

# Characterization of Acrylic Copolymers Applied in Negative-Type Photoresist via a Ternary Composition Diagram

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**ABSTRACT:** Three-component acrylic copolymers used as a binder for negative-type photoresists were synthesized and characterized. First, free radical polymerization was employed to synthesize two-component binders, i.e., acrylic ester copolymers with different ratios of benzyl methacrylate (BZMA) and methacrylic acid (MAA). Thermal behavior, viscosity and molecular weight of the prepared two-component binders were studied. Then, a series of three-component binders were prepared through incorporation of another monomer, 2-hydroxyethyl methacrylate (2-HEMA). FTIR was used to examine the evolution of chemical bonds at various stages of the synthetic process. Thermal analyses, TGA and DSC, were used to evaluate

the level of enhancement on thermal stabilities of the prepared three-component binders. Finally, an optimal region in the ternary composition diagram of BZMA, MAA, and 2-HEMA can be identified by comparing the results of acid value, viscosity, and molecular weight of the binder. A negative-type photoresist was prepared using an optimized composition, for which resolution of the circuit could reach the level of 6  $\mu\text{m}$ . © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 467–474, 2008

**Key words:** acrylic copolymer; binder; ternary composition diagram; negative-type photoresist; copolymerization; photoresists

## INTRODUCTION

Photoresist is generally a type of photosensitive polymer solution. The classification of photoresist is commonly based on the reaction mechanism during the exposure process.<sup>1–4</sup> If a positive-type photoresist is exposed to photo irradiation, the exposed area could be removed by dissolution in an alkaline developer liquid in the developing process. In contrast, the dissolved area of a negative-type photoresist is the unexposed area because the exposed area is cross-linked upon irradiation. After development, the desired circuit or pattern is formed on a substrate. Photoresists are widely used for the manufacture of microelectronics, silk screen printings, printed circuit boards, optical disks, color filter resists, and so on.<sup>5–7</sup>

Typically, a negative-type photoresist consists of polymer binder, photosensitive polyfunctional monomer, photoinitiator, solvents and additives.<sup>8,9</sup> Acrylic monomers used to synthesize the binder contain the desired functional groups, such as benzyl, hydroxyl, carboxyl groups, etc. The former two functional groups can improve both the dispersion of pigments

and the adhesion of photoresist on glass substrate. On the other hand, carboxyl group can provide sufficient acid value of the prepared photoresist.<sup>10–14</sup> However, it should be noted that when the content of polar functional groups, such as hydroxyl and carboxyl groups, is too high, the solubility of the synthesized binders in organic solvent decreases. As a binder for industrial applications, there are several basic criteria that should be obeyed. For example, the acid value has to be larger than 100 mg KOH/g and the molecular weight be controlled in the range of  $1.5\text{--}3.5 \times 10^4$  g/mol. If the binder is to be used for the manufacture of photoresist applied in color filter, the resolution should be less than 10  $\mu\text{m}$ . In this research, a series of binders were synthesized by free radical copolymerization of three kinds of acrylic monomers (BZMA, MAA, and 2-HEMA), and their properties were studied to find the optimal compositions for the binder, cf. Schemes 1 and 2. More importantly, the optimal composition of the synthesized binders was determined using a ternary composition diagram. Following that a negative-type photoresist was prepared and its resolution was determined.

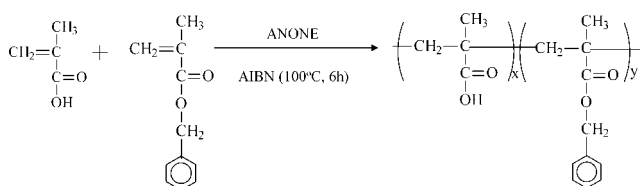
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## EXPERIMENTAL

### Materials

Materials for the preparation of negative-type photoresist include benzyl methacrylate (BZMA), methacrylic



**Scheme 1** Preparation of two-component binders, poly(BZMA-MAA), by free radical polymerization.

acid (MAA), 2-hydroxyethyl methacrylate (2-HEMA), 2,2'-azobisisobutyronitrile (AIBN), 1-dodecanethiol (Thiol), cyclohexanone (ANONE), ethyl 3-ethoxypropionate (EEP), propylene glycol methyl ether acetate (PMA), and dipentaerythritol hexaacrylate (DPHA). All of them were reagent-grade and purchased from Aldrich Chemical, Milwaukee, WI. Photoinitiators,  $\alpha$ -aminoketone (Irgacure 369) and isopropyl thioxanthone (ITX), were supplied by Ciba-Geigy, Tarrytown, NY. All materials were used as received.

