Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

THREE-COMPONENT PHOTORESISTS CONTAINING VINYL ETHER CROSSLINKING AGENTS

Seong-Yun Moon[a]; Chan-Moon Chung[b]
[a] Japan Atomic Energy Research Institute, Takasaki, Gunma, Japan [b] Department of Chemistry, Yonsei University, Korea

To cite this Article Moon, Seong-Yun and Chung, Chan-Moon(2001) 'THREE-COMPONENT PHOTORESISTS CONTAINING VINYL ETHER CROSSLINKING AGENTS', Journal of Macromolecular Science, Part A, 38: 3, 243 — 252

To link to this Article: DOI: 10.1081/MA-100103346

URL: http://dx.doi.org/10.1081/MA-100103346

J. MACROMOL. SCI.—PURE APPL. CHEM., A38(3), 243–252 (2001)

THREE-COMPONENT PHOTORESISTS CONTAINING VINYL ETHER CROSSLINKING AGENTS

Seong-Yun Moon[1],* and Chan-Moon Chung[2]

[1]Department of Material Development, Takasaki Radiation Chemistry
Research Establishment, Japan Atomic Energy Research Institute,
1233 Watanuki, Takasaki, Gunma 370-1292, Japan
[2]Department of Chemistry, Yonsei University, Wonju,
Kangwon-do 220-710, Korea

ABSTRACT

Thermal crosslinking reactivity and lithographic performance were investigated for three-component photoresists composed of a Brønsted acid-based binder polymer, a vinyl ether monomer as a crosslinking agent, and a photoacid generator. Poly(*p*-hydroxystyrene) (PHS) and poly(styrene-*co*-acrylic acid) (PST/PAA) were used as the binder polymers. The resists acted as highly sensitive, chemically amplified resists based on thermal crosslinking between a binder resin and a vinyl ether monomer and subsequent acidolytic cleavage of the crosslinks. The rate constants and activation energies for the thermal crosslinking reactions were determined, and the resists based on PST/PAA showed higher thermal crosslinking reactivity than PHS resists. The resists in this study exhibited high photosensitivity and afforded positive-tone images by alkaline development.

Key Words: Photoresist; Thermal crosslinking reactivity; Vinyl ether.

---

*Corresponding author.

INTRODUCTION

High sensitivity and high resolution of a photoresist for microlithography can be accomplished by the incorporation of chemical amplification concept into resist systems. Since a series of onium salts, which photochemically generate strong acids, were reported (1–3), a number of chemically amplified resist systems have been studied. These involve the acid-catalyzed deprotection of acid-labile pendant groups (4–9), acid-catalyzed depolymerization of polymer main chains (10–13), and acid-catalyzed electrophilic aromatic substitution (14–17). In addition, electron beam-induced polymerization of pendant oxirane ring (18) and free radical polymerization of acrylated diols (19) are important examples.

The authors previously reported (20–22) that a two-component photoresist composed of poly{*p*-hydroxystyrene-*co*-*p*-[2-(vinyloxy)ethoxy]styrene}, and a PAG, and a three-component photoresist composed of a polymer bearing carboxyl groups (or a phenolic polymer), a vinyl ether monomer, and a PAG, exhibit positive working behavior with high resolution. In our very recent work (23), triphenylsulfonium salt PAGs containing vinyl ether groups were synthesized and used as thermally crosslinkable PAGs in a two-component system. In each case, vinyl ether groups react with hydroxyl groups of the Brønsted acid-based binder polymer on prebaking by electrophilic addition reaction to form acetal crosslinks. Upon exposure to ultraviolet (UV) light and subsequent postexposure bake (PEB), the crosslinks are decomposed acid-catalytically by photogenerated acids to give alcohol and aldehyde, and consequently, a positive-mode image is obtained after alkaline development. In the present study, the kinetics of the thermal crosslinking have been investigated for three-component systems composed of a Brϕnsted acid-based binder polymer, a vinyl ether crosslinker, and a PAG. Poly(*p*-hydroxystyrene) (PHS) and poly(styrene-*co*-acrylic acid) (PST/PAA) were employed as the binder polymers and their thermal crosslinking reactivity was compared. Measurements of lithographic sensitivity and preliminary imaging tests for the resists were also performed to evaluate their applicability to microlithography.

