Preparation, Characterization, and Lithographic Applications of Glycidyl Methacrylate/Methacrylic Acid/t-Butyl-4-vinylphenyl Carbonate Terpolymers

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ABSTRACT: At present, most negative working lithographic plates use organic solvents as a developing medium. These developers have the obvious disadvantages of toxicity, fire risk, and are more expensive than the aqueous developers. This work describes the synthesis and characterization of materials that have similar photoactive properties to existing materials, but are soluble in water or aqueous medium rather than organic solvents. These materials are terpolymers comprising of one sort of material to induce water solubility, such as methacrylic acid (MAA) and another material to give the photoactive response such as glycidyl methacrylate (GMA). The *tertiary*-butyl-4-vinyl phenyl carbonate (*t*-BOCVP) was added as a chemically amplifying agent. Various terpolymers were prepared via free-radical solution polymerization, typically in methyl ethyl ketone (MEK). Crosslinking reaction was induced using mixed arylsulphonium hexafluoroantimonate (MAS+ -SbF$_6^-$) as a photogenerating acid. It was found that the films of the terpolymer containing 85 mol % of GMA unit with the addition of 5 mol % rather than 2 mol % of the *t*-BOCVP in the feed ratio gave good acid resistance and good adhesion to the surface of the zinc plate. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2467–2471, 2008

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

INTRODUCTION

Current-resist materials employ organic compounds as casting solvents, and in some cases as developers. A typical resist formulation consists of ∼ 70 wt % of organic solvents. Although the photoresist based on photocationic polymerization of epoxides or vinyl ethers have been reported, most of them are not alkaline-developable. The use of organic solvents as developer has a number of drawbacks. They are expensive, toxic, highly flammable, difficult to dispose off, and harmful to the environment. Moreover, developing by organic solvents causes an undesirable image distortion caused by swelling. Recent studies have shown that negative resists based upon the crosslinking reaction exhibit no deformation of the image when developed in an aqueous base.[1]

Recent progress in onium salt chemistry, particularly the work of Crivello and coworkers,[2–4] has opened new avenues for research in resist chemistry. The photolysis of onium salts may lead to cationic polymerization and crosslinking reactions, which unlike free-radical reactions are not inhibited by atmospheric oxygen. In imaging techniques such as those used for microlithography, numerous systems have relied on the use of photogenerating acid for their success.[5,6] In contrast, the use of photogenerating base has not been explored, with a few notable exceptions.[7]

During the past decade, chemically amplifying resists have attracted a great deal of attention because of their high sensitivity and versatility in lithographic applications.[8,9] Early work by Hult et al.[10] led to a chemically amplifying, water-soluble resist involved synthesis of acrylamide-based water-soluble homopolymers and copolymers.

In the present study, a series of terpolymers based on poly(glycidyl methacrylate/methacrylic acid/t-butyl-4-vinylphenyl carbonate) have been synthesized, characterized, and their applications as negative-tone resist system was studied.

EXPERIMENTAL

Materials and their purification

Monomers

All materials were commercially available from Aldrich chemical company (UK), except azobisisobutyro-

TABLE I
Characterization Data for MAS$^+$-SbF$_6^-$ Salt

PAG	(MAS+-SbF$_6^-$)
Yield %	Quantitative
Melting point (°C)	95–106
Melting point (°C) lit[a]	98–107
λ_{max} (nm)	300[m]
λ_{max} (nm) lit[b]	296[m]

m, in methanol.
[a] From Ref. 11.
[b] From Ref. 12.

nitrile (AIBN) from Fluka chemical company (UK), and glycidyl methacrylate (GMA) and methacrylic acid (MAA) were deinhibited by passage through a deinhibitor column and kept refrigerated. The *tert*-butyl-4-vinylphenyl carbonate (*t*-BOCVP) was used without purification.

Initiators

AIBN initiator was used as received for free-radical solution polymerization.

Solvents

Methyl ethyl ketone (MEK) was used as solvent for free-radical solution polymerization without any purification; also, cyclohexane or *n*-hexane was used as nonsolvent for polymer precipitation.

Synthesis of photo acid generator

An aqueous solution of arylsulphonium chloride (Fluka; 30 mL) was added to sodium hexafluoroantimonate (13.75 g) in water (400 mL) and the reaction mixture stirred well. After standing for 1 h in the dark, the solid product was isolated by filtration, washed with small portion of water, dried under vacuum, and stored in the dark.

