Novel Dual-Mode Photoresist Based on Cationic Polymerization and Acidolysis

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Copolymers of *p*-hydroxystyrene and *p*-(2-(vinyloxy)ethoxy)styrene were synthesized, and positive resists with sensitivities of ca. 25 mJ/cm^2 at 365-nm light by using diphenyliodonium 8-anilinonaphthalene-1-sulfonate and ca. 106 mJ/cm^2 at 248-nm light by using triphenylsulfonium trifluoromethanesulfonate as photoacid generator were obtained. A copolymer of *p*-hydroxystyrene and *p*-(2-(vinyloxy)ethoxy)styrene containing a photoacid generator had either positive or negative working behavior, depending on process conditions such as prebaking temperature or exposure energy. This complicated behavior is caused by the diverse reaction modes of vinyl ether groups. The pendant vinyl ether group reacts with the hydroxyl group of phenol with the aid of thermal energy to form cross-linked networks. The cross-links are cleaved by photogenerated acids. The vinyl ether groups also undergo competing reactions between cationic polymerization and acidolysis by photogenerated acids.

1. Introduction

Several reports show that poly[*p*-(2-(vinyloxy)ethoxy)-styrene] (polyVES) containing a photoacid generator (PAG) offers a negative resist based on the photoinitiated cationic polymerization of vinyl ether moieties. Nishikubo[1] et al. examined the photochemical reactivity of polyVES in the presence of several PAGs. Watanabe[2] et al. also obtained a negative resist with the sensitivity of 10–25 mJ/cm^2 by exposing polyVES containing diphenyliodonium salts to deep UV. However, it has not yet been reported that copolymers (PVESs) of *p*-hydroxystyrene (HS) and *p*-(2-(vinyloxy)ethoxy)styrene (VES) containing a PAG exhibit positive working behavior.

We studied two-component systems composed of a copolymer (PVES) and a PAG and found that these have either positive or negative working behavior, depending on process conditions such as prebaking temperature or exposure energy. This behavior results from the intricate reactions of the vinyl ether moieties. The pendant vinyl ether groups react with the hydroxyl group of phenol at high temperature to form cross-linked networks. These cross-links are cleaved by photogenerated acids. The vinyl ether groups also undergo the competing reactions of cationic polymerization[3–6] and acidolysis by photogenerated acids.

A variety of onium salts[7–10] which photochemically generate strong acids have been reported by Crivello et al. and the application of onium salts to chemically amplified resists has been studied[11–14] by Fréchet et al.[13] The spectral sensitivity of photopolymers is determined by that of PAG. For the present study, a novel onium salt[15] which is sensitive to near UV light was synthesized and used, because onium salts reported so far are sensitive only to deep UV light.

This paper describes the details of the thermal and photoacid catalyzed reactions of PVES and the possibility of application to lithography.

2. Experimental Section

Materials. Poly(*p*-hydroxystyrene) (PHS, M_n = 2400, M_w = 4300) from Maruzen Petrochemical Co. Ltd. and 2-chloroethyl vinyl ether (CEVE) from Tokyo Kasei Kogyo Co. Ltd. were used as received. *p*-Ethylphenol (EP), potassium hydroxide, sodium hydroxide, and tetra-*n*-butylammonium bromide (TBAB) as a phase-transfer catalyst (PTC) were supplied by Wako Pure Chemical Ind., Ltd. and used as received. Diphenyl iodonium 8-anilinonaphthalene-1-sulfonate (ANS-DPI) as a photoacid generator (PAG) was synthesized according to the literature.[15]

Measurements. IR spectra were measured with a Hitachi infrared spectrometer (Model 26 0–10), and FT-IR spectra were measured with a Horiba FT-200 Fourier transform infrared spectrometer. NMR spectra were recorded on a JEOL GSX-400 spectrometer. The molecular weights of the polymers were determined on a TOSO HLC-802 UR gel permeation chromatograph (GPC) with a TSK-GEL H-type column (styrene gel column) in tetrahydrofuran using styrene as the standard. Fast atom bombardment mass spectra (FAB-MS) were measured with a JEOL JMS-HX 110 mass spectrometer. 3-Nitrobenzyl alcohol was used as a matrix solvent for measurement of fast atom bombardment mass spectra (FAB-MS). Resist film thickness was measured with a Tencor Alphastep 200.