EXPERIMENTAL

Materials and Instruments

PHS ($M_n = 2400$, $M_w = 4300$, $M_w/M_n = 1.79$) and PST/PAA ($M_n = 2450$, $M_w = 4420$, $M_w/M_n = 1.80$) were supplied by Maruzen Petrochemical Co. Ltd. and Johnson Polymer Co. Ltd., respectively, and used as received. The percentage of acrylic acid units in the copolymer PST/PAA was determined to be 45% from proton nuclear magnetic resonance (^{1}H NMR) spectroscopy by comparing the integral ratio of 5H for benzene ring at 6.2 to 7.4 ppm to that for aliphatic chain at 0.8 to 2.5 ppm. 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 (polystyrene gel column) in tetrahydrofuran (THF) using polystyrene as a standard. 1,1,1-Tris{4-[2’-(vinyloxy)ethoxy]phenyl}ethane (TPE-TEVE), 2,2-bis{4-[2’-(vinyloxy)ethoxy]phenyl}propane (BPA-DEVE), and 1,2,3-tris[2’-(vinyloxy)ethoxy]benzene (PYRO-TEVE) were synthesized according to the literature (22) and 1,4-bis(vinyloxymethyl)cyclohexane (CHM-DEVE) was supplied by Aldrich Chemical Co. Ltd. Diphenyliodonium 8-anilinonaphthalene-9,10-dimethoxyanthracene-2-sulfonate (DIAS) was synthesized according to the literature (24–26). Fourier transform infrared (FT-IR) spectra were measured with a Horiba FT-200 FT-IR spectrometer.

Determination of Rate Constant of Thermal Crosslinking

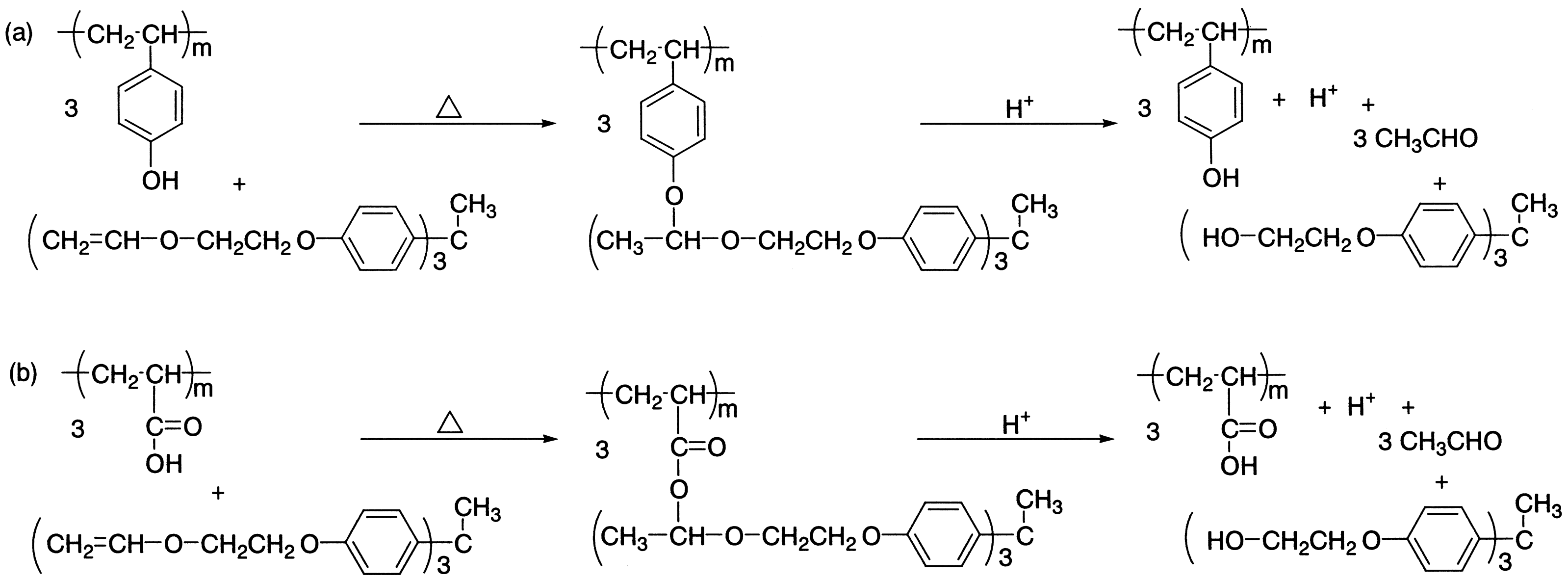
A propylene glycol monomethyl ether acetate (PGMEA) solution of a binder resin and TPE-TEVE with a molar ratio of acid moiety: TPE-TEVE of 60:1 was spin-coated on a Si wafer with a known size. The film on the wafer was dried under vacuum. From the thickness, area, and weight of the film, the initial concentration of the acid moiety was calculated. The film was cut into a small size and then used for FT-IR measurement. The bake was conducted up to 30 min in a convection oven at temperatures between 80°C and 120°C. A decrease in concentration of vinyl ether groups was measured by tracing an absorption change of the vinyl ether groups (δ_{CH}, 982 cm^{-1}). The temperature was raised to 130°C, and the bake was performed again until the peak attributable to δ_{CH} (982 cm^{-1}) attained the datum point with no further change. The point was taken as the reference standard.

