Polymer Journal (2010) 42, 86–94

www.nature.com/pj

ORIGINAL ARTICLE

Development of chemically amplified reaction development patterning

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Various carboxylate and sulfonate esters were synthesized as acid amplifiers by reacting carboxylic acid chlorides and sulfonic acid chlorides with alcohols. The synthesized acid amplifiers were introduced into a photosensitive polyetherimide (PEI) system on the basis of reaction development patterning (RDP) composed of PEI (Ultem) and a diazonaphthoquinone compound (PC-5) as a photosensitive agent, and the availability of the resulting chemically amplified RDP (CARDP) system was examined. It was found that the amount of photosensitive agent and the exposure dose required for the formation of fine patterns were closely related to the structure of acid amplifiers. Consequently, the use of 2SCE with two sulfonate groups in a molecule enabled the formation of clear patterns with 5 wt% of the photosensitive agent and a 300-mJ/cm^2 exposure dose, which achieved a sharp reduction of 30 wt% and 2000 mJ/cm^2, respectively, in the amount of the photosensitive agent and exposure dose used in conventional RDP. Good thermal properties of the patterns prepared by CARDP were also indicated.
Polymer Journal (2010) **42,** 86–94; doi:10.1038/pj.2009.308

Keywords: acid amplifier; chemically amplified reaction development patterning; photoresist; photosensitive agent; polyetherimide

INTRODUCTION

Photosensitive polymers, known as photoresists, have been widely used in the micropatterning of electronics such as semiconductor devices, printed wiring boards and color filters for liquid crystal displays.[1,2] High sensitivity, high resolution and good resistance to dry-etching are needed for photoresists that are used for microlithography in semiconductor technology. However, long-term properties are not very important for these photoresists because they are removed after dry-etching.[3] By contrast, there is another type of photoresist that is used for producing printed wiring boards and for protecting integrated circuits. The resolution needed for such photoresists is not very high (10–100 μm), but resist films require good mechanical, thermal and insulating properties because of the permanence of films in products. Thus, photosensitive polyimides (PIs), or polyamic acids as their precursors, have been used as photosensitive polymers for such purposes.[4,5] However, all these polymers require the introduction of functional groups to polymer frameworks to achieve photosensitivity and, as a result, they have the disadvantages of a reduction in the excellent properties of PI frameworks and of a high cost in preparing polymers. Thermal imidization processes are also needed for poly(amic acid) resists.

We have reported a new patterning process, reaction development patterning (RDP),[6] which is fundamentally different from previously developed processes. In RDP, the introduction of any specific functional groups or photosensitive groups to polymers is not necessary. In the process of RDP, films of commercially available engineering plastics containing a photosensitive agent are irradiated and developed by a hydrophilic nucleophilic developer. An acid generated from the photosensitive agent by irradiation reacts with amine in the developer to form salt, and the salt gives hydrophilicity to the polymer film. Therefore, at the exposed areas, infiltration of the hydrophilic developer into the polymer occurs more rapidly. Thereafter, reaction of the infiltrated amine in the developer with carboxylic acid derivatives (-C(O)-X-) in the main chain of engineering plastics leads to degradation of the polymer, and dissolution of the resulting low-molecular-weight compounds yields positive-tone patterns. We examined the applications of RDP to engineering plastics with -C(O)-X- linkages in the main chain such as PI[7] and commercially available polyetherimide (PEI),[8] polycarbonate (PC)[9] and polyarylate.[10,11] Clear patterns were formed with all polymers by RDP. However, a large quantity of photosensitive agent (30 wt% for the polymer) is needed for selective infiltration of the developer into exposed areas. In addition, a clear pattern can be obtained only with a large ultraviolet exposure dose (2000 mJ cm^{-2}) because of its low sensitivity.

Chemically amplified photoresist systems based on photoacid generators (PAGs) and functionalized polymers, such as polystyrene containing a *tert*-butoxycarbonyl group, have been studied to reduce the amount of photosensitive agent required and to achieve high sensitivity in comparison with traditional photoresists.[12] Acid groups (for example, a carboxyl group) protected with groups deprotectable by acid from PAGs are used as functional groups in polymers. At the exposed areas only, the deprotection reaction by the acid from PAGs

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Received 9 July 2009; revised 4 September 2009; accepted 12 September 2009

occurs through post-exposure baking (PEB), and the following development with an alkaline developer results in clear patterns.

In this study, we apply the principle of chemical amplification to RDP by adding a small quantity of photosensitive agent as a PAG and acid amplifier instead of a large quantity of photosensitive agent as used in conventional RDP. Acid amplifiers are protected low-molecular-weight acid molecules. A small amount of acid generated from the photosensitive agent by irradiation is expected to act as a catalyst for deprotection of the acid amplifier. The deprotection of the acid amplifier at PEB after irradiation will increase the amount of acid only at exposed areas. The produced acid can form salt with the developer, and the salt can promote preferential infiltration of the developer into exposed areas (Figure 1). When sulfonic acid esters are used as acid amplifiers, the generated sulfonic acid during PEB can also act as a catalyst for further deprotection reactions, and acid can be proliferated as reported by Ichimura *et al.*[13,14] Thus, the application of chemical amplification to RDP is expected to reduce the amount of photosensitive agent required and to achieve a higher sensitivity than that obtained with conventional RDP. In this study, we examined the effect of the structure of acid amplifiers on pattern-forming properties in chemically amplified RDP (CARDP) and explored the most suitable conditions for pattern formation. The sensitivity and amount of photosensitive agent required for pattern formation were also examined. In addition, the thermal properties of patterns obtained by CARDP were investigated.

EXPERIMENTAL PROCEDURE

Materials

Commercially available PEI (Ultem) (Scheme 1a) was kindly provided by Sabic Innovative Plastics Japan (Tokyo, Japan). 1,2-Naphthoqiunonediazide-5-sulfonic acid *p*-cresol ester (PC-5) (Scheme 1b) was purchased from Toyo Gosei Kogyo (Ichikawa, Chiba, Japan). Other reagents and solvents were purchased from Sigma-Aldrich Japan (Tokyo, Japan), TCI (Tokyo, Japan) and Wako Chemicals (Osaka, Japan).