General preparation of GMA/MAA/*t*-BOCVP terpolymers

GMA, MAA, and *t*-BOCVP comprising (10 g) mass in total were combined with MEK (40 mL) and AIBN (0.2 g) in a round-bottom flask. The reaction mixture stirred for further 4 h at 60°C. Finally, the reaction terminated by a rapid cooling in ice. The polymer that formed was precipitated by dropwise addition to cyclohexane before being washed and dried at room temperature under vacuum.

General solubility of the polymers prepared

All the terpolymers prepared were tested by solubility experiments using the following solvents [H$_2$O, THF, CHCl$_3$, 0.5M NaOH, and 10% aqueous tetramethyl ammonium hydroxide (TMAH)]. About 10 mg of the polymer was taken with 0.5 mL solvent in half-dram ampoules. All the samples were shaken for 5–30 min to see whether they dissolved or not. If at the end of the shaking, the sample solution was clear and homogeneous, it was assumed that the dissolution was complete.

Characterization and testing

Characterization procedures

The onium salt photoinitiator mixed arylsulphonium hexafluoroantimonate (MAS$^+$-SbF$_6^-$) was characterized by melting point and UV absorption measurements on a Unicam 8700 series UV/vis spectrometer. The terpolymers made were analyzed using a –JEOL_ECA 500 MHz. Fourier transform NMR spectrometer in CDCl$_3$. Infrared spectra (IR) were recorded on a Perkin-Elmer 1430X spectrometer in the form of potassium bromide discs. The molecular weight determination of the prepared polymer was not measured via GPC technique as the solubility of the polymer in THF was very poor. The melting points of the terpolymers were measured by DSC, using DSC-60A-TAD under nitrogen atmosphere at a heating rate of 10°C/min.

Spreading of films, exposure, developments, and evaluation

Zinc printing plates were prepared by gentle abrasion of their surface using a nylon pad (15% H$_2$SO$_4$ conc.). Typically, 1 g of the polymer was dissolved in 6 mL of 2-methoxy ethyl ether (diglyme) as a solvent, along with 0.1 g of photo acid generator (PAG). 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 pre-
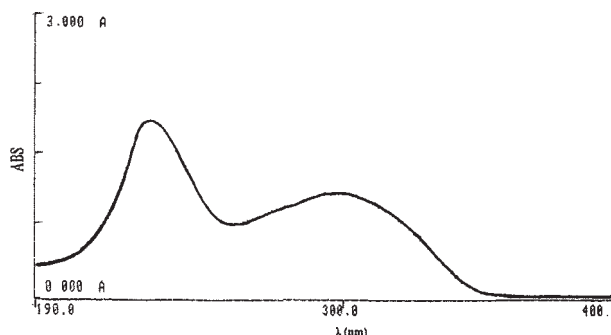

Figure 1 The UV spectrum of photo acid generator.

TABLE II
Preparation and Properties of the GMA/MAA/t-BOCVP Terpolymers

Polymer	Mole fraction of GMA in feed (%)	Melting point[a] (°C) T_m (max)	Yield (%)
1-GMA/MAA/TBOCVP 90% 8% 2%	90	175	38
2-GMA/MAA/TBOCVP 85% 13% 2%	85	180	48
3-GMA/MAA/TBOCVP 80% 18% 2%	80	170	51
4-GMA/MAA/TBOCVP 75% 23% 2%	75	177	55
5-GMA/MAA/TBOCVP 70% 28% 2%	70	176	82

[a] Measured via DSC.

pared zinc plates using a wire-wound drawdown bar or spin-coater to give films ~ 20–200-μm thick.

The films were dried at 80°C for 1 min before exposure. Exposure was carried out using UV lamp with the output of $\lambda_{max} = 365$ nm, for different periods of times. Standard printing negatives and test images were used in the imagewise exposure of the films. Development of the films was attempted in water; 10% TMAH and 0.5M NaOH with detergent. Image quality was assessed by eye, using a watchmaker's glass. Etching was carried out by immersion of the plates in 10% nitric acid.

RESULTS AND DISCUSSION

Onium salt (MAS$^+$-SbF$_6^-$) synthesis

The photo acid generator MAS$^+$-SbF$_6^-$ was successfully synthesized via a method previously published.[10] The MAS$^+$-SbF$_6^-$ salt was made from commercially available triphenyl sulphonium chloride. The product, in this case, is not pure substance but mixtures of different components. This reaction was explored further by Crivello, who named these mixtures MAS salts.[11] Further works have suggested

that these mixtures contain more than 12 UV absorbing components, which may play a part in the photoproduction of acidic species.[12] The MAS$^+$-SbF$_6^-$ salt was made in good yield as a white powder. The characteristic data for this material is shown in Table I.

