Three-Component Photopolymers Based on Thermal Cross-Linking and Acidolytic De-Cross-Linking of Vinyl Ether Groups. Effects of Binder Polymers on Photopolymer Characteristics

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A series of terpolymers with carboxyl and aliphatic alcohol groups in the side chain were synthesized and used for the three-component photopolymers, consisting of the terpolymer as a binder, the vinyl ether monomer, and a photoacid generator. These photopolymers act as a positive working photoresist with the process of prebaking, exposure to light, and postexposure baking. The effect of the physical properties of the polymers, such as acid value, molecular weight, acid component, and glass transition temperature on the characteristics of the photopolymer, including the thermal cross-linking reactivity and the sensitivity due to acidolytic de-cross-linking, was investigated. An increase in the acid value and molecular weight and decrease of glass transition temperature in the binder polymer increase the insolubilization rate based on the thermal cross-linking reaction. An increase in the acid value and glass transition temperature and a decrease in the molecular weight enhance the sensitivity of the positive resist based on the chemically amplified de-cross-linking reaction. A positive working photoresist with a sensitivity of 0.7 mJ/cm^2 and a high γ value was obtained by optimizing the structure of the terpolymer.

1. Introduction

Since a series of onium salts which produce strong acids radiochemically were reported,[1–4] the application of them to the design of a number of chemically amplified resist system has been studied. These include the photoacid-catalyzed ring-opening polymerization of oxirane pendant groups,[5,6] acid-catalyzed depolymerization of polymer main chains,[7–10] and acid-catalyzed deprotection of acid-labile pendant group[10–18] or dissolution inhibitor.[19]

We previously reported[20] that two-component photopolymers composed of *p*-hydroxystyrene-*p*-(2-(vinyloxy)ethoxy)styrene copolymer (PVES) and a photoacid generator (PAG) have either positive or negative working behavior, depending on such process conditions as prebaking temperature and exposure energy. This behavior results from the intricate reactions of the pendant vinyl ether groups. The vinyl ether groups react with the hydroxyl group of phenol at high temperature to form cross-linked networks with an acetal structure. These cross-links are cleaved acid-catalytically via protonation by photogenerated acids and subsequent hydrolysis to give alcohol and aldehyde. We also reported that the vinyl ether groups undergo the competing reactions of cationic polymerization[21–23] and acidolysis by photogenerated acids, depending on the process conditions.[20]

For the present study, terpolymers with carboxyl and aliphatic alcohol groups in the side chain were prepared and used for the three-component photopolymer systems which consisted of the binder polymer, the vinyl ether monomer, and PAG. The effects of the physical properties of the binder polymers, such as their acid value,

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(1) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307.

(2) Crivello, J. V., Lam, J. H. W. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 977.

(3) Yamaoka, T.; Morita, H. *Kankousei Jushi*, **1988**.

(4) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Macrmolecules* **1988**, *21*, 2001.

(5) Schlesinger, S. I. *Polym. Sci. Eng.* **1974**, *14*, 513.

(6) Schlesinger; S. I.; *Photogr. Sci. Eng.* **1974**, *18*, 387.

(7) Frechet, J. M. J.; Bouchard, F.; Eichler, E.; Houlihan, F. M.; Iizawa, T.; Kryczka, B.; Willson, C. G. *Polym. J.* **1987**, *19*, 31.

(8) Frechet, J. M. J.; Bouchard, F.; Houlihan, F. M.; Eichler, E.; Kryczka, B.; Willson, C. G. *Makromol. Chem. Rapid. Commun.* **1986**, *7*, 121.

(9) Jiang, Ying; Frechet, J. M. J. *Macromolecules* **1991**, *24*, 3528.

(10) Wilson, C. G.; Ito, H.; Frechet, J. M. J.; Tessier, T. G.; Houlihan, F. M. *J. Electrochem. Soc.* **1986**, *133*, 181.

(11) Yamaoka, T.; Nishiki, M.; Koseki, K. *Polym. Eng. Sci.* **1989**, *29*, 856.

(12) Hayashi, N.; Ueno, T.; Hesp, S.; Toriumi, M.; Iwayanagi, T. *Polymer* **1992**, *33*, 1583.

(13) Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. *Microelectron. Eng.* **1991**, *13*, 33.

(14) Ito, H.; Ueda, M. *Macromolecules* **1988**, *21*, 1475.

(15) Ito, H.; Ueda, M. *Macromolecules* **1990**, *23*, 2885.

(16) Ito, H.; Ueda, M. *J. Photopolym. Sci. Technol.* **1990**, *3*, 335.

(17) Frechet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1983**, *24*, 995.

(18) Frechet, J. M. J.; Tessier, T. G.; Willson, C. G.; Ito, H. *Macromolecules* **1985**, *18*, 317.

(19) Pawlowski, G.; Przybilla, K. J.; Spiess, W.; Wengenroth, H.; Roschert, H. *J. Photopolym. Sci. Technol.* **1992**, *5*, 55.

(20) Moon, S.; Naitoh, K.; Yamaoka, T. *Chem. Mater.* **1993**, *5*, 1315.

(21) Crivello, J. V.; Lee, J. L.; Conlon, D. A. *J. Radiat. Curing*, **1983**, Jan, 6.

(22) Crivello, J. V.; Lee, J. L. *J. Radiat. Curing* **1983**, *21*, 1097.

(23) Yamamoto, K.; Higashimura, T. *J. Radiat. Curing* **1974**, *12*, 613.