Synthesis of acid amplifiers

Synthesis of tert-butyl 2-naphthoate (NTB). 2-Naphthoyl chloride (5.00 g, 26.2 mmol), *tert*-butanol (5.83 g, 78.6 mmol) and anhydrous pyridine (6.22 g, 78.6 mmol) were added to a 30-ml two-necked flask. *tert*-Butanol was used as the solvent, and pyridine was added as an acid scavenger and solvent. The mixture was stirred at 30 °C for 24 h under a nitrogen atmosphere. The white suspension that formed during the reaction was poured into a large amount of pure water. After stirring for 1 h at room temperature, a white precipitate was collected by filtration and washed with pure water. This process was repeated five times to completely remove salt, unreacted reactants and pyridine. Thereafter, the obtained white precipitate was dried under reduced pressure at 60 °C for 5 h to remove water. The resulting product was obtained with an 86% yield, melting point 85.6–88.2 °C, ^{1}H NMR (in dimethylsulfoxide (DMSO)-d_6) (δ, p.p.m.) 1.60 (-CH_3, s, 9H), 7.57–8.59 (Ar-H, m, 7H).

Synthesis of isopropyl 2-naphthalenesulfonate (SIP).[15,16] In a 100-ml two-necked flask, 2-naphthalenesulfonyl chloride (5.0 g, 22.0 mmol), 2-propanol (9.26 g, 154.0 mmol), pyridine (12.20 g, 154.0 mmol) and toluene (41.7 ml) were added at 0 °C. The mixture was stirred for 60 h at room temperature under a nitrogen atmosphere. The white precipitate that formed during the reaction was filtered, and the resulting filtrate was extracted with 5 wt% $NaOH_{aq}$. The organic layer was dried with $MgSO_4$, filtered and evaporated to yield a white solid. The crude ester was further purified by recrystallization with hexane–ether. The pure product was obtained after drying under reduced pressure for 5 h at room temperature at a 48% yield, melting point 54.8–55.8 °C (lit. 51%, 55.0–56.0 °C), ^{1}H NMR (in DMSO-d_6) (δ, p.p.m.) 1.20 (-CH_3, d, 6H), 4.74 (-CH-, m, 1H), 7.70–8.64 (Ar-H, m, 7H).

Synthesis of 2-phenylethyl 2-naphthalenesulfonate (SPE). 2-Naphthalenesulfonyl chloride (5.0 g, 22.0 mmol) and 2-phenylethanol (21.10 g, 154.0 mmol) were added to pyridine (12.20 g, 154.0 mmol) and toluene (41.70 ml) at room temperature, and the mixture was stirred for 68 h. The resulting suspension was filtered, and the filtrate was extracted with 5 wt% NaOHaq and 2 mol l^{-1} HClaq. Thereafter, the organic layer was distilled under high vacuum to remove unreacted alcohol. Ether was added to the obtained oil-like solid, and the ether-soluble part was collected and evaporated. The product was further purified by

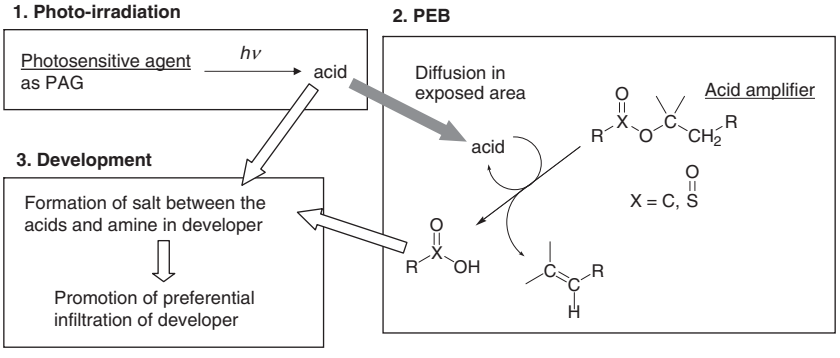
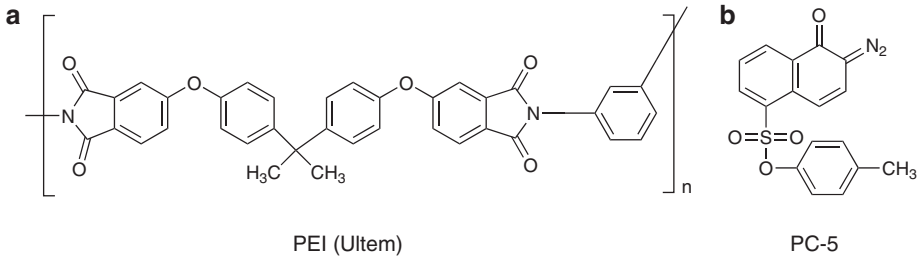


Figure 1 Mechanism of chemical amplification with an acid amplifier in reaction development patterning.



Scheme 1 Structures of polyetherimide (Ultem) and PC-5.

recrystallization using hexane–ether. The pure product was obtained after drying overnight under reduced pressure at room temperature at a 41% yield, melting point 50.7–51.4 °C, ^{1}H NMR (in DMSO-d_6) (δ, p.p.m.) 2.90 (-CH_2-Ar, t, 2H), 4.30 (-O-CH_2-, t, 2H), 7.12–8.57 (Ar-H, m, 12H).

Synthesis of di-tert-butyl terephthalate (2TB).[17] Terephthaloyl chloride (5.00 g, 25.0 mmol), *tert*-butanol (3.70 g, 50.0 mmol) and pyridine (4.00 g, 50.0 mmol) were added to a 50-ml two-necked flask. The mixture was stirred at 30 °C for 15 h. To a white solid that formed during the reaction, a large amount of diethyl ether was added, and the insoluble part was filtered off. The filtrate was extracted seven times with 10 wt% NaOHaq, twice with 2 mol l^{-1} HClaq and once with pure water. The organic layer was dried with $MgSO_4$, filtered and evaporated to yield a white solid. The product was further purified by recrystallization using H_2O–ethanol. The pure product was obtained after drying overnight under reduced pressure at room temperature with a 45% yield, melting point 116.9–117.8 °C (lit. 62%, 116.0–117.0 °C), ^{1}H NMR (in DMSO-d_6) (δ, p.p.m.) 1.56 (-CH_3, s, 18H), 8.00 (Ar-H, s, 4H).