Synthesis of Copolymer (PVES).[1,16–18] PHS (20.43 g, 0.170 mol) was dissolved in 90 mL of dimethyl sulfoxide (DMSO). Into

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Scheme I. Synthesis Scheme for *p*-Hydroxystyrene-*p*-(2-(vinyloxy)ethoxy)styrene Copolymer (PVES)

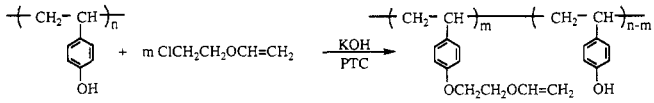

Table I. General Composition of Photopolymer (Parts by Weight)

copolymer	PVES	15
photoacid generator	ANS-DPI[a]	1.5
solvent	1,4-dioxane	67
	methanol	33

[a] Diphenyliodonium 8-anilinonaphthalene-1-sulfonate.

a 300-mL round-bottom flask flushed with nitrogen and fitted with paddle stirrer, reflux condenser, dropping funnel, and thermometer were placed this solution and 4.49 g (0.080 mol) of 85% KOH pellets. The flask contents were stirred at 60–65 °C for 2 h, and then a solution of 3.06 g of TBAB dissolved in 8.52 g (0.080 mol) of CEVE was added. Then, the mixture was held at 60–65 °C for 36 h. The reaction mixture was cooled to room temperature, and 10 g of acetic acid was added. This mixture was poured into 2 L of distilled water, and the polymer was precipitated. After filtration and drying, the polymer was dissolved in acetone and reprecipitated in distilled water. It was then dried under reduced pressure. The vinyl ether moiety content was determined from ^{1}H NMR spectra by comparing the integral ratio of 4H for the benzene, ^{1}H for the vinyl ether group of the VES unit, and 5H for the phenol of the HS unit at 6.2–7.2 ppm to 6H for the (vinyloxy)ethoxy group of the VES unit at 3.9–4.3 ppm. The synthetic process is shown in Scheme I, and the molecular weight data of the synthesized PVESs (PVES-39, 20, and 9) are listed in Table II. IR OH at 3370 cm^{-1}, C=C at 1637, 1610 cm^{-1}, C–O–C of vinyl ether group at 1200 cm^{-1}, CH of vinyl ether group at 980 cm^{-1}; ^{1}H NMR (acetone-d_6) 6.2–7.2 ppm (5H of phenol, 1H of vinyl ether group), 3.9–4.3 ppm (6H of vinyl oxy ethoxy group).

Synthesis of 4-(2-(Vinyloxy)ethoxy)-1-ethylbenzene (VEB).[4] Into a 300-mL, three-necked flask fitted with an overhead stirrer, reflux condenser, thermometer, dropping funnel, and nitrogen inlet were placed 12.20 g (0.1 mol) of *p*-ethylphenol (EP), 50 mL of DMSO, and 6.0 g (0.15 mol) of 93% NaOH pellets. The flask contents were stirred at 60–65 °C for 1 h, and then a solution of 1.83 g of TBAB dissolved in 16 g (0.15 mol) of CEVE was added. The mixture was held at 60–65 °C for 5 h. The reaction mixture was cooled. This mixture was poured into distilled water at a temperature below ca. 15 °C, and crystallized to produce white crystalline VEB. IR C=C at 1637, 1610 cm^{-1}, C–O–C of vinyl ether group at 1200 cm^{-1}, CH of vinyl ether group at 980 cm^{-1}; ^{1}H NMR (acetone-d_6) 1.17 ppm (t, 3H of 4-ethyl group), 2.57 ppm (q, 2H of 4-ethyl group), 3.98–4.26 ppm (m, 6H of vinyl oxy ethoxy group), 6.55 ppm (q, 1H of vinyl ether group), 6.85–7.13 ppm (m, 4H of benzene); ^{13}C NMR (acetone-d_6) 16.35, 28.52, 67.27, 67.58, 87.03, 115.23, 129.52, 137.25, 152.75, 157.85 ppm.

Lithographic Evaluation.[19] The typical composition of the resist solution is shown in Table I. Resist films were prepared by spin-coating this photosensitive solution on Si wafer to give a 0.5–1.0-μm-thick film. The films were prebaked and exposed to 365-nm light with a filtered super-high-pressure mercury lamp and postbaked. Development was done in an aqueous solution of tetramethylammonium hydroxide (TMAH). The thickness of the film remaining after development was measured as a function of the exposure energy. The film thickness was normalized to that obtained after postexposure baking (PEB).

3. Results and Discussion

3.1. Thermal Behavior of PVES. All of the synthesized PVESs (PVES-9 to PVES-39) are soluble in aqueous base, because the content of the vinyl ether groups that replace the phenol groups of the parent polymer is low enough and at least 61 mol % of the phenol group remains unblocked (Scheme I). Before the photochemical functionality of PVES was studied, its thermal behavior was investigated.

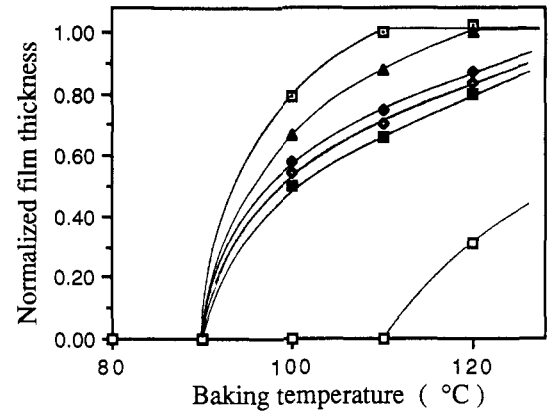

Figure 1. Change of film thickness remaining after development; bake 10 min, developing 60 s, 20 °C. ⊡: PVES-39, TMAH 2 wt %:methanol = 6:5 by weight. ◆: PVES-39, acetone. ▲: PVES-20, TMAH 2 wt %:methanol = 2:1 by weight. ◇: PVES-20, acetone. ■: PVES-9, TMAH 2 wt %. □: PVES-9, acetone.