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Table 1. Physical Properties of Binder Polymers

	components (mol %)						av mol wt[g]					
terpolymers	BzMA[a]	MAA[b]	HEMA[c]	HexMA[d]	AA[e]	acid value[f]	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_g[h] (°C)	min[i] (%)	max[j] (%)
SP-1	63.1	28.2	8.7			193	14 200	30 000	2.11	111	66	76
SP-2	65.2	15.2	19.5			123	13 000	26 200	2.02	91.5	42	51
SP-3	63.4	13.7	22.9			58	14 300	32 100	2.25	81.4	39	68
SP-4	66.4	13.6	20			121	32 100	75 200	2.34	94.2	29	61
SP-5	68.7	13.6	17.7			107	25 700	180 400	7.01	93.5	12	49
SP-6		20.1	20.1	59.8		127	16 300	33 200	2.04	66.4	49	98
SP-7	62.1		28.2		9.8	48	15 700	34 800	2.22	71.8	44	83

[a] Benzyl methacrylate. [b] Methacrylic acid. [c] 2-Hydroxyethyl methacrylate. [d] *n*-Hexyl methacrylate. [e] Acrylic acid. [f] mg of KOH/g of resin. [g] Measured by GPC (relative to polystyrene standards), g/mol. [h] Measured by DSC. [i] Minimum amount of reacted vinyl ether group for insolubilization. [j] Maximum amount of reacted vinyl ether group.

molecular weight, acid component, and glass transition temperature (T_g), on the characteristics of the photopolymers were investigated. In addition, a similar investigation was carried out with novolac resin as the binder polymer for comparing with the terpolymers.

2. Experimental Section

Materials. Diphenyliodonium 8-anilinonaphthalene-1-sulfonate (ANS-DPI)[24] and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS)[25-27] as PAGs and 2,2-bis(4-(2-(vinyloxy)ethoxy)phenyl) propane (BPA-DEVE)[28,29] as a cross-linking agent were synthesized according to the literature.

Synthesis of Terpolymers. The series of terpolymers listed in Table 1 were synthesized in a similar manner. A typical example is given as follows: To a round-bottomed flask, equipped with an overhead stirrer, reflux condenser, thermometer, dropping funnel, and nitrogen inlet were added 447.61 g of 2-methoxy-1-propanol (MPO), 158.60 g (0.9 mol) of benzyl methacrylate, 25.83 g of methacrylic acid, and 39.04 g of 2-hydroxyethyl methacrylate. The flask contents were stirred at 70 °C and then 3.72 g of 2,2′-azobis[2,4-dimethylpentanenitrile] (AMPN) was added as a free-radical initiator. The mixture was held at 70 °C for 4 h. An additional 0.93 g of AMPN and 73.82 g of MPO were then added to the mixture. Total AMPN was 1.25 mol % of total monomer concentration. After 2 h, the reaction was complete. The reaction mixture was diluted with methyl ethyl ketone and reprecipitated in distilled water. The product was characterized by FT-IR and ^{1}H and ^{13}C NMR. The composition of the resulting terpolymer was determined by comparing the integral ratios on ^{13}C NMR spectra.

IR OH stretch of aliphatic alcohol at 3500 cm^{-1}, OH stretch of carboxylic acid at 3180–3320 cm^{-1}, CH stretch at 2900–3100 cm^{-1}, C=O stretch at 1730 cm^{-1}; ^{1}H NMR (acetone-d_6) 7.4 ppm (5H of phenyl group), 3.7–4.0 ppm (CH_2CH_2 of 2-hydroxyethyl group), 5.0 ppm (CH_2 of benzyl group); ^{13}C NMR (acetone-d_6) 60–67 ppm (CH_2 of benzyl group, 2C of 2-hydroxy ethyl group), 136 ppm (C1 of phenyl group), 129 ppm (C2, C3, C4 of phenyl group), 176–178 ppm (C=O).

Measurements. FT-IR spectra were measured with a Horiba FT-200 Fourier transform infrared spectrometer. NMR spectra were recorded on a JEOL GSX-400 spectrometer. UV–visible spectra were recorded on a Hitachi U-3000 spectrophotometer. The molecular weights of the terpolymers were determined on a TOSO HLC-802 UR gel permeation chromatograph (GPC) with a TSK-GEL H-type column (polystyrene gel column) in tetrahydrofuran (THF) using polystyrene as the standard. T_g's of the terpolymers were measured under increasing temperature by 10 °C/min with differential scanning calorimetry (DSC) on a Rigaku Denki Co. CN805E1 thermal analyzer. The acid values were determined by titrating each terpolymer dissolved in THF with a 0.1 N aqueous solution of KOH. The resist film thickness was measured with a Tencor Alphastep 200.

Evaluation of Gel Fraction. The photosensitive solution was formulated with the terpolymer, 3.3 mol % BPA-DEVE, which was equivalent to ca. 9 mol % of the sum of the carboxylic acid unit and the aliphatic alcohol unit in all the terpolymers, and 2 mol % ANS-DPI of the terpolymer. The photosensitive films were prepared by spin-coating this solution on a Si wafer to give a 1.0-μm-thick film. The films were baked at 60–120 °C for 1–10 min and developed in DN-3C aqueous base developer: H_2O = 1:2 in weight ratio and postbaked at 120 °C for 10 min. The thickness of the film remaining after postbaking was measured and normalized to that obtained after baking.

Evaluation of the Amount of Reacted Vinyl Ether Group. The amount of reacted vinyl ether group required for insolubilization was measured by FT-IR internal reflectance spectroscopy. The photosensitive films were dried under vacuum at room temperature. The ratio of the absorbance of the peak due to $\nu_{C=C}$ (1608 cm^{-1}) of the vinyl ether group to that of the peak (1581 cm^{-1}) due to ANS-DPI was evaluated. The film was taken as the sample with an unreacted vinyl ether group. The ratio of the two peaks of the film containing no vinyl ether monomer was also evaluated. This film was taken as the sample for a 100% reacted vinyl ether group. The amount of reacted vinyl ether group required for insolubilization was obtained by evaluating the proportional relation of the ratio of the two peaks of the desired film between the sample with an unreacted vinyl ether group and that with a 100% reacted vinyl ether group.