Synthesis of diethyl chlorobenzene-2,4-disulfonate (2SCE).[18] In a 100-ml two-necked flask, *p*-chlorobenzenesulfonyl chloride (10.00 g, 47.6 mmol) and chlorosulfonic acid (25.00 g, 214.6 mmol) were added and heated at 130 °C for 20 h under a nitrogen atmosphere. The cooled reaction mixture was cautiously poured onto cracked ice, and a white precipitated solid was obtained. Thereafter, the white precipitate was filtered and dissolved in toluene. The solution was extracted four times using pure water. The organic layer was dried with $MgSO_4$, filtered and evaporated to yield a solid. The crude acid chloride was further purified by recrystallization using hexane–carbon tetrachloride. Pure chlorobenzene-2,4-disulfonyl chloride was obtained after drying overnight under reduced pressure at 40 °C with a 53% yield, melting point 89.2–90.3 °C (lit. 69%, 89.0–90.0 °C), ^{1}H NMR (in DMSO-d_6) (δ, p.p.m.) 7.36–7.39 (=CH-C(Cl)=, d, 1H), 7.53–7.57 (=CH-C(SO_2Cl)-, dd, 1H), 8.16–8.17 (-C(SO_2Cl)=CH-C(SO_2Cl)=, d, 1H).

Chlorobenzene-2,4-disulfonyl chloride (5.98 g, 19.3 mmol) was added to toluene (60 ml) in a 200-ml flask. To the solution, ethanol (25.00 g, 47.0 mmol) and pellet sodium hydroxide (1.6 g) were added, and the reaction mixture was stirred at room temperature for 6 h. A white precipitate that formed during the reaction was filtered, and the resulting filtrate was extracted four times using pure water. The organic layer was dried with $MgSO_4$, filtered and evaporated to yield a solid. The crude ester was further purified by recrystallization using hexane–ethanol. The pure white product was obtained after drying under reduced pressure at 35 °C for 5 h with a 24% yield, melting point 71.1–71.9 °C (lit. 30%, 72.0–73.0 °C), ^{1}H NMR (in DMSO-d_6) (δ, p.p.m.) 1.20–1.34 (-CH_3, m, 6H), 4.08–4.36 (-CH_2-, m, 4H), 7.70–8.33 (Ar-H, m, 3H).

Preparation of PEI films containing a photosensitive agent and an acid amplifier

Polyetherimide (17.5 wt%) was dissolved in *N*-methyl-2-pyrrolidinone. The diazonaphthoquinone (DNQ) compound PC-5 as a photosensitive agent (5–10 wt% for PEI) and an acid amplifier (0–20 wt% for PEI) were dissolved in *N*-methyl-2-pyrrolidinone solution. The resulting photosensitive PEI solutions were degassed and spin-coated onto the shiny side or matte side of a copper foil, and photosensitive PEI films of 7.6–12.5 μm thickness were obtained after prebaking at 90 °C for 7–10 min in a far-infrared oven.

Irradiation, PEB and development

Films were irradiated with an ultrahigh-pressure mercury lamp without any filter (exposure dose of 300 mJ cm^{-2} when converted to the i-line) through a positive photomask in a contact technique. Thereafter, the exposed films were treated at 110 °C for 15–60 s in a far-infrared oven for PEB, developed in a mixture of ethanolamine (EA)/*N*-methyl-2-pyrrolidinone/H_2O at 40 °C under ultrasonication, and rinsed with pure water.

Measurement

^{1}H NMR spectra were recorded on a JEOL JNM-270 spectrometer (270 MHz) (JEOL, Akishima, Tokyo, Japan) at room temperature using DMSO-d_6 as a solvent and tetramethylsilane as the internal standard. The glass transition temperature (T_g) was determined as the onset temperature in differential scanning calorimetry (DSC) analysis (Shimadzu, Kyoto, Japan, DSC-60) at a heating rate of 10 °C min^{-1} under N_2. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 under N_2 or air. Film thickness was measured with a contact-type thickness analyzer (Nikon, Tokyo, Japan, DIGIMICRO MFC-101). Irradiation was conducted by a ultraviolet exposure apparatus (ORC, JP-2000-EXC), and the exposure dose was measured in the wavelength range of 320–390 nm (ORC, UV-331AP2). Scanning electron micrographs (SEMs) were taken with a HITACHI S-2600N (Hitachi, Tokyo, Japan) and a JEOL JSM-6390LV instrument (JEOL).

RESULTS AND DISCUSSION

Synthesis of acid amplifiers

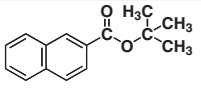
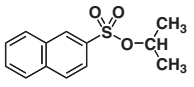
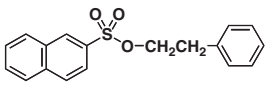
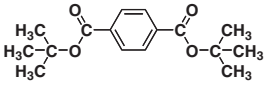
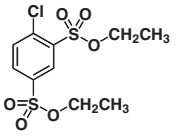
All acid amplifiers with ester groups were synthesized by reacting carboxylic acid chlorides or sulfonic acid chlorides with the corresponding alcohols. Pure products were obtained after appropriate purification procedures and recrystallization, and all products were solid at room temperature. There are two kinds of acid amplifiers, that is, those with one functional group (**NTB**, **SIP** and **SPE**) and those with two functional groups (**2TB** and **2SCE**). The structures of the acid amplifiers are shown in Table 1. All acid amplifiers were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **SPE** is shown in Figure 2.

The thermal properties of the acid amplifiers prepared in this study were investigated by TGA, and the results are shown in Figure 3. $T_{d\ onset}$, the onset temperature of degradation, of the acid amplifiers is shown in Table 1. The $T_{d\ onset}$ values of the acid amplifiers were 146–228 °C and were found to be higher than the prebaking temperatures of films. The PEB temperature for CARDP should be lower than the degradation temperature of acid amplifiers to avoid nonselective generation of acid both at the exposed and unexposed regions. Thus, in this study, PEB was carried out at 110 °C.

Lithographic evaluation

To evaluate the effect of acid amplifiers, PEI films containing the DNQ compound PC-5 as a photosensitive agent (Scheme 1) and each acid

Table 1 Structure and properties of acid amplifiers

Acid amplifier	*Structure*	*Yield (%)*	*mp (°C)*	*$T_{d\ onset}$[a] (°C)*
NTB		86	85.6-88.2	179
SIP		48	54.8-55.8	146
SPE		41	50.7-51.4	228
2TB		45	116.9-117.8	179
2SCE		24	71.1-71.9	186

[a]Determined by TGA.

