Formation of Fine Pattern from Polyarylate-Silicone Copolymer by the Application of Reaction Development Patterning

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Multi-block copolymers between polyester (polyarylate) and polydimethylsiloxane were prepared by polycondensation using polydimethylsiloxane having p-hydroxyphenyl groups at its both chain ends as a diol monomer. The copolymer gave positive-tone fine pattern by the reaction development patterning with developer containing ethanolamine as a nucleophile. The silicone unit hybridized with polyarylate enabled pattern formation from dry film by contributing not only to high photosensitivity but also to high dissolution rate at the photo-irradiated area. Use of polyarylate instead of the copolymer resulted in unsuccessful pattern formation from dry film.

Keywords: Reaction development patterning (RDP), Photosensitive polyarylate, Polyarylate-silicone copolymer, Diazonaphthoquinone (DNQ)

1. Introduction

Photo-patternable polymers with good thermal, mechanical, and electrical properties play an important role in the production of buffer coat layers [1], interlayer dielectric films [2] and optical wave guides [3] because the patterned polymers for those applications are used in the harsh environment for a long time. Engineering plastics such as polyimides (PIs) and polyarylates (PArs) are suitable candidates for the above uses.Conventionally, photosensitivity has been added to PIs by covalently introduced photoreactive functional groups or by the use of poly(amic acid)s (PAAs) as the precursors along with photo-acid generators (PAGs) [4]. For instance, photoinitiated crosslinking reaction of methacryl groups leads to negative-tone pattern. In contrast, acids generated from PAGs increase solubility of PAAs to alkaline developer, leading to positive-tone pattern. The covalent-type photosensitive PIs tend to be high costs due to complicated synthetic procedures, and the PAA-type photosensitive PIs require thermal imidization after pattern formation. Moreover, the introduced photosensitive groups and PAGs often damage physical and chemical stability of PIs.

To leave out the additional functionalization and the use of precursors for photosensitivity, we have developed reaction development patterning (RDP) method [5-7]. RDP is based on nucleophilic acyl substitution (NAS) between carboxylic-acid-derivative (-C(O)-X-) bonds in main-chains of engineering plastics and nucleophiles in developer (Fig. 1). Cleaving the main chains by NAS decreases the molecular weight and increases the solubility to the developer. In typical positive-type RDP, diazonaphthoquinone (DNQ) as a photosensitive agent is mixed with engineering plastics, followed by photo-irradiation with a photomask. DNQ at the photo-irradiated areas is converted to indenecarboxylic acid. The acid forms salt with a nucleophile in developer, promoting permeation of developer into the film. Hence, the photo-irradiated areas selectively dissolve in the developer containing nucleophiles, affording patterned engineering plastics. Nowadays, RDP can be applied to PIs [5-7], PArs [8-10] and polycarbonates [11].

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For improving properties of organic polymers, hybridization with inorganic block is useful methodology. Organic polymer/silica hybrids often increase thermal stability, surface planarity and optical transparency as compared with the corresponding organic polymers [12-14]. In our previous work, PI-silicone copolymer afforded negative-tone pattern by RDP using tetramethylammonium hydroxide/water/NMP/methanol as developer [15]. The successful pattern formation probably indicated that RDP could be applied to any hybrid copolymers containing (-C(O)-X-) bonds. Herein, we studied positive-tone pattern formation of the PAr-silicone copolymer by RDP.

2. Experimental

2.1. Materials

2,2-Bis(4-hydroxyphenyl)propane (Bis-A), isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) were purchased from Tokyo Chemical Industry Co., Ltd. Polydimethylsiloxane having p-hydroxyphenyl groups at its both chain ends (KF-2200) was purchased from Shin-Etsu Chemical Co., Ltd. 1,2-Naphthoquinonediazide 5-sulfonic acid p-cresol ester (PC-5) was purchased from Toyo Gosei Kogyo Co., Ltd. Polyarylate (U polymer®, U-100) was kindly donated from Unitika Ltd. Other reagents and solvents were commercially available.

2.2. Measurement

$^1$H NMR spectra were obtained with a Bruker DRX300 spectrometer (300 MHz) at room temperature using CDCl$_3$ as a solvent and tetramethylsilane as an internal standard. Molecular weight was determined with gel permeation chromatography (GPC) using a Tosoh TSK gel GMMH-M column coupled with UV and RI detectors (Tosoh, UV-8020 and RI-8021) and DMF containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L) as the mobile phase. The GPC system was calibrated by using polystyrene standards. Photo-irradiation was conducted with a UV exposure apparatus equipped with 2kW 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-6390LV instrument.

2.3. Synthesis of polyarylate-polydimethylsiloxane copolymer (PAR-A/Si)

To a 300 mL three-necked flask with magnetic stirring bar and 4.58 g of Bis-A (20 mmol) under N$_2$ were added 5.75 g of KF-2200 (4 mmol) and 50 mL of 1,2-dichloroethane. The mixture was cooled to 10 °C, followed by addition of 6.8 mL of triethylamine. After stirring at 10 °C for 1 h, 2.44 g of TPC (12 mmol) and 2.44 g of IPC (12 mmol) in 15 mL of 1,2-dichloroethane was added. The resulting mixture was stirred at 10 °C for further 2 h and poured into ethanol. The precipitate was collected by filtration and dried under vacuum overnight at 80 °C to yield 12 g of PAR-A(11)/Si as a white solid. PAR-A(23)/Si was also obtained from 6.84 g of Bis-A (30 mmol), 4.26 g of KF-2200 (3 mmol), 3.37 g of TPC (12 mmol) and 2.44 g of IPC (12 mmol) in 15 mL of 1,2-dichloroethane was added. The resulting mixture was stirred at 10 °C for further 2 h and poured into ethanol. The precipitate was collected by filtration and dried under vacuum overnight at 80 °C to yield 12 g of PAR-A(23)/Si as a white solid. PAR-A(23)/Si was also obtained from 6.84 g of Bis-A (30 mmol), 4.26 g of KF-2200 (3 mmol), 3.37 g of TPC (16.5 mmol) and 3.37 g of IPC (16.5 mmol), according to the similar procedure.