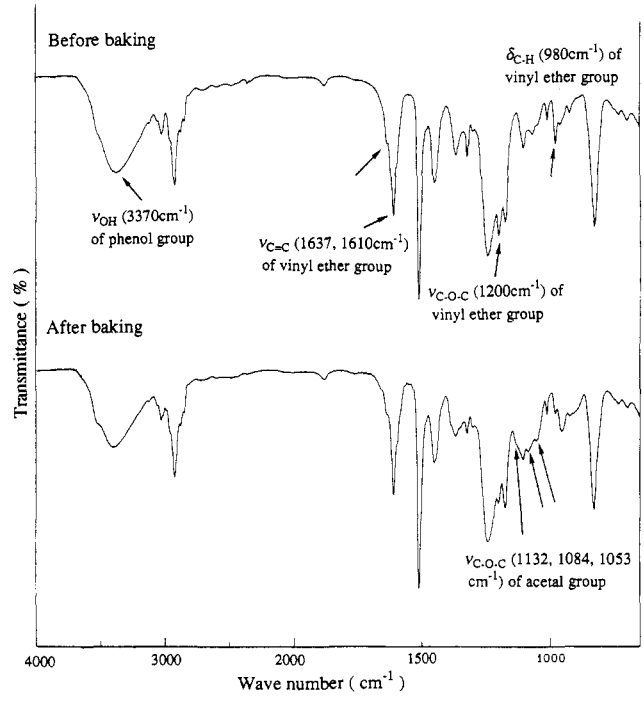

Figure 2. Change of FT-IR spectrum of PVES-39 by baking; bake 120 °C, 10 min.

It was found that PVES films prebaked at temperatures above 100 °C are insolubilized not only in aqueous base but also in organic solvents.

Figure 1 shows the gel fraction of PVESs plotted against the baking temperature. The PVESs start to come insoluble at 90 °C and are almost completely insoluble at temperatures above 120 °C. Even PVES-9 with the lowest vinyl ether group content was insolubilized at temperatures above 110 °C. These facts mean that PVESs are cross-linked by thermal reaction at temperatures above 90 °C.

Figure 2 shows FT-IR spectra of PVES-39 films before and after baking at 120 °C for 10 min. The measurements were made on a NaCl plate coated with PVES-39 dissolved

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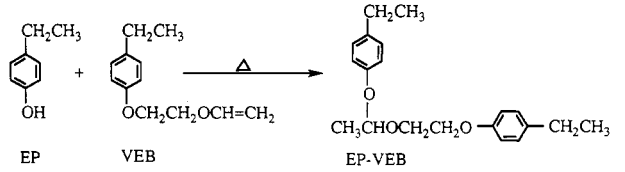
Scheme II. Cross-Linking Process for the Adduct EP–VEB



in acetone. Comparison of these spectra shows that the absorption peaks due to ν_{C-O-C} (1200 cm^{-1}) and δ_{CH} (980 cm^{-1}) of the vinyl ether group, and ν_{OH} (3370 cm^{-1}) of the phenol group decreased after baking. The doublet due to $\nu_{C=C}$ (1637, 1610 cm^{-1}) of the vinyl ether group overlapping ν_{C-C} (1610, 1600, 1510, 1450 cm^{-1}) of the benzene ring also decreased after baking. On the contrary, the weak absorption peaks due to ν_{C-O-C} (1070 cm^{-1}) of the aryl alkyl ether and the overlapping (1103 cm^{-1}) of ν_{C-O} of phenol and ν_{C-O-C} of the vinyl ether group changed to strong peaks due to ν_{C-O-C} (1132, 1084, 1053 cm^{-1}) of the acetal group after baking. These results suggest that a certain cross-linking reaction occured between hydroxyl groups and vinyl ether groups.

To clarify this thermal reaction in films, the reaction of the model compounds was investigated. As a model reaction, *p*-ethylphenol (EP) and 4-(2-(vinyloxy)ethoxy)-1-ethylbenzene (VEB) were mixed in 1:1 weight ratio and reacted in a capped flask at 110 °C. Qualitative observation of a silica gel thin-layer chromatography (TLC) plate using hexane–ethyl acetate (1:1, volume ratio), revealed a large spot and two small spots, suggesting that the product has three components. The large spot may be due to the main product. The main product is important in elucidating the reaction mechanism, so the products were characterized spectroscopically without seperation. In ^{13}C NMR and DEPT spectra of the products, the peak due to the tertiary carbon atom of the acetal group was observed at 100.7 ppm, and the peaks due to the two secondary carbons of the ethoxy group were observed at 65 and 68 ppm. FAB-MS also showed the peak at m/z = 314 to be the parent peak, which agreed exactly with the molecular weight (M) of the adduct of EP and VEB. This observation shows that the main product is the adduct of EP and VEB (EP–VEB). On the basis of these experimental results, the product and the reaction mechanism shown in Scheme II are proposed.