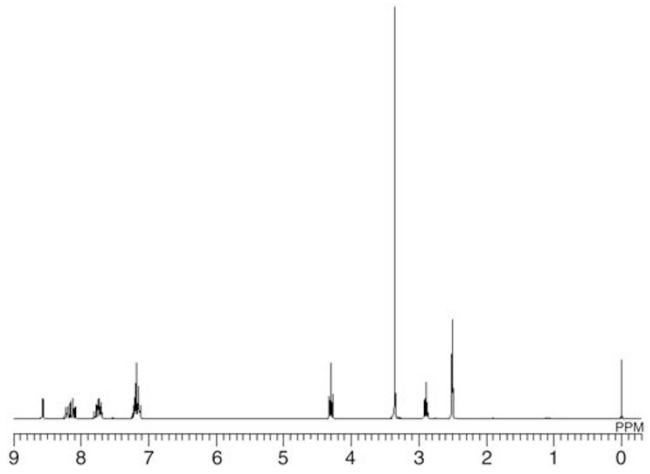


Figure 2 ^{1}H NMR of **SPE** (in DMSO-d_6).

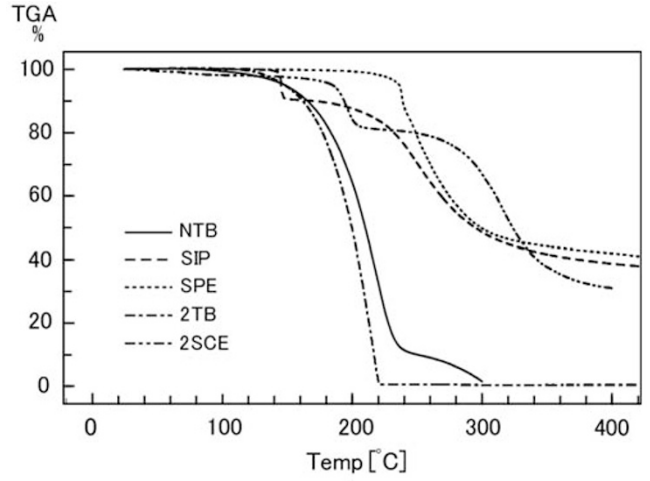


Figure 3 Thermogravimetric analysis traces of acid amplifiers (heating by 10 °C min^{-1} in N_2).

amplifier were used for patterning. The films prepared by spin-coating and prebaking were irradiated with an ultrahigh-pressure mercury lamp (i-line and g-line) through a positive photomask (exposure dose of 300 mJ cm^{-2}) and heated at 110 °C for PEB. The following development in a mixture of EA/*N*-methyl-2-pyrrolidinone/H_2O at 40 °C under ultrasonication and rinsing with pure water resulted in positive-tone patterns. The results of the pattern formation of the photosensitive PEI films and SEMs of the obtained patterns are shown in Table 2 and Figure 4, respectively.

In conventional RDP, clear patterns were obtained only when the amount of photosensitive agent was more than 30 wt% for the polymer.[6–11] Thus, we fixed the total amount of the photosensitive agent and acid amplifier in this study to be less than or equal to 30 wt%. The application of CARDP to PEI with a small amount of photosensitive agent and without any acid amplifier resulted in the formation of unclear patterns (entry 1 in Table 2, Figure 4a). This is because of a shortage of acid at the exposed areas and is in accordance with our previous studies.[6–11] The use of **NTB** as the acid amplifier improved the pattern shapes (Figure 4b). However, the film thickness at the unexposed area after development was largely decreased (entry 2 in Table 2). To differentiate the acidity between exposed and unexposed areas, we examined the use of esters from sulfonic acid with stronger acidity. When **SIP** was used instead of **NTB**, clear line and space (L/S) patterns were obtained with larger residual film thickness (entry 3 in Table 2), despite the fact that the same amounts of photosensitive agent and acid amplifier were used as in the **NTB** system. The superior property of **SIP** is because of the higher acidity of sulfonic acid compared with carboxylic acid, which enhances the permeation of EA in the development process (see 'Pattern-forming mechanism' section). The catalysis of degradation of **SIP** not only by carboxylic acid from DNQ but also by sulfonic acid from **SIP** during PEB would contribute to successful pattern formation in the **SIP** system.[13,14] A reduction in development time in the **SIP** system was achieved when the permeability of the developer was increased by omitting water from the developer system (entry 4 in Table 2).[11] A decrease in the amount of **SIP** used from 20 to 10 wt% was also achieved, although it was accompanied by an increase in development time and a decrease in residual film thickness (entry 5 in Table 2 and Figure 4c). 2-Phenylethyl ester of sulfonic acid (**SPE**) was also examined as an acid amplifier (entries 6–8 in Table 2). Although the tendency of the development time in **SPE** systems was the same as that of **SIP** systems, the residual film thicknesses in **SPE** systems were found to be better than those in **SIP** systems, probably because the higher number of aromatic rings in **SPE** compared with **SIP** afforded more hydrophobic properties to **SPE**. In RDP, the infiltration of hydrophilic developer into unexposed areas is considered to be inhibited by hydrophobic DNQ.[6–11] Thus, the addition of more hydrophobic **SPE** in place of **SIP** would assist the inhibition at unexposed areas and result in improved residual film thicknesses in **SPE** systems. SEM photographs of the patterns reported in entries 6 and 8 in Table 2 are shown in Figures 4d and e, respectively, and clear L/S patterns can be observed.