Sensitivity Measurement

Resist films were prepared by spin-coating the photosensitive solutions on bare Si wafers, followed by prebake at 120°C for 10 min. The films were exposed to 365 nm light with a super-high-pressure mercury lamp, postbaked at 100°C for 10 min, and then developed in a 2.38 wt% 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 PEB.

RESULTS AND DISCUSSION

The authors had clarified the mechanism of the thermal crosslinking and acid-catalyzed cleavage of photoresists composed of a polymer bearing carboxylic groups (or a phenolic polymer), a vinyl ether monomer, and a PAG (21, 22). The results are described in Scheme 1: the thermal crosslinking of the binder polymer occurs through electrophilic addition reaction with vinyl ether groups in the prebake step, and upon exposure and subsequent PEB, the crosslinks with acetal



Scheme 1. Thermal crosslinking and acid-catalyzed cleavage of the crosslinks. a) Phenolic resin containing TPE-TEVE and b) polyacrylic acid containing TPE-TEVE.

structure are cleaved by photogenerated acid to give the original binder polymer, alcohol, and acetaldehyde.

In the present study, PHS and PST/PAA were used as the binder polymers to compare their thermal crosslinking reactivity and lithographic sensitivity. In the case of PST/PAA, a copolymer of styrene and acrylic acid having 55:45 mol-% composition was used because a lithographic testing indicated that the best resolving capacity could be achieved with the composition. Molecular weights of both polymers were almost the same as described in the Experimental section.

Figure 1 shows insolubilization curves for PHS and PST/PAA films, each containing 7 mol-% (with respect to the polymer) of TPE-TEVE as a crosslinker. The films were baked for 10 min in a convection oven and developed for 1 min in a 2.38 wt% aqueous solution of TMAH. The PHS film began to come insolubilized at 100°C, but the PST/PAA film started to come insoluble at a lower temperature of 80°C, indicating higher thermal crosslinking reactivity of PST/PAA.