The MAS$^+$-SbF$_6^-$ salt is easily seen to be a mixture on examination of the melting point measurement, as it shows a wide range. The UV spectrum of the MAS+-SbF$_6^-$ is shown in Figure 1. It can be seen from the spectrum that the absorption is broad and stretches beyond 300 nm.[13,14]

Poly(GMA/MAA/t-BOCVP) terpolymers

The GMA monomer was chosen, as it has a pendant epoxide group that has the ability to enter into a large number of chemical reactions.[15–17] The high reactivity of the epoxide group is due to the considerable strain in the three-membered ring. The MAA monomer was chosen to provide water solubility. It was hoped that the addition of 2–5 mol % of the t-BOCVP monomer using MAS$^+$-SbF$_6^-$ as a photo acid generator could help to improve the performance of this system.
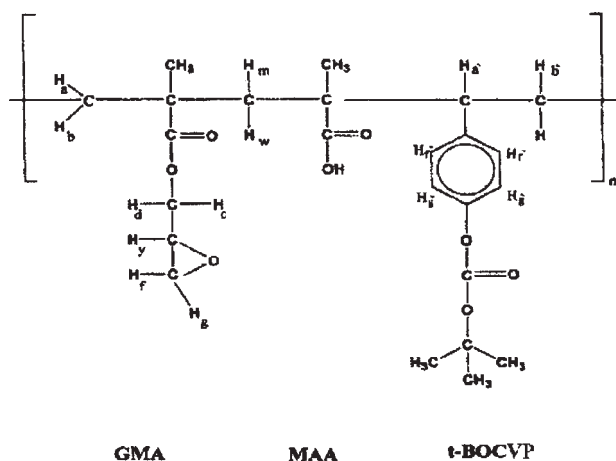

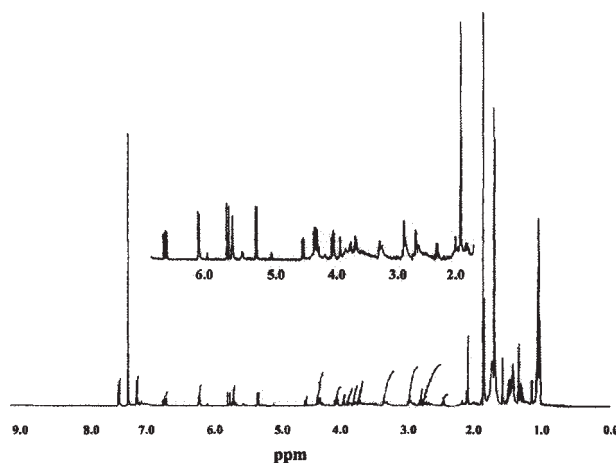Figure 2 The structure of the (GMA/MAA/t-BOCVP) terpolymer.

Figure 3 ^{1}H NMR of GMA/MAA/t-BOCVP terpolymer with 90% of GMA in the molar feed ratio.

TABLE III
Assignments of ^{1}H-NMR Spectrum of GMA/MAA/t-BOCVP Terpolymer

Chemical shifts relative to TMS in ppm	Multiplicity	Number of protons	Peak
1 ppm	s	6	CH$_3$(GMA)+CH$_3$ (MAA)
1.6 ppm	s	6	Back bone methylene groups of GMA+MAA + t-BOCVP
1.8 ppm	s	9	O—C(CH$_3$)$_3$ of t-BOCVP
2.7 ppm	d, d	1	H$_f$ (GMA)
2.9 ppm	d, d	1	H$_g$ (GMA)
3.9 ppm	d, d	1	H$_d$ (GMA)
4.2 ppm	Penta	1	H$_y$ (GMA)
4.4 ppm	d, d	1	H$_c$ (GMA)
6.6 ppm	d, d	1	H$_á$ (t-BOCVP)
7.1 ppm	d	2	H$_f$ (t-BOCVP)
7.4 ppm	d	2	H$_ġ$ (t-BOCVP)

The polymerization of the GMA/MAA/t-BOCVP terpolymers was carried out in MEK as a solvent. Reaction times of 4 h were found suitable for this system. Five GMA/MAA/t-BOCVP terpolymers with molar feed ratios of GMA were varied between 70 and 90%, with 5% increments. The reaction was terminated by immersion in ice followed by precipitation in n-hexane or cyclohexane.