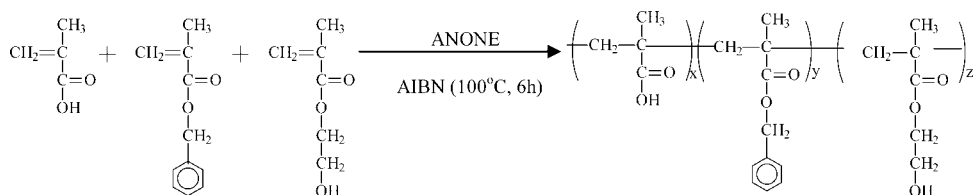
### Preparation of binders

Copolymer binders were prepared by free radical polymerization of three kinds of acrylate monomers, BZMA, MAA, and/or 2-HEMA in cyclohexanone (cf., Scheme 1, 2; the monomers = 40 wt %). The monomer solution was preheated at 100°C and stirred under nitrogen atmosphere. Then, initiator (AIBN, 1 wt % of total monomers) and chain-transfer agent (Thiol, 1 wt % of total monomers) dissolved in the same solvent were dropped slowly into the monomer solution. Free-radical polymerization was carried out for 6 h, and then the product was cooled down to room temperature. The obtained acrylate resin, poly(BZMA-MAA-2-HEMA), was used as the binder of the photoresist. Binder samples were named according to the rule: the first letter of the monomer name followed by their respective compositions in molar percentage. For instance, the molar composition of BZMA/MAA/2-HEMA of the prepared binder B54M36H10 was 54/36/10 (cf. Tables I–IV). To prepare samples for characterization of thermal property, acid value, or chemical structure, the formed binder solution was diluted with tetrahy-

drofuran (THF) and then poured into hexane to induce polymer precipitation. The precipitation procedure was repeated twice to ensure free of residual monomers. Finally, the white polymer precipitate were separated by filtration and then dried *in vacuo* at 60°C.

### Characterization

1. Differential scanning calorimeter (DSC) was employed to measure the glass transition temperature ( $T_g$ ) of the binder and the formed photoresist film. DSC, model 2010, TA Instrument, New Castle, DE, was first calibrated with indium standard before running the tests. An appropriate amount of a dried sample was sealed in an aluminum pan and placed in the heating chamber together with an empty reference pan. Temperature was raised from 50 to 170°C at a constant rate of 20°C/min under nitrogen flow.  $T_g$  of the sample was determined from the thermogram of the second heating cycle.
2. Thermal gravimetric analyzer (TGA), Hi-Res TGA 2950 from TA instruments, New Castle, DE, was used to measure the thermal decomposition temperature ( $T_d$ ) of the binder and the cured films of the photoresists. Samples (8–12 mg) were heated from room temperature to 600°C with a heating rate of 10°C/min under nitrogen flow.
3. Gel permeation chromatography (GPC, Waters 1515, Isocratic HPLC Pump, Milford, MA) was performed with THF as the mobile phase at 40°C with a polystyrene gel column (AM GPC Gel). Molecular weights of the binders were reported based on polystyrene standards.
4. Infrared absorption spectra of the prepared binders were taken using a Fourier Transform Infrared Spectrophotometer (Nicolet spectrometer 550, Madison, WI). Powders of the formed binder were ground with KBr to form a disc (1 : 50) for FTIR scanning. For all scans, the spectra were collected over the wavenumber range of 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .
5. Acid values of the prepared binders were determined by titration using a 0.1 mol/dm<sup>3</sup> potassium hydroxide solution. The definition of acid



**Scheme 2** Preparation of three-component binders, poly(BZMA-MAA-2-HEMA), by free radical polymerization.

**TABLE I**  
**Thermal Behavior, Viscosity, and Molecular Weight of the Prepared Two-Component Binders**

Sample	MAA content (mol %)	Thermal behaviors		Viscosity (cP)	Molecular weight ( $\times 10^4$ g/mol)
		$T_g$ ( $^{\circ}\text{C}$ )	$T_{dmax1,2}$ ( $^{\circ}\text{C}$ )		
B90M10H0	10	73.7	316.1, 408.6	85.1	2.45
B80M20H0	20	87.6	317.6, 414.9	152.7	2.30
B70M30H0	30	106.4	318.0, 426.4	240.8	2.37
B60M40H0	40	131.6	320.6, 430.7	502.7	2.26

value is the amount of KOH in milligrams needed to reach the equivalent point for one gram of the prepared binder (mg/g).

6. Viscosity of the as-synthesized binder solution was measured using a viscometer (RVDV-II+CP, Brookfield, Middleboro, MA), and the spindle LV2 was used.

#### Preparation of negative-type photoresists

Negative-type photoresists were prepared by mixing binder (8 wt %), polyfunctional monomer DPMA (8 wt %), photoinitiator, and photosensitizer (0.6 wt %, Irgacure 369/ ITX = 5) and a tri-solvent at room temperature. The composition of the tri-solvent was adjusted to ANONE/EEP/PMA = 0.87/1/1 in molar ratio. Viscosity of the photoresist could be adjusted by the amount of tri-solvent to give a satisfactory coatability. Resolution of the negative-type photoresist was determined by examining the developed circuit diagram under microscope. The exposure-development procedure was as follows:

1. The negative-type photoresist was uniformly spread on a glass substrate using a spin-coator (1500 rpm), and then pre-baked at  $80^{\circ}\text{C}$  for 5 min.
2. Following UV irradiation under a photomask at  $250\text{ mJ}/\text{cm}^2$  (broadband), it was then developed with a developer liquid, IPA/ $\text{H}_2\text{O}/\text{Na}_2\text{CO}_3 = 3/2/0.02$ .
3. Before using optical microscope to examine the resolution, the photoresist was post-baked at  $200^{\circ}\text{C}$  for 1 h to obtain a cured coating (about 1-2  $\mu\text{m}$  in thickness).