Evaluation of the Acidolytic Rate for the Adducts of BPA-DEVE and Para-Substituted Phenols. To an adduct in acetonitrile solution, a definite amount of HCl aqueous solution was added. The concentration of the acid in the acetonitrile solution was calculated. The ratio of the decreasing concentration with an increasing reaction time for the adduct, using the peak at 271 nm on UV spectra, was evaluated by tracing a change of the ratio of the absorbance to the molar extinction coefficient with an increase in reaction time. As the decomposition reaction proceeded, the absorption band due to aromatic $\pi\rightarrow\pi^*$ transitions of the adduct was reduced and shifted bathochromically to the peak with no further change. Hammett substituent constants were obtained from the literature.[30]

Sensitivity Measurements. The photosensitive films were prepared by spin-coating a solution composed of each terpolymer listed in Table 1, 3.3 mol % BPA-DEVE, and 2 mol % DIAS of the terpolymer. The films were prebaked at 120 °C for 10 min, exposed to 365-nm light from a filtered super-high-pressure mercury lamp, and postexposure-baked under the same conditions as the prebake. Development was done in a 2 wt % aqueous solution of tetramethylammonium hydroxide (TMAH):methanol = 1:1 in weight ratio, or DN-3C aqueous base developer:H_2O = 1:2 in weight ratio. The developed film was postbaked at 120 °C for 10 min. The film thickness was normalized to that obtained after postexposure baking (PEB).

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(24) Naitoh, K.; Ishi, K.; Yamaoka, T.; Omote, T. *Polym. Advan. Technol.*, in press.

(25) Yamaoka, T.; Adachi, H.; Matsumoto, K.; Watanabe, H.; Shirosaki, T. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1709.

(26) Naitoh, K.; Yamaoka, T.; Umehara, A. *Chem. Lett.* **1991**, 1869.

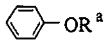
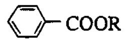
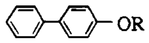
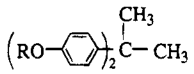
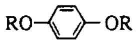
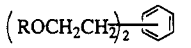
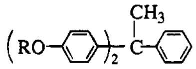
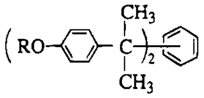
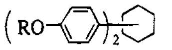
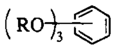
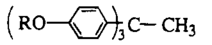
(27) Naitoh, K.; Yamaoka, T.; Umehara, A. *Polym. Advan. Technol.* **1992**, *3*, 117.

(28) Gallucci, R. R.; Going, R. C. *J. Org. Chem.* **1983**, *48*, 342.

(29) Crivello, J. V.; Conlon; D. A. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1785.

(30) Nihonkagakukai; *Kagakubinran Kisohen II*; Maruzen Co. Inc.: Tokyo, 1966.

Table 2. Dissolution Rates and Sensitivities in Novolac Resin Films Containing Vinyl Ether Monomers

binder polymer	cross-linking agent	structure	dissolution rate (nm/s) (sensitivity (mJ/cm^2)) 50 °C	80 °C	120 °C
novolac resin	none		20.1	16.6	14.5
	P-EVE[b]		2.69 (3.7)	1.06 (3.8)	0.52 (132)
	B-EVE[c]		3.03	2.08	0.94
	BP-EVE[d]		1.0	0.95	0.43
$\bar{M}_n$: 12 500[p]	BPA-DEVE[e]		0.75 (2.7)	0.43 (15.2)	0.03 (152)
$\bar{M}_w$: 15 400[p]	HP-DEVE[f]		0.76 (9.0)	0.56 (36)	0.07 (216)
	DEB-DEVE[g]		0.87 (5.4)	0.65 (9.0)	0.35 (18)
	TBE-DEVE[h]		0.29	0.02	0.00
	BHPB-DEVE[i]		0.13	0.01	0.00
	BHPCH-DEVE[j]		0.21	0.05	0.03
	THB-TEVE[k]		0.30 (3.5)	0.08 (7.0)	0.02 (162)
	THPE-TEVE[l]		0.46	0.13 (20)	0.03
	BHE-DEVE[m]	R—O—R	1.52	1.38	0.93 (203)
	BHET-DEVE[n]	$\mathrm{RO{-}(CH_2)_2{-}OR}$	1.19	1.21	0.53
	BHB-DEVE[o]	$\mathrm{RO{-}(CH_2)_4{-}OR}$	0.78	0.56	0.41

[a] R: $-CH_2CH_2OCH{=}CH_2$. [b] 2-Phenoxyethyl vinyl ether. [c] 2-(Vinyloxy)ethyl benzoate. [d] 4-(2-(Vinyloxy)ethoxy)biphenyl. [e] 2,2-Bis(4-(2-(vinyloxy)ethoxy)phenyl)propane. [f] 1,4-Bis(2-(vinyloxy)ethoxy)benzene. [g] 1,4-Bis(2-(2-(vinyloxy)ethoxy)ethyl)benzene. [h] 1-Phenyl-1,1-bis(4-(2-(vinyloxy)ethoxy)phenyl)ethane. [i] 1,4-Bis(2-(4-(2-(vinyloxy)ethoxy)phenyl)propyl)benzene. [j] 1,4-Bis(4-(2-(vinyloxy)ethoxy)phenyl)cyclohexane. [k] 1,3,5-Tris(2-(vinyloxy)ethoxy)benzene. [l] 1,1,1-Tris(4-(2-(vinyloxy)ethoxy)phenyl)ethane. [m] Bis(2-(vinyloxy)ethyl)ether. [n] 1,2-Bis(2-(vinyloxy)ethoxy)ethane. [o] 1,4-Bis(2-(vinyloxy)ethoxy)butane. [p] Measured by GPC (relative to polystyrene standards), g/mol.

