Positive Resist Using Crosslinking and Decrosslinking Properties

Haruyuki Okamura, Kazuo Shin, Masahiro Tsunooka, and Masamitsu Shirai

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan okamura@chem.osakafu-u.ac.jp

Polymeric materials with photoinduced-thermally cleavable property were prepared. A blended system of poly(methacrylic acid-co-ethyl methacrylate) (MAA-EMA), photoacid generator (PAG), and diepoxides having tertiary ester linkages became insoluble in methanol when baked above 120 °C for 10 min without irradiation. On UV irradiation and subsequent post-exposure-bake (PEB) treatment, the blended film dissolved in methanol. The dissolusion profile of the films was strongly dependent on the type of PAG used, structure of diepoxides, fraction of methacrylic acid in MAA-EMA, and MAA-EMA/diepoxide ratio. A mechanism for the dissolution of the crosslinked films was studied by FT-IR spectroscopy. A resist pattern simulation revealed the possibility of sub-micron feature size by using this system.

Keywords: crosslinking, decrosslinking, epoxide, photoacid generator, poly(methacrylic acid-co-ethyl methacrylate), resist pattern simulation

1. Introduction

Positive resists were widely used for the production of electronic devices. Chemically amplified resist system [1] has been studied due to its high sensitivity. The system includes acid-catalyzed depolymerization of polymers, and acid-catalyzed deprotection of acid-labile pendant groups, and/or dissolution inhibitors. Enhancement of mechanical properties of resist films is important to prevent pattern collapse. Mechanical properties of resists were improved by the formation of crosslinking structure in the presence of crosslinker [2]. Positive resist using decrosslinking reactions of crosslinked polymers was designed. Yamaoka et al. [3-5] reported the system based on the thermally induced addition of phenolic hydroxyl or carboxylic acid groups to the double bonds of vinyl ethers to produce acetal linkages. Recrosslinking reaction of the crosslinked resins occurred on irradiation and post-exposure-bake (PEB) treatment in the presence of photoacid generators (PAGs). Photochemically produced acid catalyzed the decomposition of acetal linkages to generate alcohols and aldehydes.

Recently, some thermosets which are thermally or chemically degradable under a given condition have been reported [6-14]. These systems include two specific units. One is the crosslinkable units and the other is the decrosslinkable units. As crosslinking sites, epoxides [6-11], methacrylates [12], bicyclic ortho esters [13,14] and spiro ortho esters [13] have been investigated. The networks formed by epoxide and methacrylate do not decompose once the crosslinking reactions have occurred. As decrosslinking sites, linkages such as disulfide [6,7], acetal [8], primary, secondary or tertiary ester of carboxylic acid [9,12], carbamate [10], and carbonate [11] were studied.

We previously reported the photocrosslinkable systems having thermally degradable properties [15-17]. Network formation occurred by the photoinduced-acid catalyzed reactions between the epoxy moieties of the crosslinker which had tertiary ester linkages and poly(vinylphenol) (PVP) [15]. Thermal treatment of the crosslinked polymers induced the cleavage of the tertiary ester linkages.

In this study, we have studied the thermally degradable thermosets based on the blended system of polymers containing carboxylic acid units, diepoxide and photoacid generator.
Thermal crosslinking reaction of epoxide and carboxylic acid units proceeded on heating in the system. On irradiation, photo-induced acid induced the thermal cleavage of the tertiary ester linkages of the crosslinker at relatively low temperatures. This system is applicable to positive resists because the acid-catalyzed thermal decrosslinking does not occur at the unexposed areas. The concept of this system is shown in Figure 1.

Here, we report the dissolution properties of poly(methacrylic acid-co-ethyl methacrylate) (MAA-EMA) / crosslinker blended systems in the presence of PAGs on irradiation. The crosslinking and decrosslinking properties were discussed in terms of the structure of crosslinkers, MAA-EMA/diepoxides ratio, and photoacid generators used. A pattern simulation was also carried out using dissolution rates of the films.

Fig. 1. Schematic representation of the concept of a thermally crosslinkable system with photo-induced thermally cleavable property.