## RESULTS AND DISCUSSION

### Characterization of two-component binders

Photoresist generally consists of binder, polyfunctional monomer, photoinitiator, photosensitizer, and solvents. The acrylate monomer MAA for binder synthesis provides sufficient acid value for increasing development ability of a negative-type photoresist. In this research, we first synthesized four kinds of two-component binders, for which ANONE was chosen as the solvent (the monomers = 40 wt %, cf. Scheme 1). Thermal behaviors, molecular weights and acid values of the synthesized two-component binders with various MAA contents were studied.

#### MAA content vs. thermal behaviors

Glass transition temperatures ( $T_g$ ) of pure poly(benzyl methacrylate) and poly(methacrylic acid) are  $54$  and  $166^{\circ}\text{C}$ , respectively, as obtained from literature.<sup>15,16</sup> The compositions of the prepared two-component binders of BZMA and MAA are shown in Figure 1 (■).  $T_g$  of these copolymer binders were measured using DSC, and the results are shown in Figure 2 and Table I. It appears that  $T_g$  of the binders increased with increasing MAA content. For example,  $T_g$  of the binder B90M10H0 was  $73.7^{\circ}\text{C}$  (MAA = 10 mol %), and when MAA content was increased to 40 mol %, i.e., B60M40H0,  $T_g$  became  $131.6^{\circ}\text{C}$ . This suggested that monomer MAA could increase not only the acid value of the photoresist but also the  $T_g$  of the binder.

TGA was utilized to measure the thermal decomposition temperatures ( $T_d$ ) of the two-component

**TABLE II**  
**Properties of the Two-Component Binder, B80M20H0, Prepared by Using Different Amounts of AIBN Initiator**

Sample	AIBN content (wt % of total monomers)	Thermal behaviors		Viscosity (cP)	Molecular weight ( $\times 10^4$ g/mol)
		$T_g$ ( $^{\circ}\text{C}$ )	$T_{dmax1,2}$ ( $^{\circ}\text{C}$ )		
B80M20H0-0.5	0.5	88.5	318.2, 413.8	179.3	3.01
B80M20H0-1	1	87.6	317.6, 414.9	152.7	2.30
B80M20H0-2	2	79.2	317.9, 413.5	112.7	1.97
B80M20H0-4	4	72.3	316.8, 415.3	35.1	1.69
B80M20H0-PMA	1	82.8	316.1, 413.6	65.3	2.27

**TABLE III**  
Thermal Behaviors of the Prepared Three-Component Binders

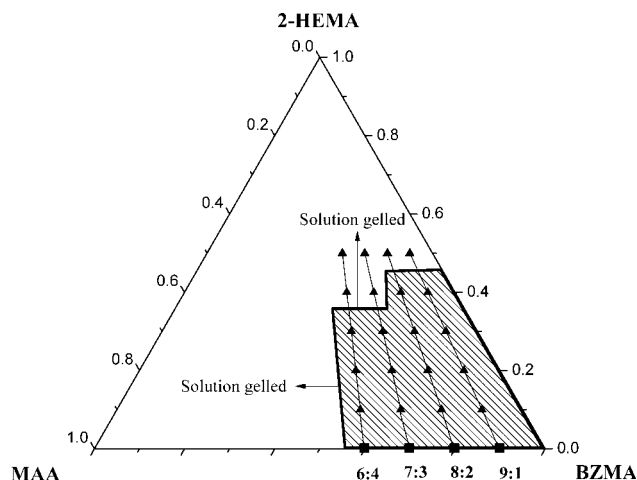
Sample name	BZMA/MAA (molar ratio)	Thermal behaviors	
		$T_g$ (°C)	$T_{d10}$ (°C)
B81M9H10	9 : 1	74.4	316.8
B72M8H20	9 : 1	74.7	314.8
B63M7H30	9 : 1	74.8	310.8
B54M6H40	9 : 1	73.6	302.5
B72M18H10	8 : 2	87.1	328.8
B64M16H20	8 : 2	86.5	314.4
B56M14H30	8 : 2	86.2	307.9
B48M12H40	8 : 2	85.8	306.6
B63M27H10	7 : 3	99.9	329.7
B56M24H20	7 : 3	99.0	322.9
B49M21H30	7 : 3	93.8	316.8
B54M36H10	6 : 4	120.4	329.8
B48M32H20	6 : 4	110.1	323.5
B42M28H30	6 : 4	109.9	318.6

binders. The obtained thermograms indicated generally a two-stage pattern, where the first- and the second-stage decomposition occurred at about 250–370°C and 370–470°C, respectively. As an example, Figure 3 shows the TGA and DTG thermograms of the binder B80M20H0. The local maxima of the 2-stage thermal decomposition ( $T_{dmax}$ ) were located at 317.6°C and 414.9°C, respectively. As was reported by Demirelli et al.,<sup>17</sup> thermal decomposition temperature of pure poly(benzyl methacrylate) was from 250 to 400°C; hence, the first- and the second-stage decompositions of the binder were attributed to the BZMA and MAA segments, respectively. It can be seen from Table I that  $T_{dmax2}$  increased with increasing MAA content, which means that thermal stability of the prepared binders could be enhanced by increasing MAA content.