3. Results and Discussion

3.1. Novolac Resin Based Photopolymers. *3.1.1. Insolubilization of Novolac Resin Film Containing Vinyl Ether Monomer.* All the resins and all the vinyl ether monomers used in this report exhibit a good solubility in diethylene glycol dimethyl ether solvent. All the photoresist solutions containing a PAG were prepared by dissolving the components in a mixed solvent (3:1 by weight ratio) of diethylene glycol dimethyl ether and methanol. An evidence of phase separation was not found in the formulations at room temperature. Upon coating, the solutions formed smooth films, with good planarizing properties.

The dissolution rates of novolac resin films containing vinyl ether monomers of 6 mol % to the polymer were investigated as shown in Table 2. The films were baked at 50−120 °C for 10 min and their dissolution rates in 2.38 wt % TMAH aqueous solution were measured.

The dissolution rate of novolac resin is inhibited by the addition of a vinyl ether monomer, while the thermal cross-linking reaction does not proceed at baking temperatures lower than 50 °C. As shown in Table 2, the novolac resin films containing bi- or trifunctional vinyl ether monomers with aromatic hydrocarbon in the structure have lower dissolution rates than those containing monofunctional monomers, or bifunctional monomers with aliphatic hydrocarbon. That is, the bi- and trifunctional vinyl ether monomers with aromatic hydrocarbon have a higher solubility inhibition effect than the monofunctional monomers, or the bifunctional monomers with aliphatic hydrocarbon.

When the baking was performed at 80 and 120 °C, the novolac resin film containing a vinyl ether monomer was insolubilized due to the thermal cross-linking reaction. The bi- or trifunctional vinyl ether monomers with aromatic hydrocarbon in the structure are more effective in insolubilizing novolac resin than the monofunctional monomers, or the bifunctional monomers with aliphatic hydrocarbon. These results mean that insolubilization of the novolac resin film, accomplished by the thermal cross-linking of vinyl ether monomers, is partially assisted by the solubility inhibition effect of the monomers.

3.1.2. Dependence of Resist Characteristics on Vinyl Ether Structure. Novolac resin films insolubilized by vinyl ether monomers offer positive resists since these become soluble in an aqueous base developer upon irradiation with ultraviolet light followed by baking at an appropriate temperature. The mechanism that gives the positive resist is due to de-cross-linking or deblocking by photogenerated acids. Therefore, the resist characteristics are dependent on various factors, such as the structure and functionality of the vinyl ether monomer, PB and PEB temperature, the quantum yield of acid generation, and the rate of acidolysis of the cross-links.

The acidolysis reaction requires a stoichiometric amount of water,[20] so the water content in air may

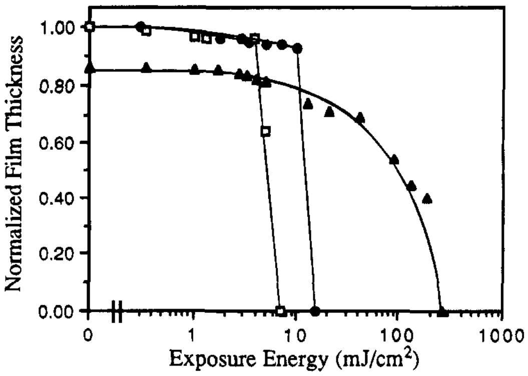


Figure 1. Comparison of characteristic curves of the positive resists consisting of novolac resin and mono- ((▲) BP-EVE), bi- ((●) BPA-DEVE), or trifunctional ((□) THB-TEVE) vinyl ether monomer. PAG: DIAS, PB, PEB: 80 °C 10 min.

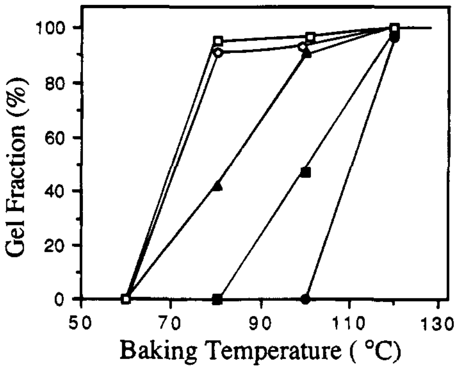


Figure 2. Insolubilization of a series of terpolymers due to thermal cross-linking by BPA-DEVE. (■) SP-1, (●) SP-2 and SP-3, (▲) SP-4, (O) SP-5 and SP-7, (□) SP-6.

influence the lithographic performance. All lithographic evaluation performed in this paper was carried out under the circumstances of relative humidity ranging from 63% to 74%, which was measured with psychrometer.

Figure 1 demonstrates the effect of vinyl ether monomer functionality on the characteristic curves. These curves as positive working resists were determined with novolac resin films containing mono-, bi-, or trifunctional monomer, in which the concentration of the monomer was adjusted so that the vinyl ether group was equivalent to 6 mol % of the phenol group. The monofunctional vinyl ether monomer results in the low sensitivity and imperfect insolubility of the unexposed areas of the novolac resin layer. The bi- and trifunctional monomers show the drastically improved resist characteristics involving sensitivity and contrast. The sensitivity values of the resists listed in Table 2 reveal the effect of the vinyl ether monomers as cross-linking agents.

3.2. Aqueous Base-Soluble Terpolymer. *3.2.1. Effect of Acid Value on Thermal Behavior.* Differences in physical properties of binder polymers such as acid value, molecular weight, acid component, and T_g influence thermal cross-linking reactivity, insolubility, and developability in an aqueous base developer. The effect of acid value on thermal behavior was investigated prior to the other factors by using binder polymers with physical properties different from one another (Table 1).