2. Experimental
2.1. Materials
Methacrylic acid (MAA) and ethyl methacrylate (EMA) were distilled twice before use. 2,2’-Azobisisobutyronitrile (AIBN) was purchased from Aldrich and purified by recrystallization from ethanol. Triphenylsulfonium triflate (TPST) was obtained from Midori Kagaku.

2.2. Polymerization
A series of poly(MAA-co-EMA) (MAA-EMA) was prepared by radical copolymerization in degassed N,N-dimethylformamide (DMF) solution at 60 °C using AIBN as an initiator. The resulting polymers were purified by reprecipitation from tetrahydrofuran (THF)/hexane system. The composition of the copolymers was determined from 1H NMR spectra. The structures of the polymers are shown in Scheme 1. Polymerization condition and characteristics of the polymers are summarized in Table 1.

2.3. Photocrosslinking
All sample films were prepared on silicon wafer by spin-casting from solutions of cyclohexanone containing MAA-EMA, crosslinker, and PAG. The sample films were dried on a hot plate at 90 °C for 1 min. The thickness of films was about 0.5 μm.

Table 1. Polymerization conditions and characterisics of poly(MAA-co-EMA)\(^a\)

<table>
<thead>
<tr>
<th>polymer</th>
<th>monomer in feed</th>
<th>DMF (mL)</th>
<th>polymerization time (h)</th>
<th>yield (%)</th>
<th>(M_n) x (10^{4})</th>
<th>(M_w/M_n)</th>
<th>content of MAA in polymer (mol%)(^c)</th>
<th>(T_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAA(27)-EMA</td>
<td>22.0</td>
<td>6.2</td>
<td>3.0</td>
<td>30</td>
<td>15.1</td>
<td>2.2</td>
<td>27</td>
<td>118</td>
</tr>
<tr>
<td>MAA(46)-EMA</td>
<td>11.0</td>
<td>5.0</td>
<td>4.5</td>
<td>43</td>
<td>20.2</td>
<td>2.3</td>
<td>46</td>
<td>134</td>
</tr>
<tr>
<td>MAA(67)-EMA</td>
<td>36.0</td>
<td>9.0</td>
<td>3.0</td>
<td>33</td>
<td>4.3</td>
<td>2.6</td>
<td>67</td>
<td>158</td>
</tr>
</tbody>
</table>

\(^a\) Polymerization was carried out at 60 °C in DMF. [AIBN]=1.5~1.7 mol% to total monomers. \(^b\) Determined by GPC (THF, polystyrene standards). \(^c\) Determined by \(^1\)H NMR. \(^d\) Glass transition temperature determined from DSC.
except for the sample films for FT-IR measurements (1.0 μm). Irradiation was performed at 254 nm in air using a low-pressure mercury lamp (Ushio ULO-6DQ, 6 W) without a filter. The intensity of the light was measured with an Orca Light Measure UV-M02. Insoluble fraction was determined by comparing the film thickness before and after developments in THF. Thickness of films was measured by interferometry (Nanometrics Nanospec M3000).

2.4. Measurements

1H NMR spectra were observed at 400 MHz using a JEOL LA-400 or at 270 MHz using a JEOL GX-270 spectrometer. FT-IR measurements were carried out using a JASCO IR-410. In-situ FT-IR measurements were carried out by using Litho Tech Japan PAGA-100. Dissolution rate of the blended film was measured using a resist development analyzer RDA-750 (Litho Tech Japan). Resist pattern simulation was carried out using Sigma C SOLID-CL Optical Microlithography Simulator using dissolution rate and exposure dose. Gel permeation chromatography (GPC) was carried out in THF on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex GMNHR-H + GMNHR-N, 8.0 mm i.d. x 30 cm each) and a differential refractometer JASCO RI1530. Number-average molecular weights (Mn) and molecular weight distribution (Mw/Mn) were estimated on the basis of a polystyrene calibration.