By using the films composed of PHS (or PST/PAA) and TPE-TEVE, the kinetics of thermal crosslinking of the two binder polymers were investigated on the basis of Equations 1–4. A molar ratio of acid moiety:TPE-TEVE of 60:1 was used in this study. It was assumed that the rate-determining step of the thermal reaction is bimolecular-type second-order reaction. Because the excess amount of acid is present, the second-order reaction becomes a pseudo first-order reaction

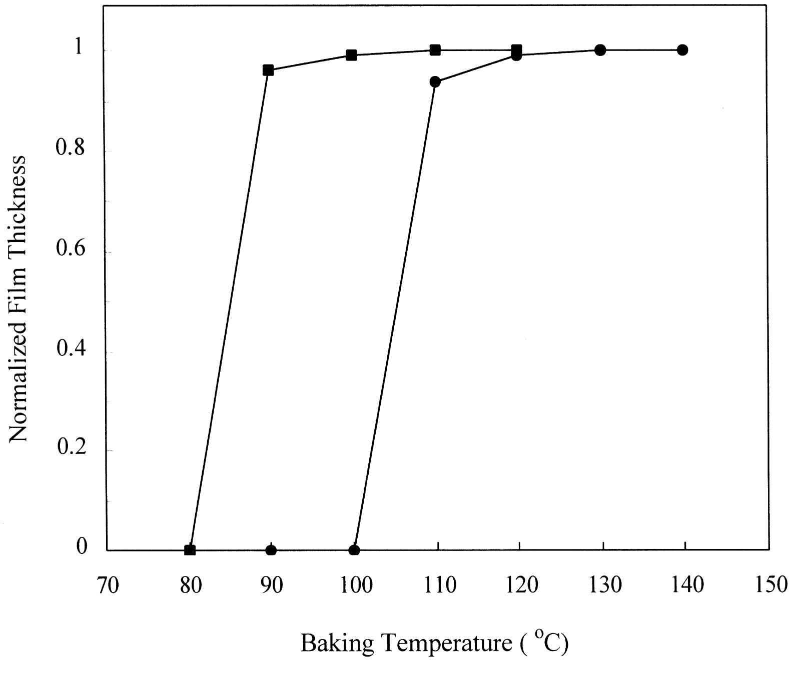


Figure 1. Insolubilization curves for PHS (●) and PST/PAA (■) films, each containing 7 mol-% TPE-TEVE: baking for 10 min; developer 2.38 wt% TMAH.

(Eq. 1–3). As can be seen in Figure 2, the plots of -ln([vinyl ether]/[vinyl ether]$_o$) versus baking time were all linear and allowed calculation of the rate constants (k) from the slopes. The activation energies were evaluated from Arrhenius plots based on Equation 4. The kinetic results are summarized in Table 1. The rate constants of the PST/PAA film were 1.9–2.6 times higher than those of the PHS film, depending on baking temperature. The activation energy (6220 cal/mol) of the PST/PAA film was determined to be lower than that (8610 cal/mol) of the PHS film.

$$\text{acid} + \text{vinyl ether} \rightarrow \text{acetal} \tag{1}$$

$$-d[\text{vinyl ether}]/dt = k[\text{acid}][\text{vinyl ether}] = k_{\text{observed}}\,[\text{vinyl ether}] \tag{2}$$

$$-\ln([\text{vinyl ether}]/[\text{vinyl ether}]_o) = k_{\text{observed}}\, t = k[\text{acid}]t \tag{3}$$

$$\ln k = \ln k_o - \Delta E/RT \tag{4}$$

where k_o is the frequency factor and ΔE is activation energy, and R is the ideal gas constant.

Figure 3 shows characteristic curves for the PHS and PST/PAA resists, each containing 7 mol-% TPE-TEVE and 2 mol-% DIAS. The prebake and PEB were done for 10 min at 120°C and 100°C, respectively, and development was performed using a 2.38 wt% aqueous solution of TMAH. The PHS film showed a sensitivity of 25 mJ/cm^2, and the PST/PAA film revealed a very high sensitivity of 0.9 mJ/cm^2. The higher sensitivity of PST/PAA resist might be partly attributable to higher solubility of the PST/PAA binder resin, because the crosslinks are decomposed by photogenerated acid and the original polymer structure before crosslinking is regenerated (Sch. 1). PHS and PST/PAA films without the crosslinker and PAG showed the dissolution rates of 1550 Å/s and 2320 Å/s, respectively, in the aqueous TMAH.