**TABLE IV**  
Viscosity, Molecular Weight, and Acid Value of the Prepared Three-Component Binders

Sample	BZMA/MAA (molar ratio)	Viscosity (cP)	Molecular weight ( $\times 10^4$ g/mol)	Acid values <sup>a</sup>
B81M9H10	9 : 1	216.2	2.25	35.8
B72M8H20	9 : 1	341.1	2.21	32.9
B63M7H30	9 : 1	670.2	2.29	31.0
B54M6H40	9 : 1	883.2	2.08	28.8
B72M18H10	8 : 2	312.8	2.19	70.2
B64M16H20	8 : 2	391.2	2.16	63.3
B56M14H30	8 : 2	716.0	2.05	58.1
B48M12H40	8 : 2	3016.8	2.01	51.6
B63M27H10	7 : 3	395.2	2.11	108.1
B56M24H20	7 : 3	782.1	2.18	98.0
B49M21H30	7 : 3	1231.8	2.16	86.4
B54M36H10	6 : 4	763.2	1.99	152.3
B48M32H20	6 : 4	983.8	2.06	136.7
B42M28H30	6 : 4	2919.0	1.92	119.8

<sup>a</sup> Milligrams of KOH/g of binder.



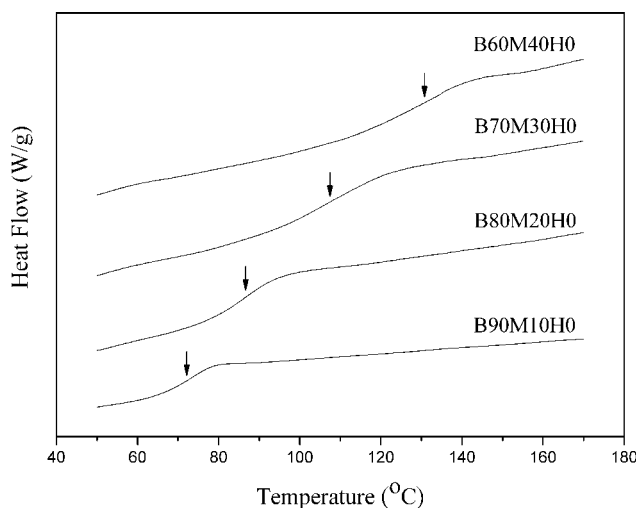
**Figure 1** Ternary composition diagram of the prepared binders. ■: copolymer of MAA and BZMA; ▲: terpolymer of MAA, BZMA, and 2-HEMA.

#### MAA content vs. viscosity

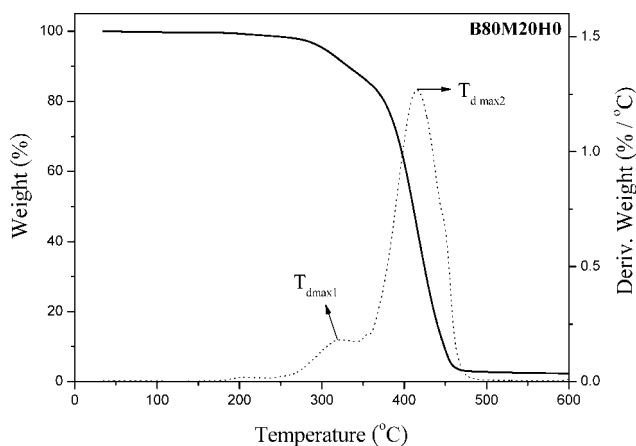
The measured viscosities of the two-component binders are summarized in Table I. It reveals that the viscosity gradually increased as the MAA content increased. For instance, viscosity of the binder B90M10H0 was about 85 cP, which is much less than the value 503 cP for B60M40H0, containing 40 mol % MAA. As the MAA content was further increased to 50 mol %, the binder solution gelled within 3 days. Therefore, the molar ratio of MAA was controlled to be less than 50 mol % in this study.

#### Molecular weight

Weight average molecular weights ( $M_w$ ) of the formed two-component binders were measured using GPC, and the results are shown in Table I.  $M_w$



**Figure 2** DSC thermograms of the prepared two-component binders.



**Figure 3** TGA and DTG thermograms of the two-component binder, B80M20H0.

of all samples was found to range from  $2.2 \times 10^4$  to  $2.5 \times 10^4$  g/mol. Because of similar molecular weight, the observed behavior in increasing viscosity with increasing MAA content could be due to the difference in molecular structure. Still, the molecular weight could be changed by changing the amount of initiator, AIBN, while keeping other reaction conditions constant. Table II shows that as the AIBN content was increased,  $M_w$  of the prepared binder decreased, and so did the viscosity. On the other hand, as the AIBN content was maintained at 1 wt % of total monomers, but the solvent was changed from ANONE to a more polar solvent PMA,  $M_w$  of the prepared binder, termed as B80M20H0-PMA, was nearly the same as B80M20H0, but its viscosity was decreased dramatically from 153 to 65 cP. That is, the observed difference in viscosity is mainly due to the “polar compatibility” between binder polymer and its solvent. The results also indicated that restricting AIBN content to 1 wt % of total monomers was reasonable in the present synthesis process, for which  $M_w$  of the formed binder met the criteria of  $1.5\text{--}3.5 \times 10^4$  g/mol.