3. Results and Discussion

3.1. Crosslinkers

The crosslinkers C1, C2, and C3 were prepared by the reaction of corresponding acid chlorides and a-terpineol, and subsequent epoxidation [15]. The thermal decomposition behavior of these crosslinkers was reported in the previous paper [15]. When heated under nitrogen at the heating rate (10 °C/min) in TGA measurements, C1, C2, and C3 started to lose their weights at 236, 211, and 222 °C, respectively. The weight loss was due to the cleavage of the tertiary ester units. The thermal decomposition temperature of tertiary esters decreased in the presence of strong acids. The onset temperatures for the thermal decomposition of C1, C2, and C3 in the presence of 2.5 wt% of p-toluene sulfonic acid were 110, 165, and 196 °C, respectively.

3.2. Crosslinking and decrosslinking

As shown in Fig. 1, the sample film irradiated and subsequently baked at a given temperature was soluble. However, the film baked without irradiation was insoluble. Thus, this system works as a positive resist.

When MAA(46)-EMA/C3 (10 mol%) blended film containing 5 wt% of PAG was irradiated with a dose of 60 ml/cm² and followed by bake treatments for 10 min, insolubilization of the film was shown in Fig. 2. When the PEB temperature was raised to 150-180 °C, the irradiated film containing FITS as a PAG completely dissolved in methanol. FITS is a photoincident generator that can generate p-toluene sulfonic acid on irradiation with UV light. The insolubilization observed at 90-140 °C was due to the photoinduced acid catalyzed crosslinking reaction of epoxy moiety of C3 and -COOH units in MAA-EMA. The decrease of the insoluble fraction of irradiated sample at higher baking temperatures (> 150 °C) was due to the acid-catalyzed decomposition of tertiary ester linkages in C3. Reaction pathway is shown in Scheme 2.

![Fig. 2. Effect of baking temperature on insolubilization of the MAA(46)-EMA/C3 (10 mol%) blended film containing 5 wt% of PAGs. Film thickness: 0.5 μm. Baking time: 10 min. Development: methanol for 10 min. (○) TPST, with irradiation at 60 ml/cm². (□) FITS, with irradiation at 60 ml/cm². (■) FITS, without irradiation.](image-url)
crosslinking reaction between the epoxy moieties in C3 and carboxylic acid in MAA-EMA proceeded. In the absence of strong acid, cleavage of tertiary ester linkages in C3 did not occur by heating below 200 °C. Thus, using MAA(46)-EMA/C3 (10 mol%)/FITS (5 wt%) blended system, negative image formation is possible if irradiation dose and bake conditions are optimized. Furthermore, this system gives a positive image when PEB treatment is done at 150-180 °C. On the other hand, if TPST was used instead of FITS, this system used as only positive resist.

![Scheme 2](image)

Figure 3 shows the effect of baking time on insolubilization of MAA(46)-EMA / C3 (10 mol%) / FITS (5 wt%) blended film with and without irradiation. When irradiated, the insoluble fraction increased, reached a maximum value at 78 % on baking for 7 min, and decreased with longer bake treatment. Insolubilization of the irradiated film was not observed after bake treatment for 14 min. On the other hand, the insoluble fraction of the unirradiated film continuously increased with baking time. Insoluble fraction of the film was 76% and 85% after bake treatment for 7 and 14 min, respectively.

![Insoluble fraction vs. Baking time](image)

Fig. 3. Effect of baking time on insolubilization of the MAA(46)-EMA/C3 (10 mol%) blended film containing 5 wt% of FITS. Film thickness: 0.5 μm. Baking temperature: 140 °C. Development: methanol for 10 min.

(□) Irradiated with a dose of 60 mJ/cm².

(■) Unirradiated.

Fig. 4. Effect of baking temperature on insolubilization of the MAA(67)-EMA/C3 (10 mol%) blended film containing 5 wt% of FITS. Film thickness: 0.5 μm. Baking time: 10 min.

(□) Irradiated with a dose of 60 mJ/cm².

(■) Unirradiated.