The FT-IR spectrum of the mixture of EP and VEB after heating further did not have the absorption peaks due to $\nu_{C=C}$ (1637 cm^{-1}), ν_{C-O-C} (1200 cm^{-1}), and δ_{CH} (980 cm^{-1}) of the vinyl ether group, but the absorption peaks due to ν_{CH} (1100 cm^{-1}) and ν_{C-O-C} (1132, 1084, 1053 cm^{-1}) of the acetal group appeared. In the FT-IR spectrum of PVES-39 film after baking, the absorption peak due to ν_{CH} (1110 cm^{-1}) of the acetal group is present inside that due to the overlapping (1103 cm^{-1}) of ν_{C-O} of phenol and ν_{C-O-C} of the vinyl ether group. This spectral behavior agrees with that of the PVES film. Therefore, the mechanism of the thermal insolubilization of PVES involves formation of cross-linking between phenol groups and vinyl ether groups as shown in Scheme III.

3.2. Reaction of PVES in the Presence of Acid. *3.2.1. Acid-Catalyzed De-Cross-Linking.* Figure 3 shows the characteristic curves of PVES-9 containing 10 wt % PAG when the prebaking and postexposure baking (PEB) temperatures are varied from 110 to 130 °C. A 1-μm-thick polymer layer coated on a Si wafer was prebaked at

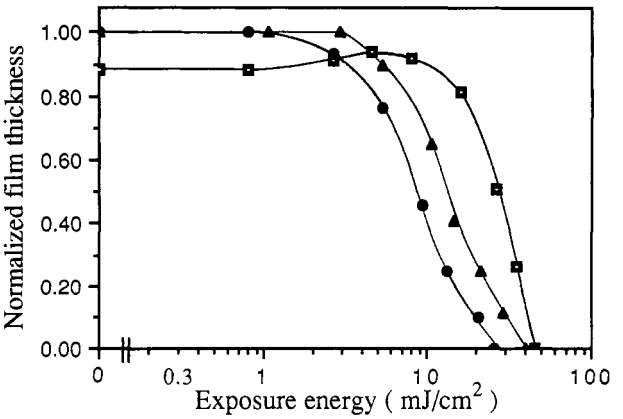
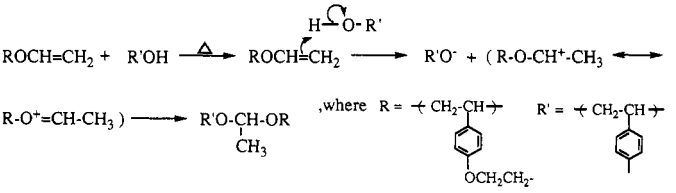


Figure 3. Characteristic curves of PVES-9 containing ANS-DPI; ANS-DPI 10 wt %, developer TMAH 2 wt %. □: prebake PEB 110 °C, 10 min. ▲: prebake PEB 120 °C, 10 min. ●: prebake PEB 130 °C, 10 min.

Scheme III. Cross-Linking Mechanism of PVES by Prebaking



110–130 °C for 10 min. In this process, a cross-linking reaction occurs by the mechanism mentioned above, so PVES-9 is insolubilized in aqueous base. The cross-linked film layer was exposed to 365-nm light followed by PEB under the same conditions as the prebake. Finally, the film layer was developed in 2 wt % aqueous solution of TMAH. The films started to dissolve at the exposure energy of 1–10 mJ/cm^2 and were completely dissolved out at 25–50 mJ/cm^2, depending on baking temperature. These curves indicate that all of the PVES-9 layers exhibit positive working behavior with sensitivities of 25–50 mJ/cm^2 at 365-nm light. It is also recognized that the cross-linked PVESs are de-cross-linked by baking at 110–130 °C in the presence of photogenerated acid.