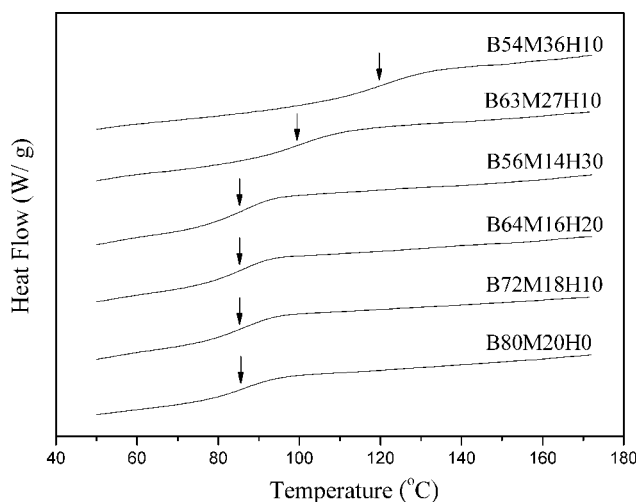
### Characterization of three-component binders

Three-component binders were prepared by incorporation of the third kind of acrylate monomer, 2-HEMA, in the synthesis process (cf. Scheme 2). Because of its hydroxyl group, 2-HEMA could enhance the adhesion between photoresist and glass substrate.<sup>9,13</sup> However, because hydroxyl group is polar, viscosity of the prepared binder will increase as 2-HEMA content increases. In the discussion that follows, thermal behavior, viscosity,  $M_w$  and acid value of three-component binders were presented and compared. Compositions of the three monomers in the binder were illustrated in terms of a “ternary composition diagram” (cf. Fig. 1 (▲)).

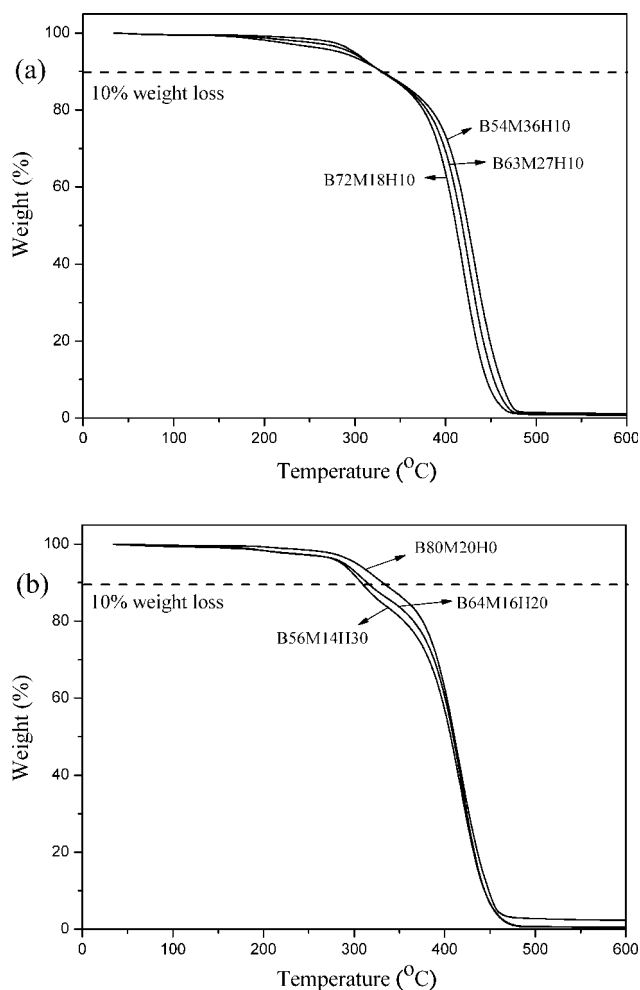
### Thermal behaviors

Glass transition temperatures ( $T_g$ ) of pure poly(2-hydroxyethyl methacrylate) is  $55^\circ\text{C}$ , as obtained from the literature.<sup>15,16</sup> Previous results of two-component binders showed that  $T_g$  increased with increasing MAA content. DSC thermograms of the three-component binders are shown in Figure 4, and  $T_g$  values are collected in Table III. It appears that  $T_g$  of the binders with the same BZMA/MAA ratio were very close to each other, regardless of the 2-HEMA content. Specifically, for the case of BZMA/MAA = 9 : 1,  $T_g$  of the four binders are all closed to  $74^\circ\text{C}$ . However,  $T_g$  of the B80M20H0 was still slightly higher than that of B56M14H30, ca.  $1.4^\circ\text{C}$ , due to the higher content of MAA. On the other hand, for samples of the same 2-HEMA content,  $T_g$  increased with increasing MAA content, in accordance with the previous results and the literature.<sup>13</sup>