Content of crosslinkers in the blended system and content of MAA moieties in the base polymers affected the insolubilization profiles. The insolubilization profiles of MAA(46)-EMA / C3 (10 mol%) / FITS (5 wt%) and MAA(46)-EMA / C3 (20 mol%) / FITS (5 wt%) on irradiation and PEB treatment at 140 °C for 10 min were compared. The insolubilization curve of the film containing 20 mol% of C3 was almost the same as that of the film containing 10 mol% of C3, except slight shift of the former one to lower baking temperature about 10 °C. Insolubilization profiles of the film MAA(67)-EMA/C3 (10 mol%) / FITS (5 wt%) is shown in Fig. 4. The insoluble fraction of the blended films with MAA(67)-EMA baked at 110-130 °C dramatically increased compared with those with MAA(46)-EMA. The irradiated blended film showed higher
insolubilization fractions than that baked at 100–160 °C after irradiation. By baking the irradiated blended films with MAA(67)-EMA at 160 °C or 180 °C after irradiation, complete dissolution was observed. When the film was baked at 200 °C after irradiation, re-insolubilization was observed. The re-increase of the insolubilization fraction is due to the formation of carboxylic anhydride moieties. Thus, it is important to optimize both MAA/crosslinker ratio and MAA unit fraction in MAA-EMA.

Fig. 5. Effect of MAA unit fraction in MAA(X)-EMA/C3 (20 mol%)/TPST(1 wt%) on insolubilization profiles. Film thickness: 0.5 μm. Baking time: 10 min. Development: methanol for 10 min.

(○, ●) X = 27. (□, ■) X = 47. (△, ▲) X = 67. Open symbol: irradiated with a dose of 60 mJ/cm². Closed symbol: unirradiated.

Figure 5 shows insolubilization profiles of MAA(X)-EMA / C3(20 mol%)/TPST(1 wt%) blended films. All of the films irradiated with 60 mJ/cm² and dissolved in methanol after PEB treatment at 80-200 °C for 10 min. Dissolution properties were slightly dependent on MAA content. Insolubilization of blended films was observed by baking at 100 °C for the film with MAA(67)-EMA and at 120 °C for the films with MAA(46)-EMA and MAA(27)-EMA, and insoluble fraction of the films increased with baking temperature, and reached more than 80 % by baking at 140-180 °C in all blended films. The irradiated MAA(X)-EMA / C3(20 mol%)/TPST(1 wt%) blended films were soluble in methanol after baking at 80-200 °C regardless of MAA unit fraction in MAA-EMA. It is because the insoluble fraction was not reflected the degree of crosslinking between MAA-EMA and C3. When certain degree of crosslinking occurred, the blended film became insoluble in solvents. The dependence of conversion of an epoxide and a tertiary ester on dissolution properties will be discussed below.

The structure of the crosslinkers also slightly affected the insolubilization properties. Insolubilization profiles of MAA(27)-EMA / crosslinker(10 mol%) / TPST blended films were shown in Fig. 6. Insoluble fraction of blended films increased, reached to maxim, and decreased with baking temperature. The insoluble fractions of the films were 0, 36, 84 % for the film with C2, C1, and C3, respectively. When the films were baked at 160 °C, the insoluble fraction of the films was about 80 % for all films. The irradiated films were soluble in methanol after baking at 80-200 °C regardless of the type of the crosslinker. In MAA(27)-EMA / C3(10 mol%) / TPST blended system, positive imaging was considered to be possible by baking at 140 or 160 °C after irradiation.

Fig. 6. Effect of crosslinker on insolubilization profile of the MAA(27)-EMA /crosslinker (5 mol%) blended film containing 1 wt% of TPST. Film thickness: 0.5 μm. Baking time: 10 min. Development: methanol for 10 min.


Figure 7 shows the effect of concentration of crosslinker on insolubilization profiles of MAA(27)-EMA/C3/TPST(1 wt%) blended films. The irradiated films dissolved in methanol regardless of concentration of C3 after PEB treatment at 160 °C for 10 min. When unirradiated sample was baked at 160 °C for 10 min, insoluble fraction of the films increased with the contents of C3 in film. Thus, positive
imaging can be obtained by using MAA(27)-EMA and 3-40 mol% of C3, and TPST (1 wt%).