Figure 2 shows the gel fraction for the terpolymer films containing BPA-DEVE when the baking was done for 3 min. The solubility inhibition effect of vinyl ether monomers was not shown differently from the case of the novolac resin. The curves for the terpolymers, SP-1, SP-2, and SP-3, with the acid values different from one another clearly show a difference in the insolubilization rate due to thermal cross-linking. SP-1 film, which has the highest acid value, starts to become insoluble at 80 °C and is completely insoluble at 120 °C, while SP-2 and -3 films, with lower acid values, start to become insoluble at 100 °C. Furthermore, SP-3 film, with the lowest acid value, was not insolubilized with the baking time of 5 min at 100 °C, but SP-2 film showed a gel fraction of 70% under the same conditions. These results indicate that a higher acid value, that is, a higher MAA content, leads to more rapid insolubilization.

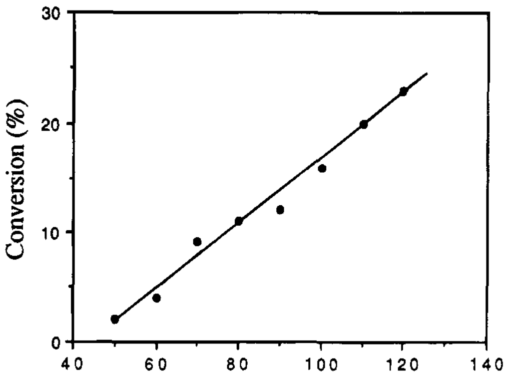


Figure 3. Conversions of vinyl ether groups in novolac resin containing BPA-DEVE depending on baking temperatures. Baking time 10 min.

This thermal cross-linking is due to the electrophilic addition reaction of acids to vinyl ether groups. The rate of addition of acid groups to vinyl ether groups increases with an increase in the acidity of the acid group. The reaction is also highly dependent on the baking temperature. Figure 3, obtained by evaluating the conversion of the vinyl ether group (δ_{C-H}, 983 cm^{-1}) to an acetal group on FT-IR spectra, supports the fact. A NaCl plate coated with the novolac resin film containing 12 mol % BPA-DEVE and 2 mol % DIAS, was baked for 10 min at baking temperatures from 60 to 120 °C and used for the measurement.

The cross-links due to the thermal cross-linking reaction are catalytically de-cross-linked by photogenerated acids. Using the adducts of BPA-DEVE with para-substituted phenols, the acidolytic rate at room temperature for the adducts with an acetal structure was investigated according to the process given by eqs 1–3. The plots between $-\ln([\text{acetals}]/[\text{acetals}_0])$ and

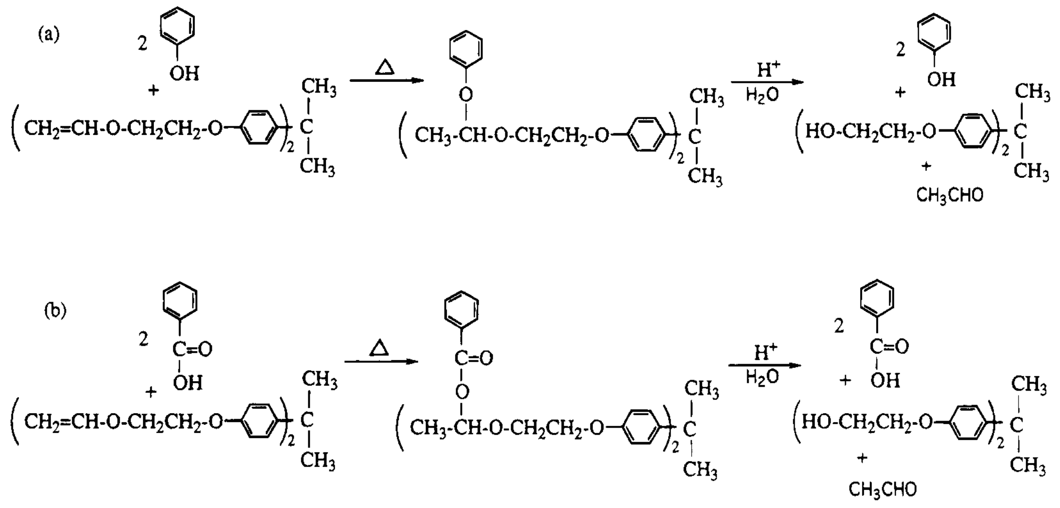
$$[\text{acetals}] + [\text{H}^+] \xrightarrow{k_{\text{H}^+}} \text{products} + [\text{H}^+] \qquad (1)$$

$$-\text{d}[\text{acetals}]/\text{d}t = k_{\text{H}^+}[\text{H}^+][\text{acetals}] \qquad (2)$$

$$-\ln\{[\text{acetals}]/[\text{acetals}]_0\} = (k_{\text{H}^+}[\text{H}^+])t = k_{\text{observed}}t \qquad (3)$$

time were all linear and allowed calculation of the rate constant (k_{H^+}) of the acidolysis from the slope. Figure 4 shows the plot of the acidolytic rates of the adducts as a function of the Hammett σ value for para-substituted phenols. It is found that the acidolytic rate is higher as the σ values are lower, that is, the substituent are less electron-attracting.

Scheme 1. Thermal Cross-Linking and De-Cross-Linking Mechanism: (a) BPA-DEVE and Phenol; (b) BPA-DEVE and Benzoic Acid



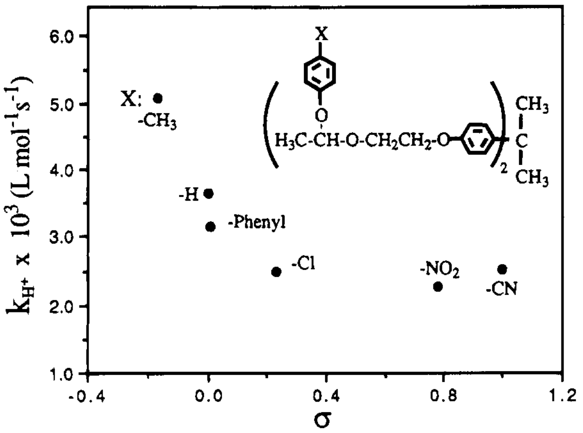


Figure 4. Hammett plot for acidolysis of the adducts of BPA-DEVE and para-substituted phenols.