The mechanism of the de-cross-linking reaction was investigated with PVES-39 and the adduct, EP-VEB. FT-IR spectra of PVES-39 films containing 15 wt % PAG were measured before and after exposure, and after exposure and PEB. The film was prebaked at 120 °C for 10 min and exposed at ca. 200 mJ/cm^2, followed by PEB under the same condition as the prebake. The absorption peaks due to ν_{C-O-C} (1132, 1084 cm^{-1}) of the acetal group disappeared after exposure and PEB. The peak due to ν_{C-O-C} (1053 cm^{-1}) of the acetal group is not visible because of overlap with that of the PAG. The absorption peak due to $\nu_{C=O}$ (1715 cm^{-1}) of the carbonyl group also appeared after exposure and disappeared after exposure and PEB. The peak due to ν_{OH} (3370 cm^{-1}) of the phenol group increased after exposure and PEB. These spectral results were confirmed by those of the adduct, EP-VEB. The adduct containing 15 wt % PAG was exposed to generate acid, followed by PEB at 120 °C for 10 min. The product was characterized by IR, NMR, and mass spectroscopy. The hydroxyl proton was observed at 4.5 ppm in the ^1H NMR spectrum and the two secondary carbons were observed at 71 and 62 ppm in the ^{13}C NMR spectrum. FAB-MS showed the peak at m/z = 166 to be the parent

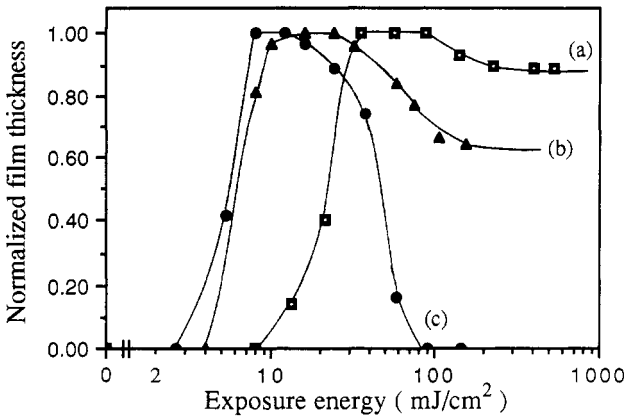
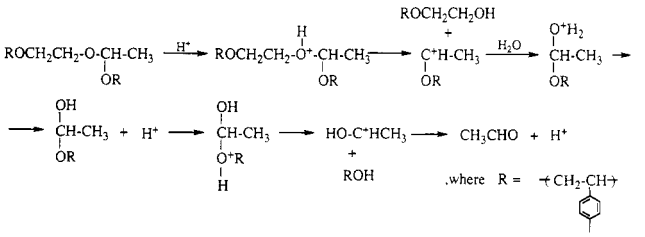


Figure 4. Characteristic curves of PVES-39 containing ANS-DPI; developer TMAH 2 wt %:methanol = 6:5 by weight, prebake PEB 80 °C, 10 min. (a) ANS-DPI 5 wt %. (b) ANS-DPI 10 wt %. (c) ANS-DPI 15 wt %.

Scheme IV. De-Cross-Linking Mechanism of the Cross-Linked PVES



peak. The IR spectra also agree with those of PVES-39. From these results, it is found that the de-cross-linking of the crosslinked PVES is accomplished by the process shown in Scheme IV.

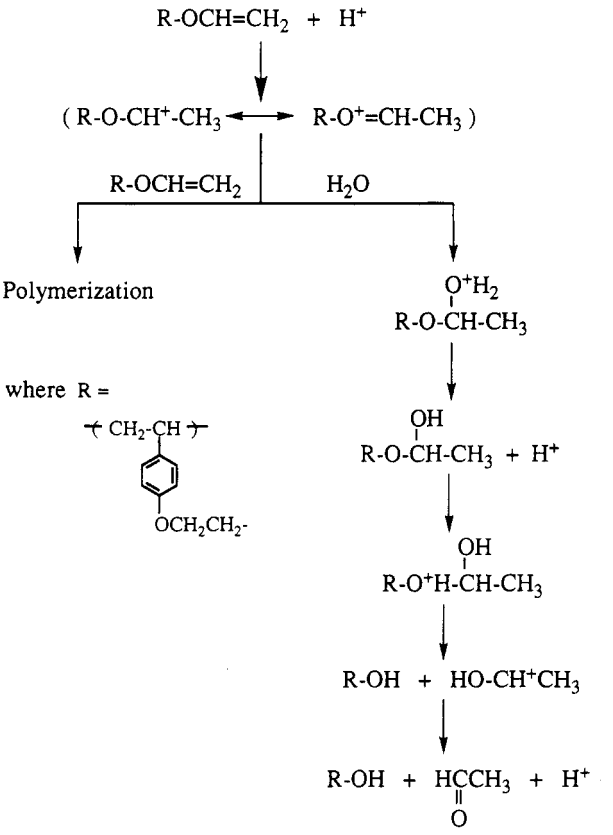
3.2.2. Photo and Thermal Behavior of PVES in the Presence of Acid. The insolubilization of PVES by exposure to light and the subsequent PEB process depends on the concentration of PAG. Figure 4 shows the characteristic curves of PVES-39 obtained by varying the PAG concentration from 5 to 15 wt %. In determining these characteristic curves, all process conditions were kept constant except PAG concentration. PVES-39 coated on a Si wafer was prebaked at 80 °C for 10 min. Under these prebaking conditions, PVES-39 is not cross-linked as described in section 3.1. The curves shown in Figure 4 are quite different from one another, which indicates that PVES-39 behavior depends on the PAG concentration.