The lithographic sensitivities of PHS resists containing bifunctional (BPA-DEVE and CHM-DEVE) and trifunctional (TPE-TEVE and PYRO-TEVE) vinyl ether crosslinkers were evaluated using a concentration of 7 mol-% (Fig. 4). Prebake and PEB were done for 10 min at 120°C and 100 °C, respectively. There were no significant differences between the sensitivity values (15–25 mJ/cm^2) obtained for the resists.

The spectral sensitivity for the resists is dependent on that of the PAGs used. The resists containing DIAS was sensitive to near UV (300-400 nm), and those made from triphenylsulfonium trifluoromethanesulfonate (TPS-T$_f$), to deep UV light. Figure 5 shows a scanning electron micrograph of positive-tone image printed in a 0.7-µm thick PHS film containing 3 mol-% BPA-DEVE and 0.4 mol-% TPS-T$_f$. The resist film was prebaked at 140°C for 90 s, exposed at a dose of 62 mJ/cm^2 to 248 nm light from a KrF excimer laser stepper (Numerical Aperture: 0.45), and postbaked under the same conditions as in the prebake. Development was done in a 2.38 wt% aqueous solution of TMAH. The micrograph shows that 0.26-µm lines and spaces are resolved.

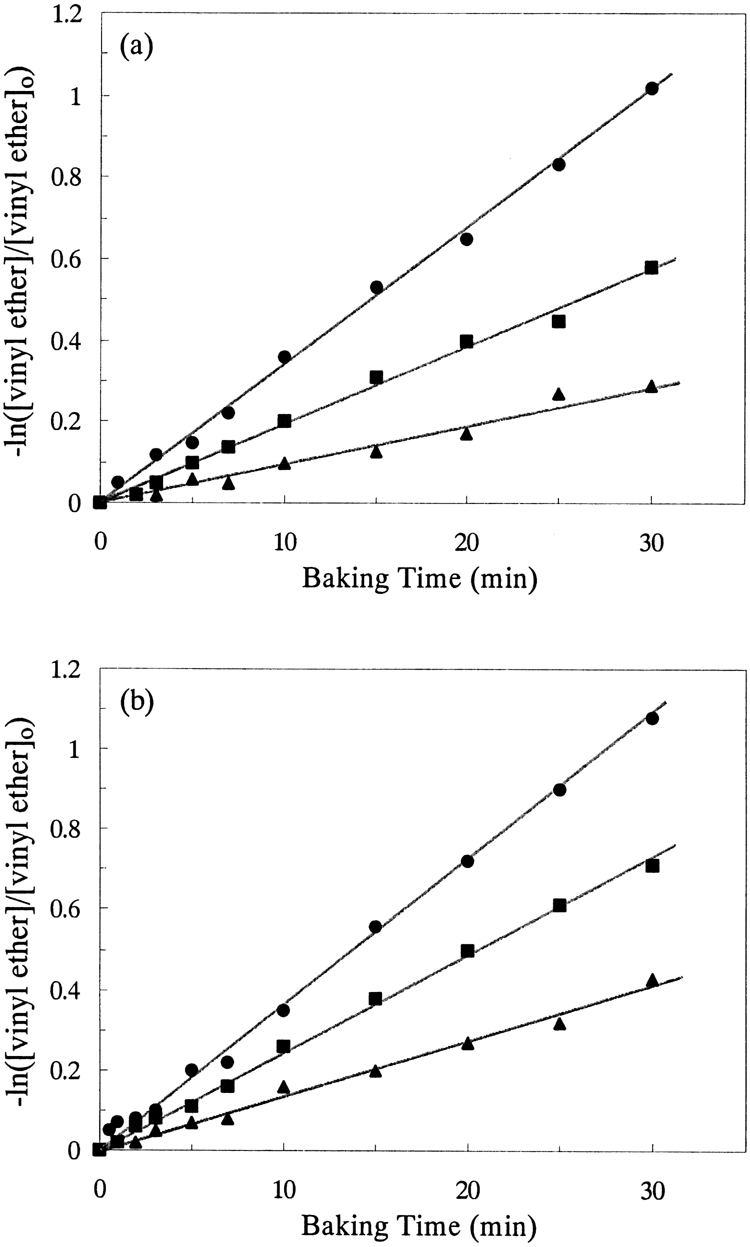


Figure 2. Thermal crosslinking reactivity of (a) PHS and (b) PST/PAA, each containing TPE-TEVE. Bake: (▲) 80°C; (■) 100°C; (●) 120°C.

Table 1. Rate Constants and Activation Energies of the Thermal Crosslinking

Polymer	PHS			PST/PAA		
Crosslinking agent	TPE-TEVE					
Baking Temperature (°C)	80	100	120	80	100	120
Rate Constant (k x 10^5 L/mol^{-1}·s^{-1})	1.30	2.51	4.46	3.36	5.71	8.60
Activation Energy (ΔE, kcal/mol)	8.6			6.2		

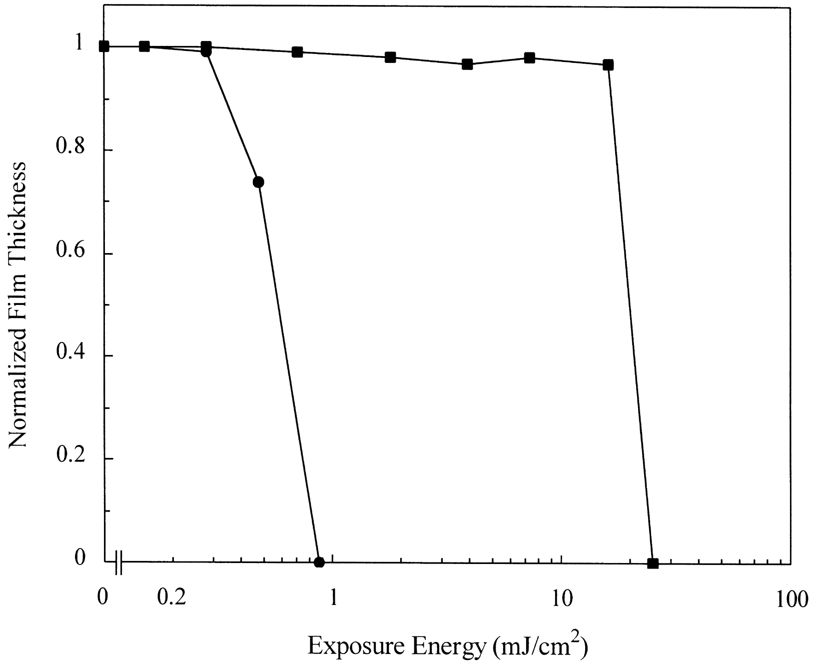


Figure 3. Characteristic curves for PHS (■) and PST/PAA (●) films, each containing 7 mol-% TPE-TEVE and 2 mol-% DIAS: prebake at 120°C for 10 min; PEB at 100°C for 10 min; developer 2.38 wt% TMAH.