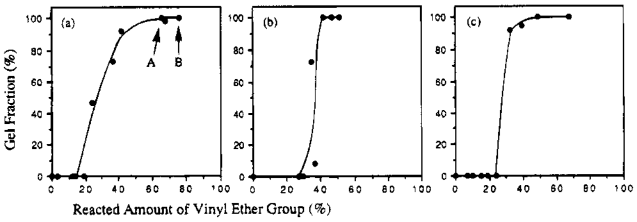


Figure 5. Reacted amount of vinyl ether group required for insolubilization for the terpolymers with acid value different from one another. (A) minimum amount of reacted vinyl ether group, (B) maximum amount of reacted vinyl ether group. (a) SP-1; (b) SP-2; (c) SP-3.

The mechanism of the thermal cross-linking and acid-catalyzed de-cross-linking for the three-component photopolymers was suggested by the model reactions shown in Scheme 1.

Figure 5 shows the amounts of the reacted vinyl ether groups required for insolubilization of the terpolymers: 66% of the vinyl ether groups in SP-1 terpolymer, 42% in SP-2 terpolymer, and 39% in SP-3 terpolymer are required for complete insolubilization.

A polymer with a higher acid value has higher solubility in an aqueous base developer. Accordingly, a polymer film with a higher acid value requires higher cross-linking density for complete insolubilization. Consequently, the amount of the reacted vinyl ether group required for complete insolubilization increases with an increase in the acid value of the binder polymer.

The vinyl ether monomer containing in SP-1 terpolymer reacts up to 76% with sufficient baking. This high value, compared with the terpolymers, SP-2 and -3, is attributable to the higher acid value. Such a maximum amount of the reacted vinyl ether group also depends on the T_g of the binder polymer, which will be discussed in the following section. The minimum and maximum amounts of the reacted vinyl ether groups for the respective binder polymers are summarized in Table 1.

3.2.2. Effect of the Other Physical Properties on Thermal Behavior. Using the terpolymers SP-2, SP-4, and SP-5, the effect of molecular weight on thermal insolubilization was investigated.

As can be seen from Figure 2, SP-2 film which had the lowest weight-average molecular weight (M_w) of 26 200 g/mol was not insolubilized with a baking time of 3 min at 80 °C. However, the insolubilization ratio increases with increasing molecular weight and gel fractions of 39% in SP-4 film with M_w of 75 200 g/mol and 92% in SP-5 film with the highest M_w of 180 400 g/mol were obtained with baking times of 3 min at 80 °C. SP-5 film was completely insolubilized with a baking of only 1 min at 120 °C.

The amount of reacted vinyl ether groups required for insolubilization also decreases in order of increasing molecular weight. SP-2 film starts to become insoluble with a amount of reacted vinyl ether group of 35% and becomes completely insoluble with reacted amount of 42%. However, SP-5 film exhibits almost complete insolubilization with only reacted amount of 12%. These results indicate that insolubilization for the terpolymers follows the gelation theory by Charlesby.[31,32]

The dependence of insolubilization on the acid component of the terpolymers was investigated using the terpolymers SP-3 and SP-7.

SP-3 film with MAA moiety as a acid component was not insolubilized with a baking time of 3 min at 80 °C, but SP-7 film with AA moiety exhibited a gel fraction of 90% under the same baking conditions (Figure 2). The film with MAA moiety also started to become insoluble with a reacted amount of the vinyl ether group of 25% and reacted up to 68% of the vinyl ether group with

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(31) Yamaoka, T. et al.; *Photopolymer Technology*; Nikkan Kogyo Simbunsha: Tokyo, 1988.

(32) Charlesby, A. *Proc. R. Soc.* **1954**, *222A*, 542.

sufficient baking time. However, the film with AA moiety started to become insoluble with only a slight reaction of the vinyl ether group and reacted up to 83% of the vinyl ether group with enough baking time.

MAA moiety and AA moiety have a similar acid strength to each other ($pK_a = 4.66$ for methacrylic acid and 4.26 for acrylic acid) and also the acid values of SP-3 and SP-7 are similar. However, the substitution of AA moiety for MAA moiety gives rise to a change in T_g (T_g = 81.4 °C for SP-3, 71.8 °C for SP-7). The abrupt cross-linking and increase in the maximum amount of reacted vinyl ether groups for SP-7 with AA moiety may be due to a change in T_g.

The effect of T_g on the thermal insolubilization was studied using SP-2 and SP-6, which have the analogous physical properties except the T_g.

SP-2 film with T_g of 91.5 °C was not insolubilized with a baking at 80 °C for 3 min, while SP-6 film with a T_g of 66.4 °C had a gel fraction of 93% under the same baking condition (Figure 2). This means that the T_g of the polymers plays an important role in the thermal cross-linking of the vinyl ether monomer.

In the polymer film with a higher T_g, it is harder for large-scale molecular motion in the long segments of the polymer chain to take place, and only motion in atoms and small groups of atoms or short sections of the main chain or the side chain is present. The more reactive carboxylic acid moiety of the binder polymer reacts with one functional group isolated from the other functional group by the long chain of hydrocarbons in the bifunctional vinyl ether monomer to form an acetal structure. The molecular motion can be neglected, compared with the distance to the neighboring molecule. Accordingly, it is difficult for the other functional group of the monomer to undergo intermolecular cross-linking with the neighboring molecule, so that the other functional group remains unreacted. Consequently, SP-2 film with a T_g of 91.5 °C starts to become insoluble only with an amount of the reacted vinyl ether group above 30% and does not react above 51% of the vinyl ether group, even with sufficient baking time.