To reduce the development time in the case of the decreased amount of acid amplifiers, the use of acid amplifiers with two functional groups within one molecule was examined. **2TB** with two carboxylate groups in an amplifier was equally ineffective as **NTB**, and round-shaped patterns were obtained (entry 9 in Table 2 and Figure 4f). We then applied **2SCE** with two sulfonate groups in an amplifier to CARDP. As a result, a shorter development time (10 min) and a higher residual film thickness (80%) were achieved in spite of the reduced amount of **2SCE** of 10 wt% (entry 10 in Table 2). A reduction in PEB time to 15 s resulted in a further decrease in development time (7 min 5 s, entry 11). Moreover, optimization of prebaking conditions (7 min at 90 °C) achieved the shortest development time (4 min 5 s) while maintaining a good residual film thickness after development (entry 12 in Table 2). The SEM images of **2SCE** systems (entries 11 and 12) are shown in Figures 4g and h, respectively. In these cases, adhesion between photosensitive polymer films and the shiny side of the copper foil was not sufficient for pattern formation, and the films were spin-coated onto the matte side of the foil. Clear L/S patterns were formed in these systems. A reduction in the amount of photosensitive agent in the **2SCE** system was also examined, and positive-tone L/S patterns were successfully prepared even when only 5 wt% of PC-5 was used (entry 13 in Table 2). The superior property of **2SCE** as an acid amplifier would result from a higher sulfonate content (6.08 mmol g^{-1}) in **2SCE** compared with **SPE** (3.20 mmol g^{-1}) and **SIP** (4.0 mmol g^{-1}). The catalysis of deprotection of a sulfonate in **2SCE** by a proton from another deprotected sulfonate in the same molecule may also contribute to the good results obtained for the **2SCE** systems. These advantages in **2SCE** promote the infiltration of the developer into exposed areas and their rapid dissolution. As a result of this fast dissolution, in spite of a reduced

Table 2 Results of pattern formation for photosensitive PEI[a,b]

Entry	*Acid amplifier (wt%)*		*Photosensitive agent[c] (wt%)*	*Prebake (°C/min)*	*PEB (°C/s)*	*Developer (weight ratio) EA/NMP/H_2O*	*Development time (min'sec)*	*Film thickness (μm)[d]*
1	None	0	10	90/10	110/60	4/1/1	61'00	12.5→5.1 (41)
2	**NTB**	20	10	90/10	110/60	4/1/1	33'09	7.6→2.3 (30)
3	**SIP**	20	10	90/10	110/60	4/1/1	42'00	9.2→5.4 (59)
4		20	10	90/10	110/60	4/1/0	9'30	9.7→5.5 (57)
5		10	10	90/10	110/60	4/1/0	21'20	10.5→3.9 (37)
6	**SPE**	20	10	90/10	110/60	4/1/1	44'00	9.1→6.3 (69)
7		20	10	90/10	110/60	4/1/0	9'10	9.5→5.8 (61)
8		10	10	90/10	110/60	4/1/0	26'30	9.4→4.1 (44)
9	**2TB**	20	10	90/10	110/60	4/1/1	34'10	10.8→4.9 (45)
10	**2SCE**	10	10	90/10	110/60	4/1/0	10'00	10.4→8.3 (80)
11		10	10	90/10	110/15	4/1/0	7'05	10.2→6.6 (65)
12		10	10	90/7	110/15	4/1/0	4'05	9.9→6.6 (67)
13		10	5	90/10	110/15	4/1/0	14'50	10.9→6.6 (61)

[a]Irradiated at 300 mJ cm^{-2} of exposure dose.
[b]Developed at 40 °C under ultrasonication.
[c]PC-5.
[d]The values in parentheses are the ratio of residual film thickness (%).

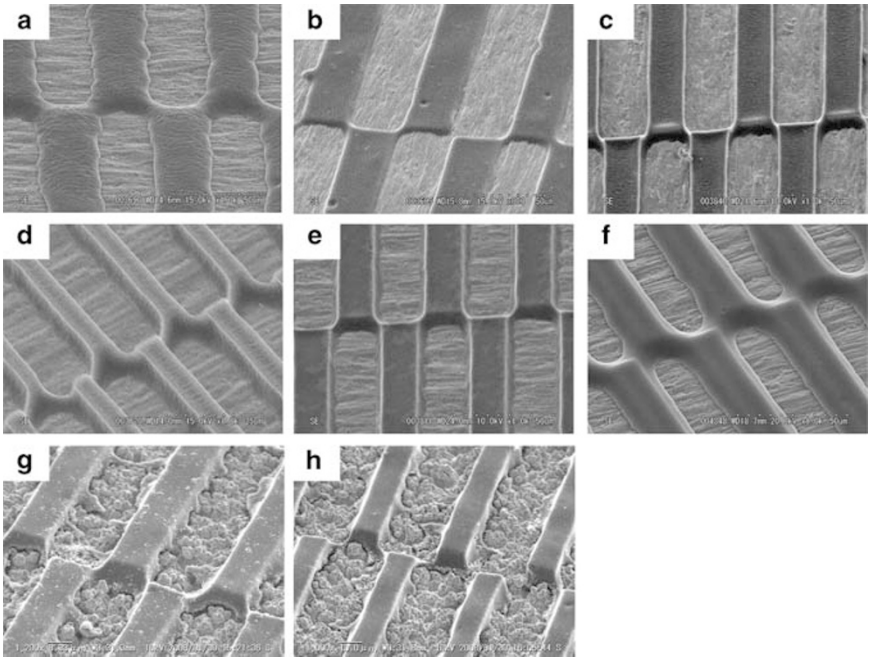


Figure 4 Scanning electron micrograph images of line and space (L/S) patterns for photosensitive polyetherimide based on CARDP. (**a**) Table 2, entry 1 (L/S=20 μm); (**b**) Table 2, entry 2 (L/S=30 μm); (**c**) Table 2, entry 4 (L/S=20 μm); (**d**) Table 2, entry 6 (L/S=10 μm); (**e**) Table 2, entry 8 (L/S=20 μm); (**f**) Table 2, entry 9 (L/S=20 μm); (**g**) Table 2, entry 11 (L/S=20 μm); and (**h**) Table 2, entry 12 (L/S=20 μm).

inhibition effect caused by less hydrophobic **2SCE** at unexposed areas as compared with the more hydrophobic **SPE** and **SIP**, dissolution at exposed areas is completed before dissolution progression at unexposed areas.

Figure 5 shows the sensitivity curves of photosensitive PEI films based on CARDP. Sensitivity (E_0) was estimated from the exposure dose at which the resist film was completely dissolved into the developer. The sensitivity of the **NTB** system was 354 mJ cm^{-2} (Figure 5a). This is a significant improvement compared with the value of 2000 mJ cm^{-2} obtained for conventional RDP. The sensitivity of the **SPE** system was 177 mJ cm^{-2} (Figure 5b). The higher sensitivity compared with that of **NTB** is in agreement with the results in Table 2 and Figure 4. This demonstrates that the esters prepared from compounds with higher acidity were effective as acid amplifiers. The sensitivity of the **2SCE** system was 125 mJ cm^{-2} (Figure 5c), and this value was the highest sensitivity among all the acid amplifiers. The difference in the dissolution rate between the exposed and unexposed regions of the **2SCE** system is shown in Figure 6. The dissolution rate of the exposed region was higher than that of the unexposed region. The residual film thickness at unexposed regions was 66% when the dissolution in the exposed region was completed.