Curve a for 5 wt % PAG concentration shows that PVES-39 starts to come insolubilized at the exposure energy of 10 mJ/cm^2 and is almost completely insolubilized by the exposure energy of 30 mJ/cm^2, indicating the negative working behavior.

Curve b for 10 wt % PAG concentration is clearly different from curve a. PVES-39 starts to come insolubilized at the exposure energy of 7 mJ/cm^2 and reaches the maximum value at 10–20 mJ/cm^2. As exposure energy increases above this exposure energy, PVES-39 becomes soluble again. In other words, PVES-39 shows negative working behavior up to the exposure energy of 10 mJ/cm^2 and positive working behavior above 20 mJ/cm^2. However, the normalized film thickness does not decrease to less than 0.6, even at exposure energies above 200 mJ/cm^2.

Curve c for 15 wt % PAG concentration clearly shows the dual-mode behavior. In this case, PVE-39 shows negative working behavior up to 8 mJ/cm^2 and positive working behavior above the value. At 100 mJ/cm^2, the

Scheme V. Competing Reactions of PVES in the Presence of Acid

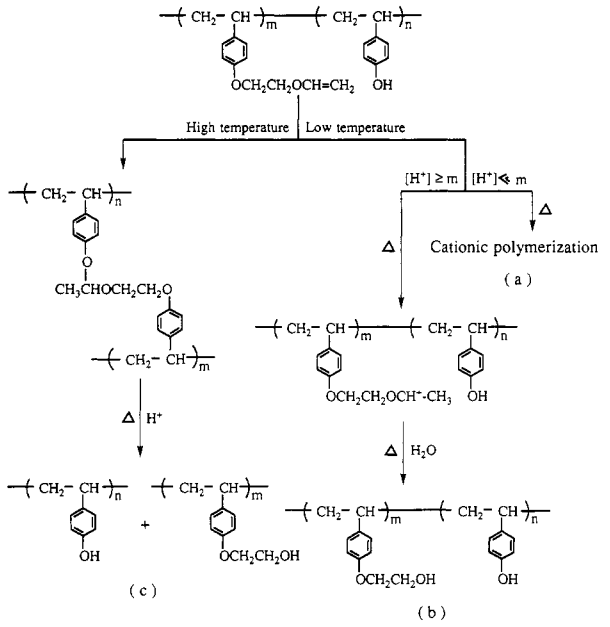


normalized film thickness after development indicates that PVES-39 is completely soluble in the developer. The difference in the characteristic curves according to the PAG concentration strongly suggests a reaction mechanism for PVESs in the presence of acid.

The mechanism of insolubilization of PVES-39 by exposure may be different from that of the thermal cross-linking described in Scheme III, because in obtaining the three characteristic curves, the prebaking conditions were kept constant at 80 °C for 10 min to prevent thermal cross-linking. FT-IR spectra of PVES-39 film containing 15 wt % PAG were measured before and after exposure, and after exposure and PEB. The film was prebaked at 80 °C for 10 min and exposed at 8 mJ/cm^2, followed by PEB under the same conditions as the prebake. PVES-39 containing 15 wt % PAG is insolubilized in developer and shows negative working behavior with the exposure energy of 8 mJ/cm^2. After exposure and PEB, the absorption peaks due to $\nu_{C=C}$ (1637 cm^{-1}), ν_{C-O-C} (1200 cm^{-1}), and δ_{CH} (980 cm^{-1}) of the vinyl ether group decreased, but the peak attributable to ν_{OH} (3370 cm^{-1}) of the phenol group showed no appreciable change. In particular, the peaks due to ν_{C-O-C} (1132, 1084 cm^{-1}) of the acetal group did not appear after exposure and PEB. The absorption peak due to $\nu_{C=O}$ (1715 cm^{-1}) of the carbonyl group did not appear after exposure. This observation means that cationic polymerization of vinyl ether groups occurs in the presence of acid and PEB, and the insolubilization of PVES-39 is due to formation of the cross-linked network by cationic polymerization of the pendant vinyl ether groups.

PVES-39 is again solubilized in developer in the presence of excess acid. PVES-39 does not undergo the cross-linking reaction by aid of thermal energy at the prebaking