![Graph showing the effect of content of C3 on insolubilization of the MAA(27)-EMA/crosslinker (20 mol%) blended film containing 1 wt% of TPST. Film thickness: 0.5 μm. Baking condition: 160 °C for 10 min. Development: methanol for 10 min. (◯) Irradiated with a dose of 60 mJ/cm². (■) Unirradiated.]

![Graph showing sensitivity curves of MAA(27)-EMA/C3(5 mol%)/TPST(1 wt%) blended films. Developer: methanol. (◯) Without prebake. PEB: 140 °C for 10 min. (□) Prebake: 160 °C for 10 min. PEB: 120 °C for 10 min.]

Dependence of the dissolution rate of the MAA-EMA/crosslinker/PAG blended films on exposure dose was investigated. Figure 8 shows the stress curves of MAA(27)-EMA/C3 (5 mol%)/TPST(1 wt%) blended films. Dissolution rate of the film was dramatically increased with exposure dose above 2 mJ/cm² and subsequent baking at 140 °C for 10 min. When the film was baked at 160 °C for 10 min before exposure, the sensitivity was 5 mJ/cm² by PEB treatment at 120 °C for 10 min. Baking temperature strongly affected the sensitivity curves.

3.3 Crosslinking and decrosslinking mechanism

Scheme 2 shows a proposed reaction mechanism of MAA-EMA/crosslinker/PAG blended system. On irradiation, FITS and TPST were photolyzed to generate p-toluenesulfonic acid and triflic acid, respectively. The acid catalyzed the crosslinking reaction of carboxylic acid moiety in MAA-EMA and epoxy moiety in the crosslinker. Proper bake treatment of irradiated films enhanced the crosslinking reactions in using FITS as a PAG. Acid-catalyzed cleavage of tertiary ester linkages in the crosslinker occurred by bake treatments. Using TPST, photo-induced crosslinking was not observed, because photo-induced acid catalyzed crosslinking and cleavage of tertiary ester linkages in crosslinker occurred simultaneously. Only thermal crosslinking reaction proceeded by bake treatments. The thermally crosslinked MAA-EMA/crosslinker/TPST was stable up to 200 °C.

![Graph showing FT-IR spectra of MAA(46)-EMA/C3(20 mol%) blended film containing 1 wt% TPST. Film thickness: 1.0 μm. Solid line: Baked at 140 °C for 10 min. Bold line: Baked at 140 °C for 10 min, irradiated with a dose of 60 mJ/cm², and baked at 140 °C for 3 min.]

Figure 9 shows the FT-IR spectral changes of crosslinked MAA(46)-EMA / C3(20 mol%) / TPST(1 wt%) blended films by PEB treatment. Crosslinking of the film was carried out by baking at 140 °C for 10 min before irradiation with 60 mJ/cm². The peak at 840 cm⁻¹ ascribed to epoxide of C3 was not observed in the crosslinked films, suggesting quantitative reaction of epoxide and carboxylic acid. After PEB treatment at 140
°C for 3 min, the peak at 1720 cm⁻¹ ascribed to carboxylate of C3 decreased. The peak was not completely disappeared because of the overlap of carboxylate units of EMA at 1720 cm⁻¹.

![Graph](image)

**Fig. 10.** Thermal and photo-thermal crosslinking or decrosslinking of MAA(46)-EMA/C3(20 mol%) / TPST (1 wt%) blended film measured by in-situ FT-IR spectroscopy. Film thickness: 1.0 μm.

- **Carboxylate group (1720 cm⁻¹):**
  - Solid line: baked at 140 °C.
  - Broken line: baked at 140 °C after irradiation with 60 mJ/cm².
  - Dotted line: baked at 140 °C after prebaked at 140 °C for 10 min and irradiated with 60 mJ/cm².

- **Epoxy group (840 cm⁻¹):**
  - Bold line: baked at 140 °C.
  - Bold-broken line: baked at 140 °C after irradiation with 60 mJ/cm².