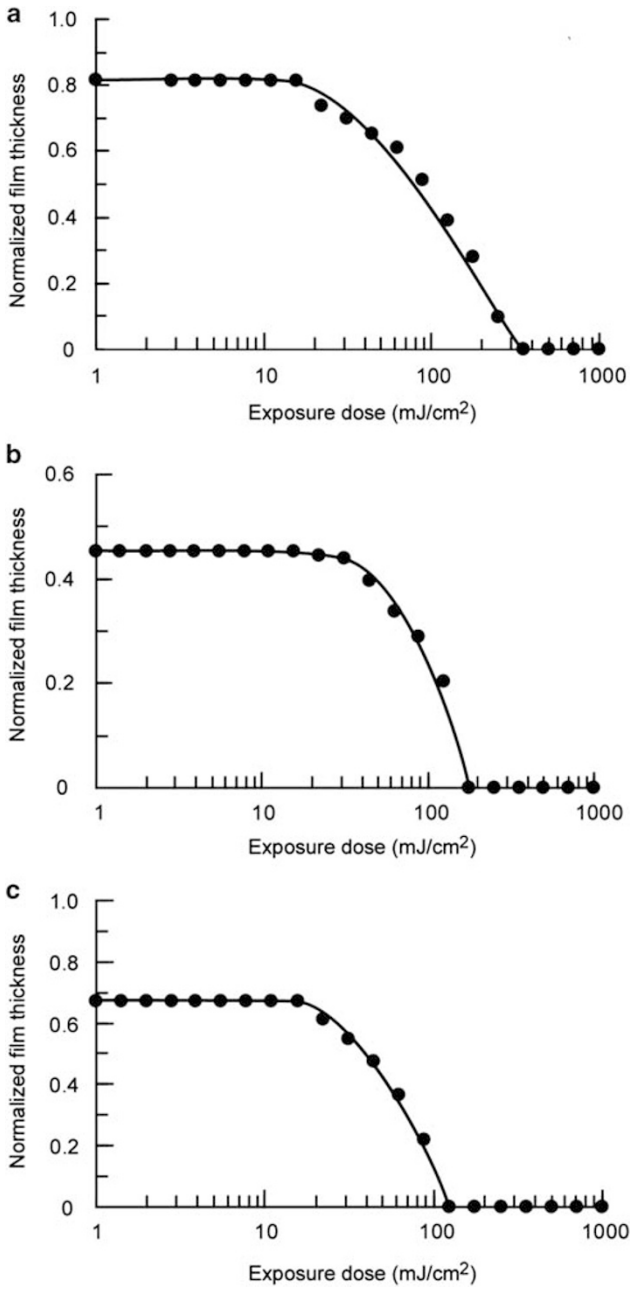


Figure 5 Sensitivity curves for photosensitive polyetherimide based on chemically amplified reaction development patterning. (**a**) PC-5 10 wt%+**NTB** 20 wt%, developed with ethanolamine (EA)/*N*-methyl-2-pyrrolidinone (NMP)/H_2O (4/1/1 by weight). (**b**) PC-5 10 wt%+**SIP** 10 wt%, developed with EA/NMP (4/1 by weight). (**c**) PC-5 10 wt%+**2SCE** 10 wt%, developed with EA/NMP (4/1 by weight).