Scheme VI. Classification of Reaction Modes of Pendant Vinyl Ether Groups in PVES Depending on Process Conditions



temperature of 80 °C. This fact indicates that PVES-39 undergoes a certain acidolysis that is different from the de-cross-linking reaction of the cross-linked PVES in the presence of excess acid. The acidolysis mechanism was investigated with PVES-39 and VEB. FT-IR spectra of PVES-39 film containing 15 wt % PAG were measured before and after exposure, and after exposure and PEB. The film was prebaked at 80 °C for 10 min and exposed at 200 mJ/cm^2, followed by PEB under the same conditions as the prebake. The absorption peak due to $\nu_{C=O}$ (1715 cm^{-1}) of the carbonyl group appeared after exposure and disappeared after exposure and PEB. The peaks due to $\nu_{C=C}$ (1637 cm^{-1}), ν_{C-O-C} (1200 cm^{-1}), and δ_{CH} (980 cm^{-1}) of the vinyl ether group also disappeared completely, and the peak due to ν_{OH} (3370 cm^{-1}) of phenol increased after exposure and PEB. VEB was dissolved in 3 wt % HCl aqueous solution (1:3, weight ratio) and heated at 80 °C for 10 min. The product was characterized by NMR and mass spectroscopy. The hydroxyl proton was observed at 4.5 ppm in the ^{1}H NMR spectrum and two secondary carbons were observed at 71 and 62 ppm in the ^{13}C NMR spectrum. FAB-MS also had the peak at m/z = 166 as the parent peak. These results indicate that the acidolysis of PVES is accomplished by the process shown in Scheme V.

4. Classification of Reaction Modes of Vinyl Ether Groups in PVES

The complicated behavior of PVES in the presence or absence of acid is caused by the diverse reaction modes of vinyl ether groups. Those reactions are classified as shown in Scheme VI. When the concentration of photogenerated acids is low, the pendant vinyl ether groups react very quickly with acids to give small amounts of carbocations. The initiated carbocations undergo cationic polymerization with remaining vinyl ether groups to form cross-linked networks. Therefore, negative working behavior is exhibited. When the concentration of acid is increased, the formation of carbocation is also increased because the reaction with acid is so fast, and conversely, the concentration of vinyl ether groups is decreased. As the result, the rate of cationic polymerization is lowered and the carbocations undergo acidolysis. Accordingly, positive working behavior is exhibited. From these results, it is recognized that the acidolysis and the cationic polymerization of PVES are competing reactions that depend on the amount of photogenerated acids, as can be seen from Scheme V.

When phenol groups exist and are prebaked at high temperature, vinyl ether groups react with hydroxyl groups of phenol with the aid of thermal energy to give cross-linked networks. The cross-links also react with photogenerated acids to give decomposition products such as aldehyde and alcohol. Consequently, the resist exhibits positive working behavior.

5. Lithographic Evaluation of PVESs

The lithographic characteristics of PVESs were evaluated by imaging experiments, based on the process described in the Experimental Section, using the resist solution of the composition shown in Table I. The results are summarized in Table II.

PVES-9 exhibits the negative working mode when the layer is prebaked at 80 °C for 10 min and exposed to light for 5 s. Under these prebaking conditions, PVES-9 is not thermally cross-linked and the layer is still soluble in developer. Only a small part of PAG reacts to release a small amount of acid when exposure is done for 5 s. Under these conditions, pendant vinyl ether groups will undergo cationic polymerization to form cross-linked networks with the aid of thermal energy in the PEB process. As a result, PVES-9 exhibits the negative working mode (Scheme VIa). PVES-9 prebaked under the same conditions exhibits the positive working mode when exposure is done for 30 or 60 s. Under these conditions, a larger amount of acid is generated to react with vinyl ether groups to form carbocations. With a larger concentration of acid, a larger amount of carbocation is formed, and hence no vinyl ether groups are left to undergo cationic polymerization. Thus, vinyl ether groups undergo acidolysis with the carbocation in exposed areas. Consequently, the resist exhibits the positive working mode (Scheme VIb).

PVES-9 exhibits the positive working mode when the layer is prebaked at 100 °C for 10 min and exposed to light for 5, 30, or 60 s. With these prebaking conditions, pendant vinyl ether groups react with the hydroxyl groups of phenol and are thermally cross-linked, and hence the cross-linked layer is insolubilized. The layer is decomposed by acids photogenerated from the PAG. As a result, the resist exhibits the positive working mode (Scheme VIc).

PVES-20 exhibits the negative working mode for exposure of 5 s (Scheme VIa) and the positive working mode for exposure of 30 or 60 s (Scheme VIb) when the layer is prebaked at 80 °C for 10 min. PVES-20 also exhibits the positive working mode when the layer is prebaked at 100 °C for 10 min and exposed to light for 30 or 60 s (Scheme VIc). Each behavior for PVES-20 is interpreted in the same manner as for PVES-9.

PVES-39 exhibits the negative working mode when the film layer is prebaked at 80 °C for 10 min and exposed to light for 5, 30, or 60 s. Under these prebaking conditions, PVES-39 is not thermally cross-linked. PVES-39 also possesses a higher content of vinyl ether groups than PVES-9 and 20, and accordingly vinyl ether groups available to undergo cationic polymerization still remain,