TGA was utilized to measure the  $T_d$  of the three-component binders. Because thermal decomposition behaviors of the three-component binders were complicate and involved several stages, the temperature corresponding to 10 wt % loss was identified as the thermal degradation temperature,  $T_{d10}$ , for easy comparison. The results are listed in Table III. Figure 5 shows the TGA thermograms of several typical three-component binders, from which it can be seen that the thermal decomposition generally follows a three-stage pattern. For all samples, the first-, second- and the third-stage occurred at about  $180\text{--}250$ ,  $250\text{--}400$ , and  $400\text{--}470^\circ\text{C}$ , respectively. The weight loss in the first-stage could be attributed to the reactions of MAA with adjacent MAA or 2-HEMA monomer unit, for which water was lost during the formation of anhydride or ester group, as pointed out in the previous works.<sup>15,18,19</sup> Because the ranges



**Figure 4** DSC thermograms of several three-component binders.



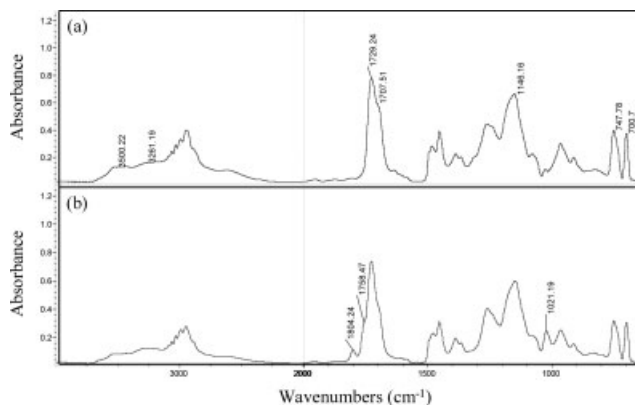
**Figure 5** TGA thermograms of the prepared binders. (a) 10 mol % 2-HEMA (b) molar ratio of BZMA/MAA = 4 : 1.

of thermal decompositions for poly(2-HEMA) and poly(BZMA) were 250–430°C<sup>19</sup> and 250–400°C,<sup>17</sup> respectively, the second-stage decomposition in Figure 5 was due to both 2-HEMA and BZMA segments. This explains why the weight loss of the binder containing 72% BZMA, B72M18H10, in Figure 5(a) was most obvious of the three samples over the temperature range 250–400°C. For the third-stage decomposition, the weight loss could largely be attributed to the MAA units (the thermal decomposition range of poly(MAA) is 370–470°C) in the binders. Therefore, the third-stage degradation temperature increased as the MAA content increased. For example, Figure 5(a) demonstrates that the highest third-stage thermal degradation temperature of the three samples was the binder B54M36H10. Figure 5(b) shows that the extent of the first-stage decomposition increased as the 2-HEMA and MAA content increased; furthermore, the decomposition of the binder “B56M14H30” was most evident over the temperature range of 250–430°C due to its high 2-

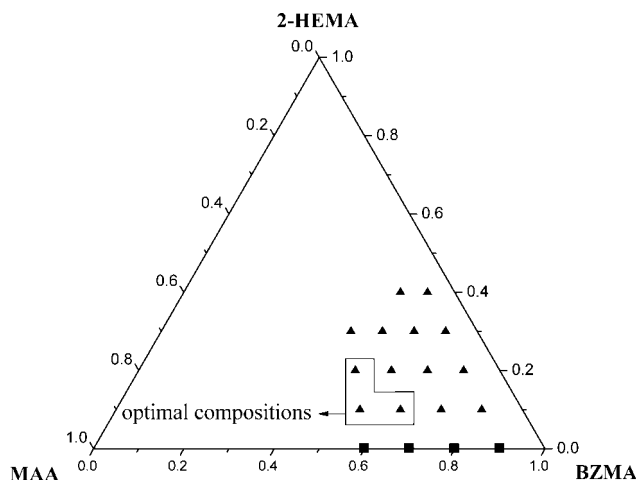
HEMA content. In addition,  $T_{d10}$  also increased with increasing MAA content in the binder, cf. Table III.

### Characterization of chemical structure

Figure 6 (a) illustrates the FTIR spectrum of a prepared three-component binder, B63M27H10. The absorption peaks at 3500 and 3261  $\text{cm}^{-1}$  were due to the —OH stretching bands of hydroxyl group and carboxyl group, respectively. The =C—H stretching band of the aromatic ring (BZMA unit) was observed from 2950 to 3065  $\text{cm}^{-1}$ , and the C=O stretching band of the carbonyl group at 1729  $\text{cm}^{-1}$  (MAA unit) and 1708  $\text{cm}^{-1}$  (2-HEMA unit) could also be observed. For the 2-HEMA unit, the stretching band of the ester group (C—O—C) was observed at 1146  $\text{cm}^{-1}$ .<sup>13</sup> Furthermore, two C—H vibration bands of monosubstituted benzene (BZMA unit) were observed at 701 and 748  $\text{cm}^{-1}$ . The spectrum suggests that the three kinds of acrylate monomers were successfully linked together to form a binder by free-radical polymerization. Figure 6(b) shows FTIR spectrum of the binder, B63M27H10, that had been baked at 220°C for 1 h. The asymmetric and symmetric stretching vibrations of the two C=O groups of a formed anhydride were observed at 1804  $\text{cm}^{-1}$  and 1758  $\text{cm}^{-1}$ , respectively. This result indicates that the anhydride was produced after the binder was baked at 220°C for 1 h. A strong band at 1021  $\text{cm}^{-1}$  was also observed, which might be formed due to the C—O—C stretching vibration in anhydride group or ester group. In addition, the relative intensity of hydroxyl absorption decreased. Therefore, as the binder contained more MAA or 2-HEMA, the weight loss in the first-stage degradation of TGA experiment would be more pronounced due to the dehydration during the formation of anhydride and ester groups, in accordance with the TGA results shown in Figure 5.