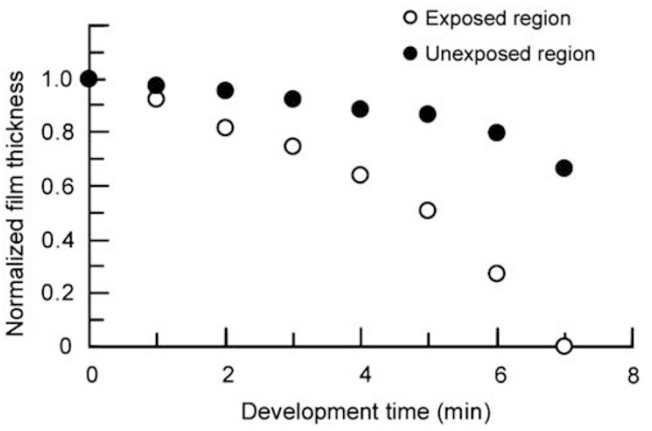


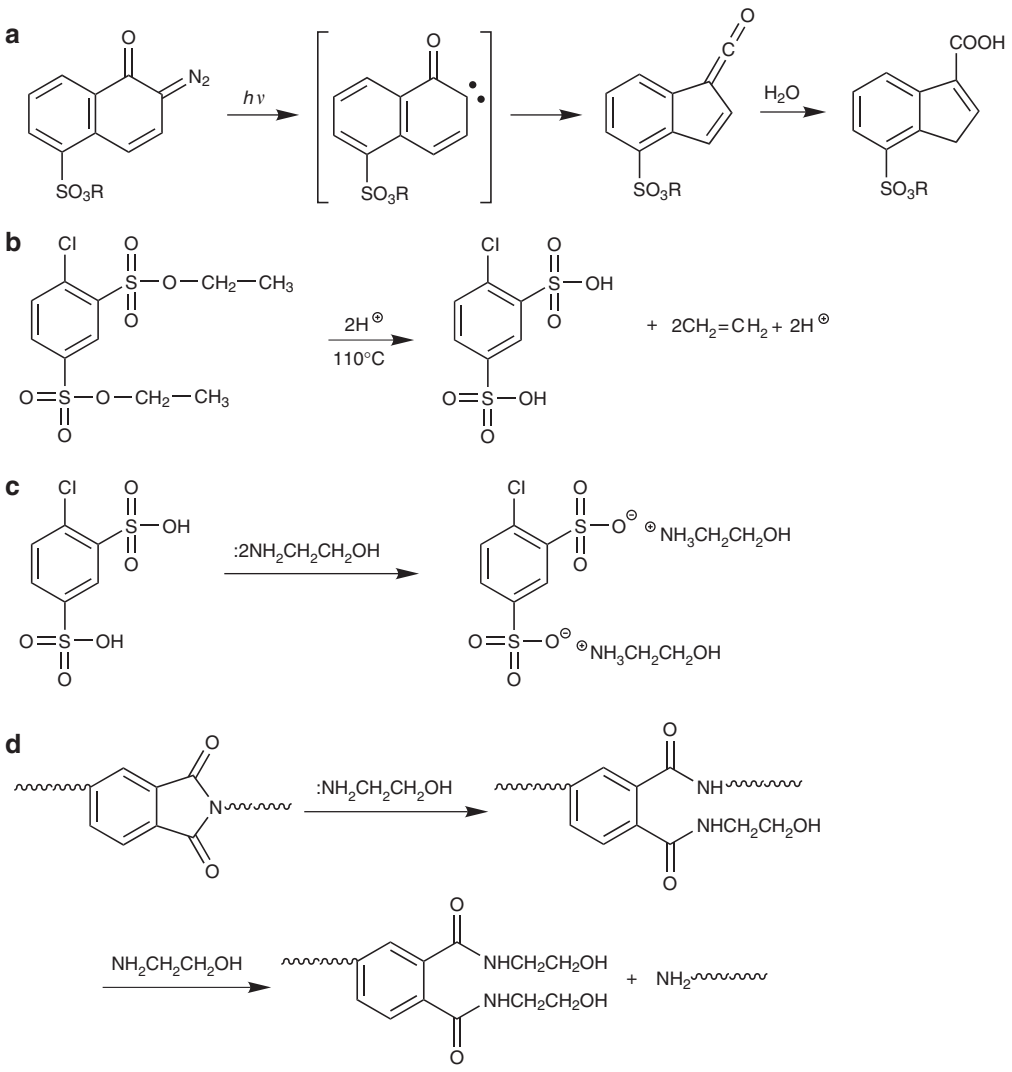
Figure 6 Dissolution curves for photosensitive polyetherimide based on chemically amplified reaction development patterning. PC-5 10 wt%+**2SCE** 10 wt%, developed with ethanolamine/*N*-methyl-2-pyrrolidinone (4/1 by weight). ○: exposed region; ●: unexposed region.

Pattern-forming mechanism

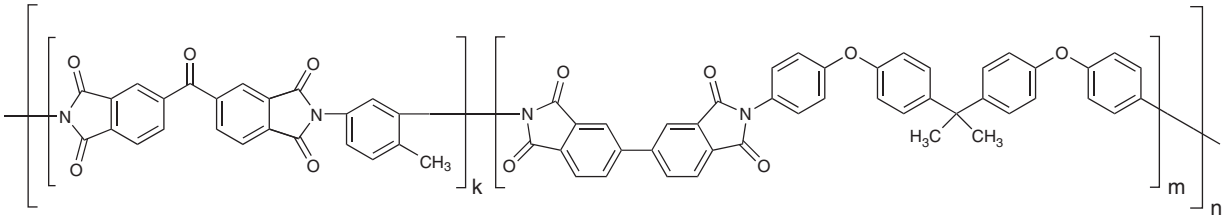
From the results shown in the previous section and those from literature,[6–11] pattern formation for CARDP should be considered to proceed as shown in Scheme 2. In exposed regions, the photosensitive agent DNQ in the film converts to indenecarboxylic acid by irradiation (Scheme 2a). Thereafter, the degradation reaction of amplifiers is caused by the proton from the indenecarboxylic acid resulting in sulfonic (or carboxylic) acid, and the proton is regenerated (Scheme 2b). The regenerated proton is used repeatedly for the degradation of amplifiers. Because this degradation reaction occurs consecutively, the amount of the acid is increased only at exposed areas. The acid from amplifiers and the photosensitive agent then reacts with EA in the developer, and salt is formed (Scheme 2c). The formation of salt leads to the infiltration of the hydrophilic developer, and the reaction of the infiltrated EA with PEI results in main-chain scission and dissolution of the corresponding low-molecular-weight compounds at exposed areas into the developer (Scheme 2d). In unexposed regions, the reaction of photosensitive agents and the succeeding chemical amplification do not occur, and therefore, infiltration of the developer does not occur either. As a result, positive-tone patterns are formed.

Thermal properties

The thermal properties of films containing a photosensitive agent (PC-5), an acid amplifier (**SPE**) and a combination of the two were examined. Soluble and thermally stable multiblock copolyimide (bPI (T_g: 256 °C), Scheme 3)[7] was used as the polymer component. A bPI film without any additives was used as a reference to obtain the weight loss derived from the residual solvent in prebaked films. All films were heated at 250 °C for 5 h, and the difference in weight loss between samples and the reference was estimated to be the weight loss derived from the photosensitive agent, the acid amplifier or from a combination of the two. After heating for 5 h at 250 °C, the films were reheated to 800 °C, and T_{d5} values were investigated. The TGA traces are shown in Figure 7. Table 3 shows the values of estimated weight losses and T_{d5} values. On the basis of the results shown in Figure 7a, the weight loss in the TGA measurement of the bPI film was found to be 16.0%. Thus, the residual solvent in the prebaked bPI film was $100\times16.0/(100-16.0)=19.0$ wt% for the polymer (entry 1 in Table 3). From this result, the weight loss derived from PC-5 (10 wt% for the polymer before thermal treatment) was estimated to be 23.5–19.0=4.5 wt% (entry 2 in Table 3). In the same way, the weight losses derived from 20 wt% of **SPE** and 10wt% of PC-5+20 wt% of **SPE** were estimated to be 8.8 and 10.7 wt%, respectively (entries 3 and 4 in Table 3). Although, as shown above, thermal treatment at 250 °C for 5 h did not remove all the additives in the photosensitive bPIs, a good thermostability of thermally treated bPIs was achieved by reheating to 800 °C (Figure 7b, Table 3). These results suggest that appropriate thermal treatment of photosensitive films can recover the thermal properties of PIs considerably.



Scheme 2 Mechanism of chemically amplified reaction development patterning. (**a**) Formation of indenecarboxylic acid by ultraviolet irradiation; (**b**) Degradation reaction of acid amplifier; (**c**) Formation of salt by reaction of the acid with ethanolamine (EA); (**d**) Reaction of imide ring with EA.