Table II. PVES Resist Behavior under Various Process Conditions[a]

polymer	content of VES unit (mol %)	av mol wt ($\bar{M}_n$, $\bar{M}_w$)	PAG (wt %)	prebake (°C, min)	exposure (s)	PEB (°C, min)	developer (TMAH wt % aq soln)	mode
PVES-9	9	2100, 4800	ANS-DPI 10 wt %	80, 10	5	80, 10	TMAH 2 wt %	N
				80, 10	30	80, 10		P
				80, 10	60	80, 10		P
				100, 10	5	100, 10	TMAH 2 wt %	P
				100, 10	30	100, 10		P
				100, 10	60	100, 10		P
PVES-20	20	2800, 9000		80, 10	5	80, 10	TMAH 4 wt %	N
				80, 10	30	80, 10		P
				80, 10	60	80, 10		P
				100, 10	30	100, 10	TMAH 2 wt %:methanol = 6:5 in wt ratio	P
				100, 10	60	100, 10		P
PVES-39	39	3150, 7750		80, 10	5	80, 10	TMAH 2 wt %:methanol = 6:5 in wt ratio	N
				80, 10	30	80, 10		N
				80, 10	60	80, 10		N
				100, 10	5	100, 10	TMAH 2 wt %:methanol = 6:5 in wt ratio	P
				100, 10	30	100, 10		P
				100, 10	60	100, 10		P

[a] Exposure energy: 3.96 mJ/cm^2 s.

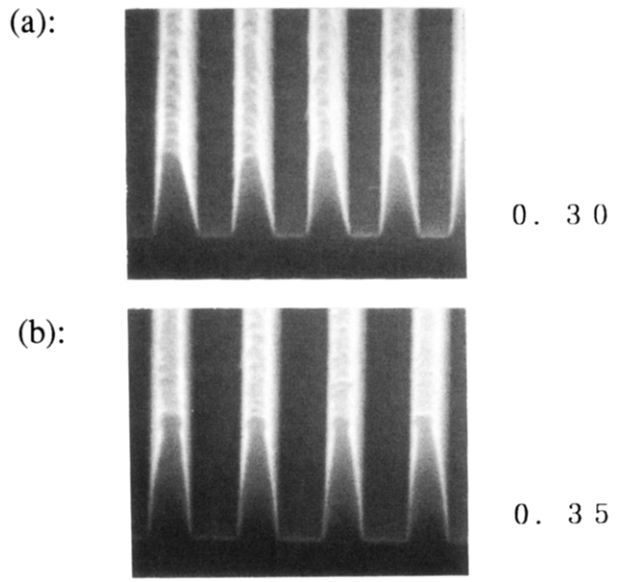


Figure 5. Scanning electron micrographs of the positive patterns obtained from PVES-9 containing 10 wt % TFMS-TPS. (a) 0.30-μm line and space. (b) 0.35-μm line and space.

even if all of the 10 wt % PAG reacts to release acids. This can be seen also from Figure 4b. When the content of PAG is 10 wt %, the normalized film thickness does not decrease to less than 0.6, even for exposure energies above 200 mJ/cm^2. Therefore, under these conditions, vinyl ether groups undergo cationic polymerization to form a cross-linked network with the aid of thermal energy in the PEB process. Consequently, PVES-39 exhibits negative working mode (Scheme VIa).

PVES-39 also exhibits the positive working mode when the layer is prebaked at 100 °C for 10 min and exposed for 5, 30, or 60 s (Scheme VIc). This behavior for PVES-39 is interpreted in the same manner as for PVES-9 and 20.

The spectral sensitivity for these resists is dependent on that of PAG. With ANS-DPI as a PAG, the resist is sensitive to near UV light (300–410 nm). When triphenylsulfonium trifluoromethanesulfonate (TFMS-TPS) is used as a PAG, the resist exhibits sensitivity to deep UV light from a low-pressure mercury lamp or a KrF excimer laser.

Figure 5 shows scanning electron micrographs of positive 0.30- and 0.35-μm line and space patterns printed in 1.03-μm-thick film. The film was prepared by spin-coating PVES-9 solution containing 10 wt % TFMS-TPS on Si wafer. The film was prebaked at 120 °C for 120 s and exposed at ca. 106 mJ/cm^2 with a KrF excimer laser, followed by PEB under the same conditions as the prebake. Development was done in 2.38 wt % aqueous solution of TMAH.

6. Conclusion

To achieve solubility in an aqueous base developer, copolymers (PVESs) containing sufficiently low vinyl ether group content were synthesized. PVES containing a photoacid generator (PAG) exhibited either positive or negative working behavior, depending on process conditions such as prebaking temperature or exposure energy. The vinyl ether groups of PVES undergo a cross-linking reaction with the aid of thermal energy to form a cross-linked network. The cross-links are decomposed by acid. The vinyl ether groups also undergo the competing reactions of cationic polymerization and acidolysis by photogenerated acids. The complicated behavior of PVES is determined by a combination of these reactions. Positive resists with sensitivities of ca. 25 mJ/cm^2 at 365-nm light by using ANS-DPI, and ca. 106 mJ/cm^2 at 248-nm light by using TFMS-TPS as PAG were obtained. When TFMS-TPS was used as a PAG, the resist exhibited 0.30- and 0.35-μm line and space patterns at 248-nm light.