**Figure 6** FTIR spectra of the three-component binder, B63M27H10. (a) before and (b) after baked at 220°C for 1h.



**Figure 7** Optimal compositions of prepared binders for a negative-type photoresist.

#### Molecular weight and viscosity

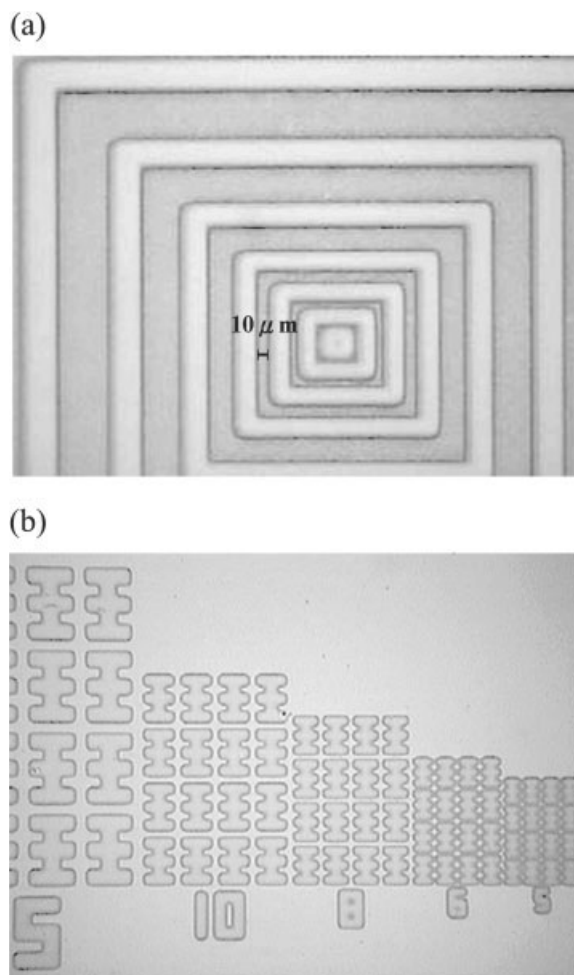
If the molecular weight of the formed three-component binder was too small, the development of the photoresist would be excessively rapid. This made it difficult to control pattern shape during the development process. Even if patterns could be formed, problems such as reduction of the final coating thickness could also occur. On the contrary, as the molecular weight of the binder was too high, the viscosity of the photoresist solution would be high, and this could affect the coatability. Furthermore, the developability might also be deteriorated making it difficult to form sharp patterns.<sup>10</sup> Molecular weights of the three-component binders, measured using GPC, are listed in Table IV. Because AIBN was maintained at 1 wt % of total monomers for all synthesis cases, molecular weights of all formed three-component binders were very close, ca.  $1.9\text{--}2.5 \times 10^4$  g/mol. The acceptable  $M_w$  of a binder in a negative-type photoresist is known to be about  $1.5\text{--}3.5 \times 10^4$  g/mol. This means that our synthesized three-component binders meet the industrial requirement.

Viscosities of the three-component binders are summarized in Table IV. It appears that viscosity increased with increasing 2-HEMA or MAA content; furthermore, the largest allowable 2-HEMA content in the binder was about 30–40 mol %, cf. Figure 1 (▲). When the amounts of carboxyl and hydroxyl groups are high enough, the hydrogen bonding could be formed. Meanwhile, viscosity of binder solution would be higher. For example, for the case of BZMA/MAA ratio maintained at 4, viscosity of the binder B80M20H0, was about 153 cP. However, as 2-HEMA was introduced, viscosities of the prepared binders increased accordingly, and when the binder contained 40 mol % 2-HEMA, B48M12H40, the viscosity reached a high value of 3017 cP. An area in

the ternary composition diagram for preparing binders that complied with the viscosity criteria could thus be sketched, as shown in Figure 1. A binder solution would gel as its composition was outside the area due to polar compatibility between binder polymer and solvent.