Scheme 3 Structure of bPI.

The difference in the shape of patterns before and after heating was also examined. Figure 8 shows the difference in shape of the same patterns prepared with bPI containing a photosensitive agent and an acid amplifier before and after heating (before: Figure 8a, after: Figure 8b). The thickness and width of the patterns were measured by using SEM, and the values are presented in Table 4. As shown in Figure 8 and Table 4, after heating at 240 °C for 1 h, the patterns were found to maintain their shapes with little shrinkage. From these results, good thermal properties of the patterns prepared by CARDP are indicated.

CONCLUSION

Various carboxylate and sulfonate compounds as acid amplifiers were synthesized, and the principle of chemical amplification was successfully applied to RDP. The acid amplifiers with sulfonate groups afforded better patterns, and the sulfonate with two functional groups was more effective as an acid amplifier than the sulfonate with one functional group. The amount of photosensitive agent was successfully reduced from 30 to 5 wt%, and high sensitivity (125 mJ cm^{-2}) compared with conventional RDP (2000 mJ cm^{-2}) was also achieved.

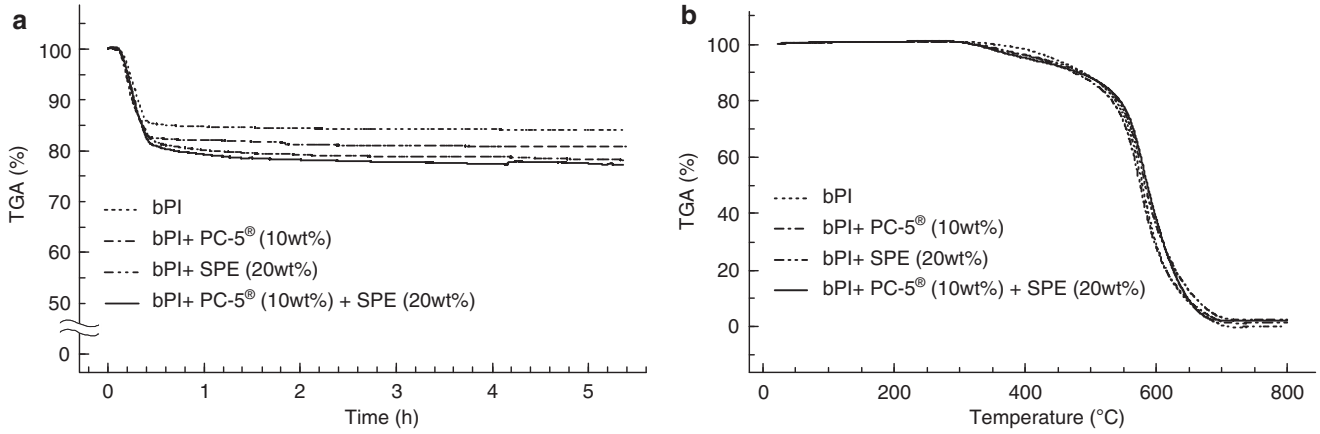


Figure 7 Thermogravimetric analysis traces of polyetherimide-containing additives. (**a**) Heating at 250 °C in air. (**b**) Reheating of the samples in (**a**) to 800 °C at 10 °C min^{-1} in air.

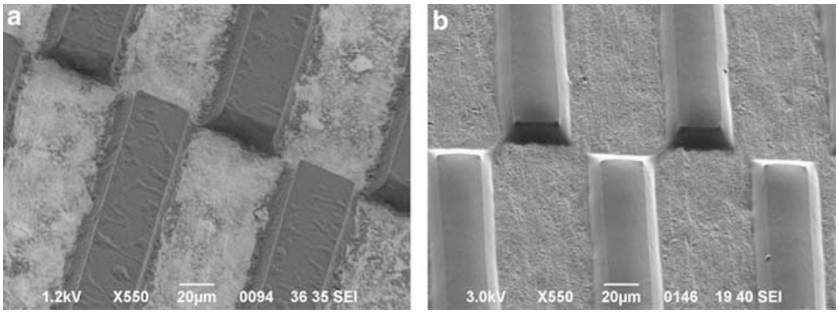


Figure 8 Scanning electron micrograph images of line and space patterns for photosensitive bPI based on chemically amplified reaction development patterning. PC-5 10 wt%+**SPE** 20 wt%. (**a**) Before heating. (**b**) After heating at 240 °C for 1 h.

Table 3 Weight losses derived from the additives and T_{d5} values of the thermally treated photosensitive bPI films[a,b]

		Weight loss[c] (wt% for polymer)[d]			
Entry	*Additive (s)*	*bPI*	*bPI+additive(s)*	*Derived from additive(s)[e]*	T_{d5}[f] *(°C)*
1	None	19.0	—	—	430.1
2	PC-5 (10wt% for bPI)	—	23.5	4.5	404.6
3	SPE (20wt% for bPI)	—	27.8	8.8	403.9
4	PC-5 (10wt% for bPI)+ SPE (20wt% for bPI)	—	29.7	10.7	382.8

[a]Determined by thermogravimetric analysis (TGA).
[b]T_g of bPI: 256 °C.
[c]Heating at 250 °C for 5 h in air.
[d]100× (weight loss in TGA (%))/(100−weight loss in TGA (%)).
[e](Weight loss for bPI+additive(s))−(weight loss for bPI).
[f]Reheating to 800 °C by 10 °C min^{-1} in air.

Table 4 Change in shape of the patterns by heating at 240 °C[a]

SEM image	*Film thickness (µm)*	*Width of the pattern (µm)*
Figure 7a	13.9	30.0
Figure 7b	12.2	25.8

[a]Determined using scanning electron micrograph (SEM).

The T_{d5} values of thermally treated PI films containing low-molecular-weight compounds were comparable with that of the PI itself. The patterns after thermal treatment were also found to maintain their shapes with little shrinkage. These results indicate good thermal properties of patterns prepared by CARDP.

ACKNOWLEDGEMENTS

We are grateful to Professor Masayoshi Watanabe (Yokohama National University) for SEM measurements. This study was partially supported by the Industrial Technology Research Grant Program in 2007 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan, the Tokuyama Science Foundation, and the Ogasawara Foundation for Promotion of Science and Engineering.

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