Formation of Fine Pattern by Reaction Development Patterning Using Photo-Base Generator and Acidic Developers

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Reaction development patterning (RDP) applicable to polyacetals was investigated by using inverse acid-base condition, namely, photo-base generator and acidic developers. Polyacetal films composed of polyacetals, O-phenylacetyl 2-acetonaphthone oxime as a photo-base generator and benzophenone as a photosensitizer gave positive-tone patterns after irradiation with an ultrahigh-pressure mercury lamp and successive dipping in developer containing carboxylic acid, methanesulfonic acid or sulfuric acid. Reduction in thickness at the unexposed area was inhibited by incorporation of trifluoromethyl groups to polyacetals.

Keywords: Reaction development patterning, Photosensitive polyacetals, Photo-base generator, Positive-tone pattern

1. Introduction

Photosensitive polymers used in the harsh environment such as buffer coat layers [1], interlayer dielectric films [2] and optical waveguides [3] require good thermal and mechanical properties like engineering plastics. Conventional photosensitive polymers for such applications vary their solubility in developer by polymer reaction under photo-irradiation. Accordingly, photosensitivity was often given to engineering plastics like polyimides by introducing specific functional groups reactive under photo-irradiation or by using acidic precursors reactive to base [4–6]. Incorporation of the photo-reactive groups to the polymers, however, leads to high synthetic cost and low preservability. Moreover, post-exposure baking to promote polymer reaction from the precursors sometimes collapse the fine pattern and damage the entire article.

In order to give photosensitivity to readily accessible engineering plastics, we have developed reaction development patterning (RDP) [7-17] based on nucleophilic acyl substitution between carboxylic-acid-derivative (-C(O)-X-) bonds in polymer main-chains and nucleophiles in developer. RDP uses polymer films prepared from varnish containing engineering plastics and photo-acid generators such as diazonaphthoquinone. In typical positive-type RDP, photo-irradiation induces no polymer reaction but generation of acids. The acids in the irradiated area promote permeation of nucleophilic developer by forming salts. The permeated nucleophiles attack the main-chain and reduce the molecular weight of polymers until the films of the irradiated areas dissolve in developer. Although RDP has been applied to polyimides, polyarylates and polycarbonates, polymers without -C(O)-X- bonds were not tolerated.

![Scheme 1. Positive-tone pattern-forming mechanism of RDP using photo-base generator and acidic developer.](image-url)
acidic developer selectively permeates the photo-irradiated area of polyacetal films, the area dissolves in developer by decomposition to low-molecular-mass fragment. Herein, we designed novel RDP for polyacetals using a photo-base generator and acidic developers (Scheme1). Photosensitive films were prepared by mixing polyacetals and O-phenylacetyl 2-acetonaphthone oxime (PaNpO) as a photo-base generator in NMP and successive spin-coating. The base generated in the photo-irradiated area of polyacetal films was considered to work as permeation promoter for acidic developers which accelerate dissolution of the polyacetal films by reduction in molecular weight.

2. Experimental

2.1. Materials

2,2-Bis(4-hydroxyphenyl)propane (Bis-A) was purchased from Junsei Chemical Co., Ltd. Bis(4-hydroxyphenyl) sulfone (Bis-S) and benzal chloride were purchased from Wako Pure Chemical Industries, Ltd. 2-(Trifluoromethyl)benzal chloride and 18-crown-6-ether were purchased from Tokyo Chemical Industry Co., Ltd. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (Bis-AF) was purchased from Central Glass Co., Ltd. PaNpO was prepared according to the literature [21].

2.2. Measurement

1H-NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270 MHz) at room temperature using dimethyl sulfoxide-d$_6$ and CDCl$_3$ as solvents, and tetramethylsilane as an internal standard. Molecular weight was determined with size-exclusion chromatography (SEC) using a Tosoh TSK$_{gel}$ GMHHR-M column coupled with UV and RI detectors (Tosoh, UV-8020 and RI-8021), and THF as the mobile phase. The SEC system was calibrated by using polystyrene standards. Photo-irradiation was conducted with a UV exposure apparatus equipped with 2 kW ultrahigh-pressure mercury lamp (ORC Manufacturing, JP-2000-EXC), and the exposure dose was measured in the 320–390 nm wavelength range with an ORC UV-331AP2. Scanning electron micrograph (SEM) measurement was carried out with a JEOL JSM-5500 instrument.

2.3. Typical procedure for synthesis of polyacetals

To a 50 mL three-necked flask with magnetic stirring bar under N$_2$ were added 7.50 mmol of bisphenols, 10.0 mmol of benzal chloride derivatives, 20.0 mmol of potassium hydroxide (85%, powder), 0.750 mmol of 18-crown-6-ether and 5 mL of N-methylpyrrolidone (NMP). The mixture was stirred at 100 °C for 3 h. After cooling to room temperature, the resulting mixture was poured into 300 mL of methanol. The precipitate was collected by filtration, washed with water and methanol, and dried under vacuum overnight at room temperature. Structures of the obtained polymers (PBAA, PBAA-F, PBAA-FF, PBSA and PBSA-F) were shown in Scheme 2.

2.4. Pattern formation from polyacetal films

A 20–30 wt% NMP solution of polyacetal was prepared and PaNpO (35 wt% for the polymer) and benzophenone (30 wt% for the polymer) were dissolved in the solution. The resulting photosensitive solution was spin-coated onto the mat side of copper foil, and prebaked at 80–90 °C for 15 min in a far-infrared oven to give a film with a thickness of approximately 8–11 µm. The film was irradiated with an ultrahigh-pressure mercury lamp without any filter through a positive photomask using the

![Scheme 2. Synthesis of polyacetals. a Determined by DSC (10 °C/min, under N$_2$). b Estimated by SEC based on polystyrene standard in THF.](image-url)
contact technique. The exposure dose was 2000–3000 mJ/cm². The exposed film was developed by immersion into a mixture of acid/methanol (or NMP)/water at 50 °C and rinsed with pure water to give a positive-tone pattern.