CONCLUSION

The three-component photoresists have been shown to act as highly sensitive, chemically amplified photoresist system based on thermal crosslinking and subsequent acidolytic cleavage of the crosslinks. The rate constants of the thermal crosslinking for the PST/PAA resist were 1.9 to 2.6 times higher than those for the PHS resist, depending on baking temperature. The resist based on PST/PAA showed higher photosensitivity than PHS resist, and especially a very

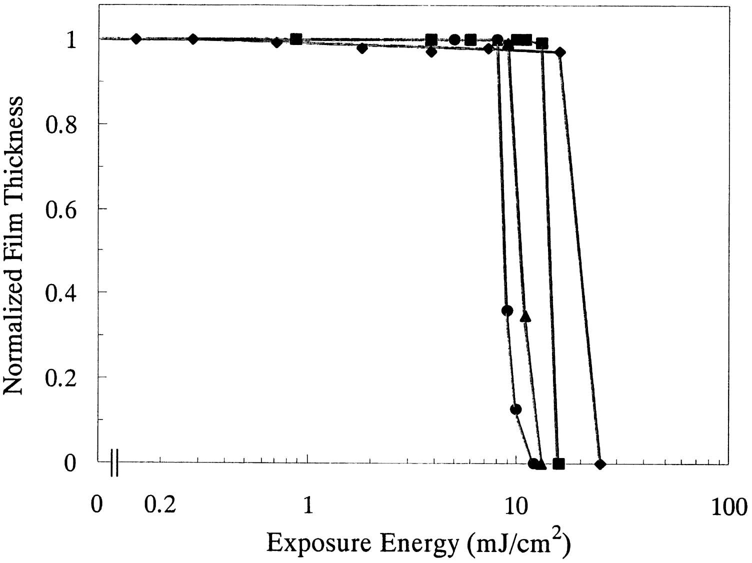


Figure 4. Characteristic curves for PHS films containing 7 mol-% TPE-TEVE (◆), PYRO-TEVE (▲), BPA-DEVE (■), and CHM-DEVE (●), and 2 mol-% DIAS: prebake at 120°C for 10 min; PEB at 100°C for 10 min; developer 2.38 wt% TMAH.

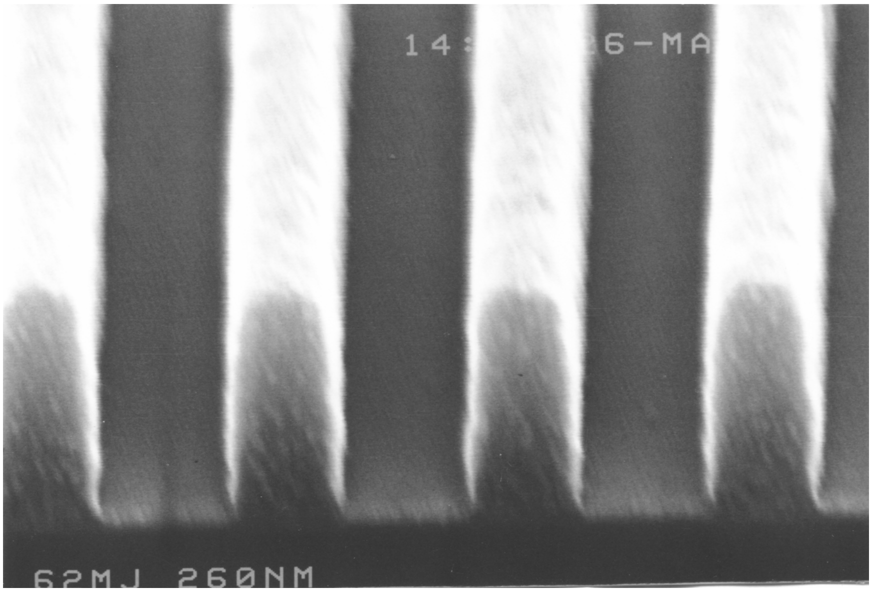


Figure 5. A scanning electron micrograph of 0.26-µm line and space positive patterns in the PHS film containing 3 mol-% BPA-DEVE and 0.4 mol-% TPS-T_f: prebake and PEB at 140°C for 90 s on a hot plate; dose 62 mJ/cm^2 to 248 nm light; developer 2.38 wt% TMAH.

high sensitivity of 0.9 mJ/cm^2 was obtained with a PST/PAA resist formulated with TPE-TEVE and DIAS.