In the polymer with the lower T_g, segments of the polymer can move with respect to one another because of an increase of the free volume. Accordingly, intermolecular cross-linking is possible and hence SP-6 film with T_g of 66.4 °C begins to be insolubilized with only a slight amount of the reacted vinyl ether group. Intermolecular cross-linking also requires the reaction of both functional groups of the bifunctional monomer. Accordingly, in SP-6 film with a T_g of 66.4 °C, the vinyl ether group disappears almost completely after enough baking.

3.3. Effect of Physical Properties of Binder Polymer on Sensitivity. The effect of the physical properties on the sensitivity was investigated using the terpolymers shown in Table 1 as binder polymers. The baking condition (120 °C, 10 min), conducted in this study, is sufficient to reach the maximum amount of reacted vinyl ether groups for all of the polymers.

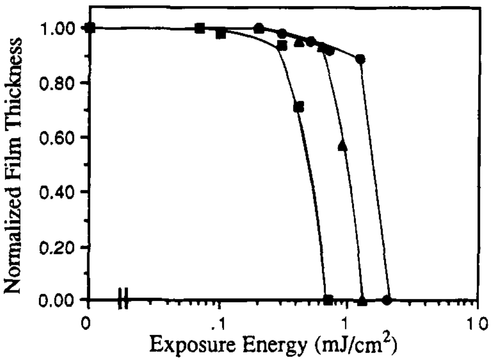

Figure 6. Comparison of characteristic curves for the terpolymers containing BPA-DEVE with acid values different from one another. PAG: DIAS, in acid value: (■) SP-1 with 193 mg of KOH/g of resin; (▲) SP-2 with 123 mg of KOH/g of resin; (●) SP-3 with 58 mg of KOH/g of resin.

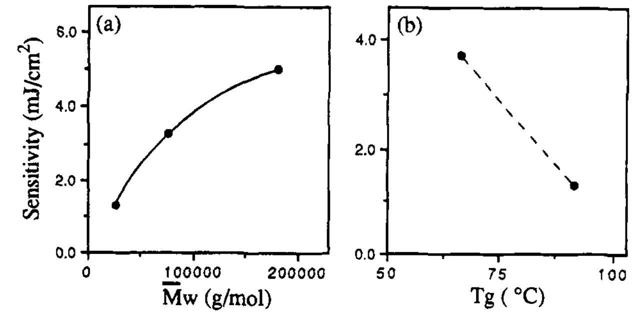

Figure 7. Sensitivities depending on physical properties of the binder polymers. (a) SP-2 with $\bar{M}_w$ = 26 200 g/mol, SP-4 with $\bar{M}_w$ = 75 200 g/mol, SP-5 with $\bar{M}_w$ = 180 400 g/mol. (b) SP-6 with T_g = 66.4 °C, SP-2 with T_g = 91.5 °C.

As can be seen from the characteristic curves in Figure 6, an increase in the acid value of the binder polymer increases the resist sensitivity of the photopolymer. SP-1 films with the highest acid value exhibits the high sensitivity of 0.7 mJ/cm^2. However, the sensitivity decreases with a decreasing acid value and SP-3 film with the lowest acid value, exhibits a sensitivity of 2.0 mJ/cm^2.

The cross-links are decomposed by photogenerated acids and return to the structure before cross-linking. That is, the binder polymer with the higher acid value before cross-linking gives a reaction product with a higher acid strength after de-cross-linking in the presence of sufficient photogenerated acids. The product with the higher acid strength also has the higher solubility in the aqueous base developer. Therefore, the sensitivity of the resist is enhanced with an increase in the acid value of the binder polymer.

Figure 7 shows the sensitivities obtained from the characteristic curves for the terpolymers. As shown in Figure 7a, an increase in the molecular weight of the binder polymer decreases the sensitivity of the photopolymer. SP-2 films with the lowest M_w of 26 200 g/mol, has a sensitivity of 1.3 mJ/cm^2. However, the sensitivity decreases with an increasing molecular weight, and a sensitivity of 3.3 mJ/cm^2 is exhibited for SP-4 film with a M_w of 75 200 g/mol. Particularly, in SP-5 film with the highest M_w of 180 400 g/mol, the normalized film thickness did not decrease to less than 0.6 under the same development conditions using a developer of 2 wt % TMAH aqueous solution:methanol = 1:1 in weight ratio. A sensitivity of 5 mJ/cm^2 for this polymer was obtained using DN-3C aqueous base developer:H_2O = 1:2 in weight ratio.

The higher the molecular weight of the binder polymer before cross-linking, the higher the molecular weight of the reaction product. Therefore, with an increase in the molecular weight in the binder polymer, the solubility of the reaction product is decreased and accordingly, the sensitivity is decreased.

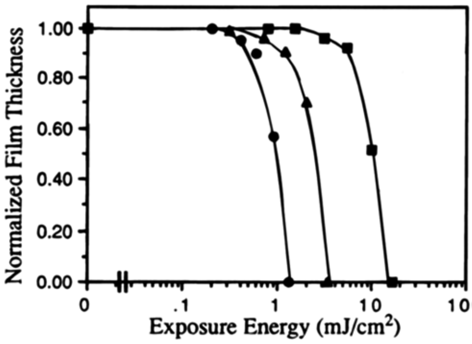

Figure 8. Characteristic curves of SP-2 terpolymer containing BPA-DEVE with different PEB time from one another. PAG: DIAS, prebake 120 °C 10 min. PEB: 120 °C (■) 1 min, (▲) 6 min, (●) 10 min.