Precise observation of crosslinking and decrosslinking reactions was carried out using in-situ FT-IR measurements. Figure 10 shows the changes of peak intensities of carboxylate ester unit and epoxy unit of C3 in MAA(46)-EMA / C3(20 mol%) / TPST(1 wt%) blended film on baking at 140 °C. The slight decrease in ester C=O was observed because small amounts of C3 in the film were vaporized by baking at 140 °C (solid line in Fig. 10). The decomposition of ester C=O of C3 did not occur in the condition. The peak due to epoxide decreased with baking time (bold line in Fig. 10). It suggests that the reaction between epoxide and carboxylic acid in MAA-EMA, or polymerization of epoxide occurred by baking. The reaction of epoxide with carboxylic acid produces a carboxylate ester. Regrettfully, the increase of the peak due to carboxylate ester C=O was not observed (bold line in Fig. 10). It suggests that degree of the formation of carboxylate ester was not so high among the reacted epoxide. When the film was irradiated with a dose of 60 mJ/cm², the decomposition of carboxylate ester was observed (broken line and dotted line in Fig. 10). The decomposition was completed within 30 seconds in both irradiated film and prebaked film before irradiation. The reaction rate of epoxide in the irradiated film was faster than that in the unirradiated film (bold broken line and bold line in Fig. 10). Comparing the reaction rate of crosslinking and decrosslinking of MAA(46)-EMA / C3(20 mol%) / TPST(1 wt%) blended film irradiated with 60 mJ/cm² and PEB at 140 °C, the rate of decrosslinking reaction was much faster than that for crosslinking reaction. Positive imaging was possible by longer bake treatment enough to crosslink the base polymer in unirradiated region. The control of two factors, acid-catalyzed cleavage of carboxylate esters and thermal crosslinking by epoxide and carboxylic acid, is important to accomplish positive imaging. With the decrease of irradiation dose, the cleavage of carboxylate esters in C3 occurred slowly. Crosslinking reaction dominates in the film irradiated lower than specific irradiation dose. The pathway of imaging in the film was effective for high-sensitive positive resist by optimizing baking conditions.

### 3.4. Resist pattern simulation

Resist pattern simulation was carried out using the simulation program SOLID-CL [20]. The simulations were performed using dissolution rate of the sample. In the case of MAA(27)-EMA / C3 (5 mol%) / TPST(1 wt%) blended film (film thickness: 1.0 μm), 0.3 μm L/S patterns were estimated to be obtained when irradiated at 2.0 μm.

![Pattern Simulations](image)

**Fig. 11.** Resist pattern simulation of MAA(27)-EMA/C3(5 mol%) blended film containing 1 mol% TPST. Film thickness: 1.0 μm. PEB: 140 °C for 10 min. Development: methanol for 6 min. NA: 0.54.
mJ/cm², baked at 140 °C for 10 min, and followed by development with methanol for 6 min (Fig. 11). When the film was baked at 160 °C for 10 min before irradiation, insolubilization of the film occurred. The process affected the resist sensitivity. However, possibility of 0.3 μm L/S pattern formation was suggested under the following condition (Exposure dose: 4.0 mJ/cm², PEB: 120 °C for 10min, development: methanol for 20 sec).

4. Conclusion

The photocrosslinkable system having thermally decrosslinkable property based on the blend of MAA-EMA and thermally degradable crosslinkers was devised. MAA-EMA/crosslinker blended films containing PAG became insoluble in solvents on UV irradiation and subsequent PEB treatment. With a rise in the PEB temperature, the insoluble fraction of the irradiated films increased, passed through a maximum value, and decreased at elevated baking temperatures. The initial insolubilization was due to the photoinduced acid catalyzed reaction between epoxy units and -COOH groups. The decrease of the insoluble fraction was due to the decrosslinking reaction because of the thermal cleavage of tertiary ester units in the crosslinker molecules. The baking temperature for the crosslinking and decrosslinking was strongly dependent on the type of PAG used and MAA-content in MAA-EMA. Thermal crosslinking was observed without irradiation. The system worked as positive resist with high sensitivity. The baking and irradiation processes affected sensitivity curves. Resist pattern simulation revealed the possibility of sub-micron feature size patterning by using the blended systems.

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