As can be seen in Table II the yield % of the terpolymers was found to increase with decreasing the percentage of the GMA in feed. Also, it was found that the melting point measurements were around 170–180°C.

The structure of the GMA/MAA/t-BOCVP terpolymer as shown in Figure 2 was confirmed by ^{1}H-NMR and IR spectroscopy. The ^{1}H-NMR of this terpolymer is shown in Figure 3 and the peak assign-ment, for this polymer is shown in Table III. The polymer composition data were found difficult to be measured quantitatively from the proton-NMR spectra, as some peaks are overlapping.

The spectrum of the terpolymer as shown in Figure 3 shows no evidence of the existence of the acidic proton of the MAA. It appeared in the various molar ratios of the terpolymer; however, it was shifted upfield to 8.9 ppm instead of 10.5 of the monomer.

The IR spectrum as shown in Figure 4 was measured using KBr discs. Table IV shows the IR band assignments of the terpolymers.[18–23]

The solubility test of the polymers indicated that all the polymers are soluble in CHCl$_3$. Poor solubility was noticed with water (cold and hot); 0.5M aqueous NaOH; and 10% aqueous TMAH solvents.

Resist solutions were prepared as detailed in the experimental section. Exposure to UV was carried out using standard printing negative mask. Development of the films was attempted by immersion of the plates in water; 10% aqueous solution of TMAH; and 0.5M NaOH with adding detergent. A latent
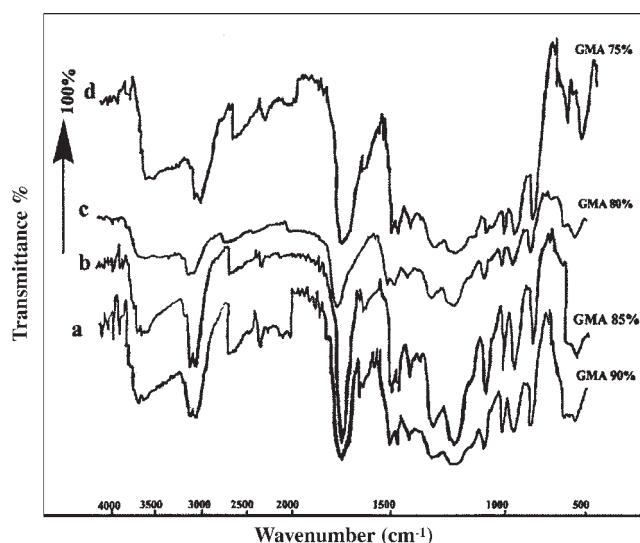

Figure 4 The IR spectra of GMA/MAA/t-BOCVP terpolymers.

TABLE IV
IR Peak Assignments for GMA/MAA/t-BOCVP Terpolymers

Frequency (cm^{-1})	Assignment
3450 (w)	OH— of absorbed water
3100 (s)	OH bonded of MAA
2850 (m)	C—H stretching vibrations
1650–1750	Carbonyl stretch
1200 (s)	Epoxy group of GMA
1100 (s)	
910 (s)	

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

image was clearly seen after exposure and before development. A poor image pattern was obtained after development for all molar ratios.

It was also found that the GMA with 85 mol % in the feed with 2 mol % of the *t*-BOCVP gave poor development in water or aqueous medium used. The adhesion was also not satisfactory and upon etching the films peal off from the plate, so that another trial was made to prepare two terpolymers with 5 mol % of the *t*-BOCVP in the feed rather than 2 mol %, to improve both adhesion and etching processes. Their resist solutions were also tested as mentioned earlier. It was found that the addition of 5 mol % of the *t*-BOCVP instead of 2 mol % in the feed gave an excellent adhesion to the plate and also good acid resistance, which lasted for more than 15 min but still with poor quality.

CONCLUSION

The terpolymers of GMA/MAA/*t*-BOCVP were successfully prepared over a wide composition range via radical polymerization. The terpolymers containing between 70 and 90 mol % of GMA with 2 mol % of the *t*-BOCVP in the feed along with the photo acid generator $MAS^+\text{-}SbF_6^-$ when coated and exposed to UV irradiation demonstrated poor development in water; 10% TMAH; and 0.5M NaOH with detergent.

The addition of 5 mol % of *t*-BOCVP instead of 2 mol % in the feed ratio showed an improvement of adhesion and acid resistance to some extent, although more future work is needed to obtain good quality image such as increasing the molar ratios of the MAA in the feed on the expense of the GMA; also changing the concentration of the PAG in the formulation.

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