REFERENCES

1. Crivello, J. V.; Lam, J. H. W. Macromolecules **1977**, *10*, 1307.
2. J. Polym. Sci., Polym. Chem. Ed. **1979**, *17*, 977.
3. Crivello, J. V.; Lam, J. H. J. Org. Chem. **1978***, 43,* 3055.
4. Yamaoka, T.; Nishiki, M.; Koseki, K. Polym. Eng. Sci. **1989**, *29*, 856.
5. Hayashi, N.; Ueno, T.; Hesp, M.; Toriumi, M.; Iwayanagi, T. Polymer **1992**, *33*, 1583.
6. Ito, H.; Ueda, M. Macromolecules **1990**, 23, 2885.
7. Frechet, J. M. J.; E. Eichler; Ito, H.; Willson, C. G. Polymer **1983**, *24*, 995.
8. Frechet, J. M. J.; Tessier, T. G.; Willson, C. G.; Ito, H. Macromolecules **1985**, *18*, 317.
9. Willson, C. G.; Ito, H.; Frechet, J. M. J.; Tessier, T. G.; Houlihan, F. M. J. Electro. Chem. Soc. **1986**, *133*, 181.
10. Frechet, J. M. J.; Bouchard, F.; Eichler, E.; Houlihan, F. M.; Iizawa, T.; Kryczka, B.; Willson, C. G. Polym. J. **1987**, *19*, 31.
11. Ito, H.; Ueda, M.; Schwalm, R. J. Vac. Sci. Technol. **1988**, *B6*, 6, 2259.
12. Frechet, J. M. J.; Houlihan, F. M.; Willson, C. G. Proc. ACS Div. Polym. Mater. Sci. Eng. **1985**, *53*, 268.
13. Houlihan, F. M.; Bouchard, F.; Frechet, J. M. J.; Willson, C. G. Macromolecules **1986**, *19*, 13.
14. Frechet, J. M. J.; Matuszczak, S.; Reck, B.; Tessier, T. G.; Stover, H. D. H.; Willson, C. G. Macromolecules **1991**, *24,* 1746.
15. Reck, B.; Allen, R. D.; Twieg, R. J.; Willson, C. G.; Matuszczak, S. Li, N. H.; Frechet, J. M. J. Polym. Eng. Sci. **1989**, *29*, 960.
16. Thackeray, J. W.; Orsula, G. W.; Rajaratnam, M. M.; Sinta, R.; Herr, D. Proc. SPIE. **1991**, *1466*, 39.
17. Fahey, J. T.; Shimizu, K.; Frechet, J. M. J.; Clecak, N.; Willson, C. G. J. Polym. Sci. Polym. Chem. Ed., **1993**, *31*, 1.
18. Thompson, L. F.; Feit, E. D.; Heidenreich. Polym. Eng. Sci. **1974**, *14*, 529.
19. Hoyle, C. E.; Keel, M.; Kim, K. J. Polymer **1988**, *29*, 18.
20. Moon, S.; Naitoh, K.; Yamaoka, T. Chem. Mater., **1993**, *5*, 1315.
21. Moon, S.; Kamenosono, K.; Kondo, S.; Umehara, A.; Yamaoka, T. Chem. Mater. **1994**, *6*, 1854.
22. Moon, S.; Chung, C.-M.; Yamaoka, T. Polymer **2000**, *41*, 4013.
23. Moon, S.; Chung, C.-M. Polym. Eng. Sci. **2000**, *40*, 1248.
24. Yamaoka, T.; Adachi, H.; Matsumoto, K; Watanabe, H.; Shirosaki, T. J. Chem. Soc., Perkin. Trans. **1990**, *2*, 1709.
25. Naitoh, K.; Yamaoka, T.; Umehara, A. Chem. Lett. **1991**, 1869.
26. Naitoh, K.; Yamaoka, T.; Umehara, A. Polym. Adv. Technol. **1992**, *3*, 117.

Received August 9, 2000
Revision received September 15, 2000