3. Results and discussion

Polyacetals were prepared by polycondensation of bisphenols and benzal chlorides under the presence of potassium hydroxide and 18-crown-6-ether (Scheme 2) [22]. Molecular weights of the obtained polyacetals were estimated as $M_n = 6,000–38,000$ and $M_w/M_n = 1.3–5.8$ by size-exclusion chromatography using polystyrene standards. Those polymers were soluble so that films of the polyacetals containing PaNpO as a photo-base generator and benzophenone as a photosensitizer were prepared on a copper foil by spin-coating of the NMP solutions and prebaking in a far-infrared oven. After photo-irradiation through a positive photomask, the films were immersed into acidic developers. Positive-tone patterns of PBAA were obtained by developing with formic acid/NMP/water and trifluoroacetic acid (TFA)/methanol/water (Table 1, entries 1 and 2). Dissolution of the exposed areas supported our proposed mechanism in which base generated by photo-irradiation promoted permeation of acidic developers and degradation of polyacetals. However, rough surface of the unexposed areas observed by SEM implied that acidic developers corroded the surface of polyacetals even at the unexposed areas (Fig. 1). Indeed, developers containing strong acid like methane-sulfonic acid (MSA) and sulfuric acid (SA) dissolved the film regardless of photo-irradiation. Relatively low $T_g$ of PBAA (87 °C), which was close to prebaking temperature of the photosensitive film, may also affect the rough surface of the pattern. Trifluoromethyl-substituted polyacetals, PBAA-F and PBAA-FF were also investigated in RDP by PaNpO and acidic developers. PBAA-F films containing PaNpO and benzophenone afforded no fine patterns by developing with formic acid and acetic acid due to low dissolution rate. More acidic developers composed of MSA (or SA)/methanol/water were, however, effective to make positive-tone patterns with high thickness at the unexposed areas (Table 1, entries 3 and 4, and Fig. 1). Photosensitive PBAA-FF films as well as the PBAA-F films gave positive-tone patterns by the MSA (or SA)/methanol/water developer (Table 1, entries 5 and 6). Compared with PBAA-F, PBAA-FF required longer developing time. Effect of trifluoromethyl groups on successful patterning could be explained by two factors, reactivity and permeability. Electron-withdrawing nature of trifluoromethyl groups reduced the reactivity of the polyacetals toward acid, resulting in slow degradation in the unirradiated area. Moreover, their hydrophobicity moderately inhibited permeation of aqueous developer in the

<table>
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<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Developer [w/w/w]</th>
<th>Development time [min'sec]</th>
<th>Film thickness [µm]</th>
<th>Residual thickness [%]</th>
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<td>1c</td>
<td>PBAA</td>
<td>formic acid (90%)/NMP/water = 16/1/1</td>
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<td>2c</td>
<td>PBAA</td>
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<td>10.8 → 10.6</td>
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<td>PBAA-F</td>
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<td>1'28</td>
<td>8.6 → 8.1</td>
<td>94</td>
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<td>4c</td>
<td>PBAA-F</td>
<td>SA (95%)/Methanol/water = 4/1/1</td>
<td>8'23</td>
<td>11.2 → 9.0</td>
<td>80</td>
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<td>PBAA-FF</td>
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<td>4'55</td>
<td>10.2 → 8.1</td>
<td>79</td>
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<tr>
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<td>14'03</td>
<td>8.4 → 5.2</td>
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Table 1. Results of pattern formation of polyacetals by positive-tone RDP.

- Films of polyacetals were prepared from their 20–30 wt% NMP solutions containing PaNpO and benzophenone (35 and 30 wt% for the polymers, respectively).
- Development: 50 °C/immersion.
- Exposure dose: 3000 mJ/cm².
- Exposure dose: 2000 mJ/cm².
- By contact-type thickness analyzer.
- Unexposed area.
Importance of hydrophobicity of the films in RDP using photo-base generator was confirmed by PBSA films containing sulfonyl groups as hydrophilic and electron-withdrawing moieties. Developers containing MSA, SA or TFA dissolved the unexposed areas, leading to unclear patterns. Trifluoromethylation of PBSA slightly improved pattern formation. Thickness of the unirradiated area of PBSA-F films after developing with MSA/NMP/water (Table 1, entry 8) was higher than that of PBSA developed by MSA/MeOH/water (Table 1, entry 7).

The sensitivity of PBAA-F film containing PaNpO and benzophenone was evaluated by photo-irradiation with various exposure doses through photographic step tablet, followed by dipping with MSA/methanol/water (8/1/1 by weight) developer for 1 min 35 s at 50 °C. The resulting sensitivity curve is shown in Fig. 2, and the sensitivity of the photosensitive PBAA-F, at which the exposed film was completely dissolved into the developer, was found to be 1500 mJ/cm². Contrast (γ value) obtained from slope of the curve was 1.45.

**Fig. 2.** Sensitivity curve of photosensitive PBAA-F film. Initial film thickness: 14.1 µm.

4. Conclusion

Photosensitive polyacetal films were obtained by spin-coating of NMP solutions containing polyacetals, PaNpO as a photo-base generator and benzophenone as a photosensitizer. Photo-irradiation followed by acidic developments afforded positive-tone patterns of polyacetals probably due to promoted permeation of acidic developers into the basic exposed area. The trifluoromethyl groups effectively inhibited the unirradiated area from dissolution, resulting in finer patterns.

**References**