#### Acid value

For a negative-type photoresist, the acid value could be adjusted by changing the amount of carboxyl group in the binder. If the acid value of the binder is too low, the solubility of the unexposed photoresist in an alkaline developer liquid would be too low, which may cause an excess amount of residue, i.e., poor developability. Meanwhile, poor adhesion to the substrate may also occur if the acid value is too low. On the other hand, when the acid value is too high, the film may dissolve too much in the developer liquid.<sup>20</sup> Acid values of the prepared three-component binders are listed in Table IV. As expected, the acid



**Figure 8** Optical microscopic image of the patterns prepared by a negative-type photoresist. (a) circuit diagram; (b) resolution test.

value increases as the MAA content is increased. Generally speaking, the acid value of a binder for a negative-type photoresist should be larger than 100. For all the prepared three-component binders, there are only four binders satisfying this requirement, which are B63M27H10, B54M36H10, B48M32H20, and B42M28H30. Among them, viscosity of the binder "B42M28H30" is too high, ca. 2919 cP, for preparing a good photoresist because of poor coat-ability. It follows that a region of optimal compositions for binders in a negative-type photoresist can be drawn in Figure 7.

### Resolution test

Binders with optimal compositions were employed to prepare negative-type photoresists. It is important to know how high resolution the photoresist can achieve after a standard exposure-development process, in case that industrial applications are sought. Figure 8 shows the microscopic images of the negative-type photoresist containing the binder, B54M36H10. It can be seen that the resolution of the photoresist reached the level of 6  $\mu\text{m}$ . This implies that the binders with optimized composition for a negative-type photoresist are suited to industrial applications such as color filter and printed circuit board.

## CONCLUSIONS

In this research, three-component binders composed of MAA, BZMA, and 2-HEMA were prepared by means of free radical copolymerization. The thermal behaviors, chemical structures, and other general properties of the formed binders were investigated. Compositions of the monomers for binder synthesis were determined with the aid of a ternary composition diagram. Several conclusions can be drawn from the experimental observations:

1. As the MAA content was increased, not only was the acid value but also the thermal stability of the binders, e.g.,  $T_g$  and  $T_d$ , enhanced.
2. As a result of the polar compatibility between binder polymer and solvent, viscosity of the binders increased as MAA or 2-HEMA content was increased. The maximum allowable feed

ratios of MAA versus 2-HEMA were ca. 40 and 30–40 mol %, respectively, for binder synthesis.

3. An optimal region in the ternary composition diagram could be constructed, in which appropriate monomer compositions could be selected to synthesize binders for preparing photoresists.
4. For the resolution test of the negative-type photoresist, the results showed that resolution of the circuit could reach the level of  $\sim 6 \mu\text{m}$ .

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## References

1. Jeng, R. J.; Chan, L. H.; Lee, R. H.; Hsiue, G. H.; Chang, H. L. *J Macromol Sci* 2001, 38, 1259.
2. Kubota, S.; Yamawaki, Y.; Moriwaki, T.; Eto, S. *Polym Eng Sci* 1989, 29, 950.
3. Kubota, S.; Moriwaki, T.; Ando, T.; Fukami, A. *J Appl Polym Sci* 1987, 33, 1763.
4. Ueda, M.; Nakayama, T. *Macromolecules* 1996, 29, 6427.
5. Chae, K. H.; Sun, G. J.; Kang, J. K.; Kim, T. H. *J Appl Polym Sci* 2002, 86, 1172.
6. Nasrullah, J. M.; Dhamodharan, R. *J Appl Polym Sci* 2004, 92, 1902.
7. Cho, H.; Kim, J.; Patil, P.; Kim, J. Y.; Kim, T. H. *J Appl Polym Sci* 2007, 103, 3560.
8. Kobayashi, K. *Solid State Technol* 1992, 11, 15.
9. Sabnis, R. W. *Displays* 1999, 20, 119.
10. Ueda, K.; Shioda, S.; Nishijima, H.; Mukaiyama, T.; Mitsuhashi, S. U.S. Pat. 6,558,858 (2003).
11. Sato, M.; Iwasaki, M.; Shinozaki, F.; Inoue, K. US Pat. 5,397,678 (1995).
12. Ueda, K.; Shioda, S.; Nishijima, H.; Mukaiyama, T.; Mitsuhashi, S. U.S. Pat. 6,432,614 (2002).
13. Lee, J.; Aoai, T.; Kondo, S.; Miyagawa, N.; Takahara, S.; Yamaoka, T. *J Polym Sci Part A: Polym Chem* 2002, 40, 1858.
14. Cheng, T. S.; Lee, H. Y.; Lee, C. T.; Chen, H.; Lin, H. T. *Mater Lett* 2003, 57, 4578.
15. Mansur, C. R. E.; Tavares, R. M. I. B.; Monteiro, E. E. C. *J Appl Polym Sci* 2000, 75, 495.
16. Krause, S.; Gormley, J. J.; Roman, N.; Shetter, J. A.; Watanabe, W. H. *J Polym Sci Part A: Polym Chem* 1965, 3, 3573.
17. Demirelli, K.; Coskun, M.; Kaya, E. *J Polym Sci Part A: Polym Chem* 2004, 42, 5964.
18. Rutkaite, R.; Buika, G.; Kreiveniene, N.; Grazulevicius, J. V. *Polym Degrad Stab* 2002, 78, 143.
19. Caykara, T.; Ozyurek, C.; Kantoglu, O.; Erdogan, B. *Polym Degrad Stab* 2003, 80, 339.
20. Baba, K.; Hozumi, S. U.S. Pat. 6,344,300 (2002).