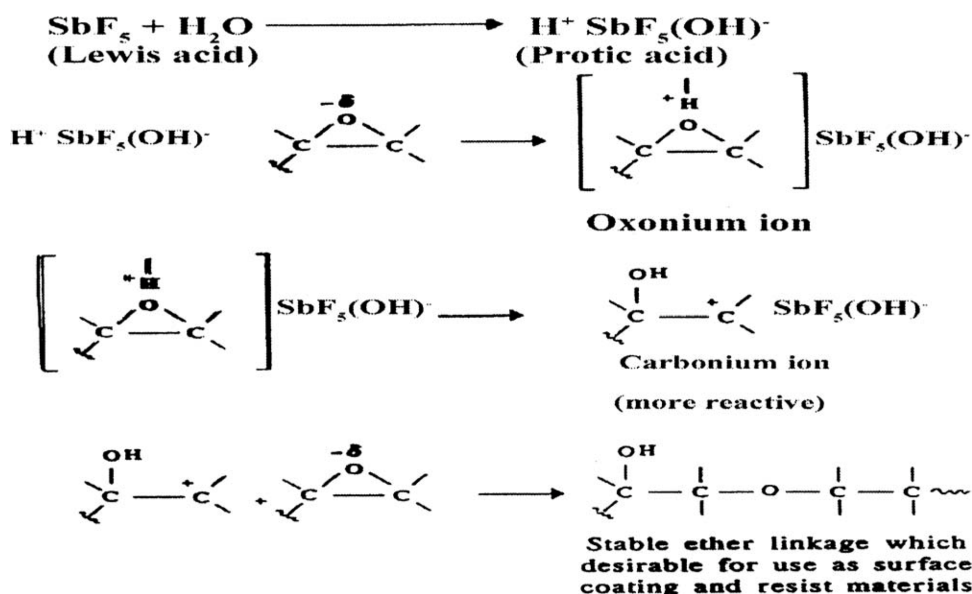


Plate 3 Imaged Cu plate with 15 mol % AA after develoopement in 0.5*M* aqueous NaOH.



Scheme 1 Crosslinking reaction of epoxide groups with photoacid generation.

than with zinc plates. A good image pattern was obtained as shown in Plate 3.

Etching was also attempted in 10% HNO_3 for zinc plates and with $H_2O : HNO_3$ with 1 : 5 with respect to copper plates. The copper plates after etching showed relatively good acid resistance but for only few min as the resist pattern was washed off completely.

CONCLUSION

The major conclusion to be drawn from this work is that GMA/AA copolymers were successfully synthesized over a wide range of composition. The copolymer with 15 mol % of AA in the feed was successfully developed with 0.5*M* aqueous NaOH for few minutes with copper plates with relatively acid resistance but just for few min rather than with zinc plates. Although further work still needed to enhance the etching process of the resist polymer via changing the concentration of the PAG; also, a crosslinking agent must be added to improve the photocrosslinking reaction. All of these factors should be taken into account.

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