A change in the acid component of the binder polymer causes a change in T_g. In SP-3 film with MAA moiety (T_g, 81.4 °C), a sensitivity of 2 mJ/cm^2 was exhibited, but in SP-7 film with AA moiety (T_g, 71.8 °C), the normalized film thickness did not decrease to less than 0.89. This is attributable to a relatively low T_g and the lowest acid value. A sensitivity of 3 mJ/cm^2 was obtained using DN-3C aqueous base developer:H_2O = 1:2 in weight ratio.

The effect of the T_g of the binder polymer on sensitivity was investigated using SP-2 with a T_g of 91.5 °C and SP-6 with a T_g of 66.4 °C (Figure 7b). In SP-2 film, a sensitivity of 1.3 mJ/cm^2 was exhibited. However, the sensitivity decreased with a decreasing T_g of the binder polymer and a sensitivity of 3.7 mJ/cm^2 was exhibited for SP-6 film.

The lower the T_g of the binder polymer, the higher the maximum amount of the reacted vinyl ether group which can be attained under enough baking. That is, the binder polymer with a lower T_g forms three-dimensional cross-linked networks by the thermal reaction with the vinyl ether monomer. Accordingly, it is difficult for the photogenerated acid to diffuse, and hence the sensitivity is decreased.

Figure 8 shows the characteristic curves for SP-2 terpolymer containing BPA-DEVE when the PEB time at 120 °C is varied from 1 to 10 min. With no PEB, the normalized film thickness did not decrease to less than 0.94 even under sufficient exposure. However, the sensitivity increased with an increase in PEB time and the sensitivity of 1.3 mJ/cm^2 was exhibited at PEB time of 10 min.

This sensitivity enhancement may be due to chemical amplification. On the basis of the mechanism shown in our previous paper, photogenerated acids catalytically react with the cross-links and are regenerated.

Figure 9 shows a scanning electron micrograph[33] of positive patterns printed in 1-μm-thick film. Photopolymer film composed of SP-2 terpolymer, 1.52 mol % BPA-DEVE, and 2 mol % DIAS of the polymer, was prebaked at 130 °C for 3 min and exposed at 50 mJ/cm^2, followed by PEB at 110 °C for 1 min. Development was done in a developer of 2.38 wt % TMAH aqueous solution:methanol = 7:3 by weight ratio. The micrograph shows that the 0.85-μm line and space patterns are resolved. The sensitivities for these resists are strongly dependent on composition of the developer, the process condition, and the amount of the monomer. This describes a difference in the sensitivities indicated in Figure 6 and Figure 9.

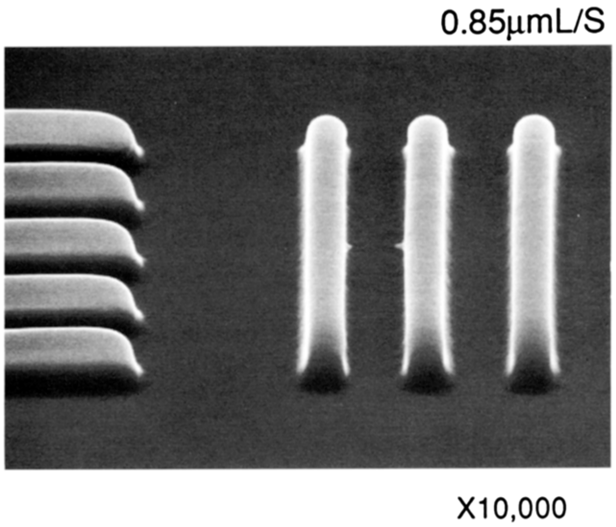

Figure 9. Resist pattern profiles. SEM picture of 0.85 μm line and space positive pattern transferred on the three-component resist (SP-2, BPA-DEVE, and DIAS). Substrate: Si wafter (pretreatment with HMDS). Coating thickness: 0.97 μm. Prebake: 130 °C/180 s. Exposure tool: i-line stepper. Exposure dose: 50 mJ/cm^2. PEB: 110 °C/60 s. Development: puddle, 60 s/23 °C using a 7:3 mixed solution of 2.38 wt % aq TMAH and MeOH. Rinse: deionized water, 20 s/23 °C.

The shelf life of the resist materials for the solution as well as the coated layer is one of the most important factors from the viewpoint of the practical use. The present resist consisting of SP-2, BPA-DEVE, and the PAG coated on an aluminum plate does not show any change in the specification at least for 5 months at room temperature. The solution is also unchanged for 5 months. However, a method for further improvement of the thermal stability as the resist is being studied.

DIAS as a PAG exhibits an exothermic peak with a maximum point at 207 °C on a DSC curve. However, a slight weight decrease accompanying a rise of base line on DSC curve is observed from 174 °C on a TGA curve, which indicates a decomposition of the PAG. Even a very little acid has a critical effect on the resist performance based on acid-catalyzed reactions. The soft bake region of 110−130 °C is suitable for our resist systems. TGA and DSC were carried out with a increasing rate of 5 °C/min.

4. Conclusion

Terpolymers with carboxyl and aliphatic alcohol groups in the side chain were synthesized and used for three-component photopolymer systems, consisting of the terpolymer as a binder, the vinyl ether monomer as a cross-linking agent and a PAG. The physical properties of the binder polymers affect the characteristics of the photopolymers, including the thermal cross-linking reactivity and sensitivity as a positive working resist. An increase in acid value increases the insolubilization rate and enhances sensitivity. An increase in molecular weight increases the insolubilization rate and decreases sensitivity. An increase in T_g decreases the insolubilization rate and enhances sensitivity.

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[33] We acknowledge Dr. Ohta, Japan Synthetic Rubber Co., for taking the SEM pictures of the transferred patterns.