2.4. Pattern formation from PAR-A/Si films

A 20 wt% cyclopentanone (CP) solution of a
PAR-A/Si was prepared and PC-5 as a photosensitive agent (30wt% for the copolymer) was dissolved in the solution. The resulting photosensitive solution was degassed, spin-coated onto the shiny side of a copper foil, and prebaked at 90 °C for 10 min in a far-infrared oven to give a film with a thickness of approximately 11–15 µm. The film was irradiated with an ultrahigh-pressure mercury lamp without any filter through a positive photomask using the contact technique. The exposure dose was 2000 mJ/cm². The exposed film was developed by immersion into a mixture of ethanolamine (EA)/water under ultrasonic treatment at 40 °C and rinsed with pure water to give positive-tone pattern.

2.5. Pattern formation from PAR films

A 17 wt% N-methylpyrrolidone (NMP) solution of a U-100 was prepared and PC-5 as a photosensitive agent (30wt% for the copolymer) was dissolved in the solution. The resulting photosensitive solution was degassed, spin-coated onto the shiny side of a copper foil, and prebaked at 90 °C for 10 min in a far-infrared oven (successive drying at 90 °C for 1 h under vacuum was necessary to obtain a dry film) to give a film with a thickness of approximately 9–12 µm. The film was irradiated with an ultrahigh-pressure mercury lamp without any filter through a positive photomask using the contact technique. The exposure dose was 2000 mJ/cm². The exposed film was developed by immersion into a mixture of EA/water under ultrasonic treatment at 40 °C and rinsed with pure water to give positive-tone pattern.

3. Results and discussion

Multi-block copolymers between polyarylate and polydimethylsiloxane (PAR-A/Si) were prepared by polycondensation of Bis-A, KF-2200, TPC, and IPC. Composition ratio of the obtained PAR-A/Si (k/m in Scheme 1) was determined by 1H NMR spectroscopy. When feeding molar ratio was Bis-A/KF-2200 = 5/1, NMR peak areas indicated k/m = 11/1 and the polymer was named PAR-A(11)/Si. Increasing the feeding ratio of Bis-A to 10/1 resulted in k/m = 23/1 (PAR-A(23)/Si). Molecular weights of the polymers were estimated by GPC, and number-average molecular weights of PAR-A(11)/Si and PAR-A(23)/Si were found to be 25,000 and 20,000, respectively.

To examine pattern formation, dry film of PAR-A(11)/Si containing PC-5 as a DNQ-type photosensitive agent was prepared on a copper foil by spin-coating of CP solution and prebake at 90 °C for 10 min in a far-infrared oven. Dryness of the film was confirmed by 1H NMR measurement after dissolving the film in CDCl₃. No CP peaks were observed in the 1H NMR spectrum. A positive-tone pattern of PAR-A(11)/Si was formed by photolysis through a photomask and successive development with EA/water = 8/1 (w/w) solution (entry 1 in Table 1, Fig. 2a). Despite high residual thickness at the unexposed area (92%), dissolution rate at the exposed area reached 78.7 nm/s. Sensitivity E₀ of PAR-A(11)/Si was estimated as 189 mJ/cm² from the exposure dose at which the exposed film was completely dissolved. Moreover, contrast γ was obtained as 0.95 from the slope of sensitivity curve. It should be noted that efficient pattern formation of PAR-A(11)/Si was achieved by...

Table 1. Results of pattern formation of PAR-A/Si and U-100 by positive-tone RDPa,b,c.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Prebaking condition</th>
<th>Development time [min'sec]</th>
<th>Film thicknessa [µm]</th>
<th>Residual thicknessd [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Irradiated</td>
<td>Unirradiated</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>PAR-A(11)/Si</td>
<td>90 °C /10 min</td>
<td>2'30</td>
<td>11.8 → 0.0</td>
<td>11.8 → 10.9</td>
</tr>
<tr>
<td>2</td>
<td>PAR-A(23)/Si</td>
<td>90 °C /10 min</td>
<td>5'18</td>
<td>15.0 → 0.0</td>
<td>15.0 → 14.7</td>
</tr>
<tr>
<td>3</td>
<td>U-100</td>
<td>90 °C /10 min</td>
<td>12'00</td>
<td>11.7 → 0.0</td>
<td>11.7 → 11.2</td>
</tr>
<tr>
<td>4</td>
<td>U-100</td>
<td>90 °C /10 min then 90 °C /1 h in vacuo</td>
<td>15'00</td>
<td>9.3 → 8.6</td>
<td>9.3 → 9.1</td>
</tr>
</tbody>
</table>

a Films of PAR-A(11)/Si and PAR-A(23)/Si were prepared from their 20 wt% CP solutions containing PC-5 (30 wt% for the polymers). b Films of U-100 were prepared from their 17 wt% NMP solution containing PC-5 (30 wt% for the polymers). c Exposure dose: 2000 mJ/cm², Development condition: EA/water = 8/1 (w/w), 40 °C /ultrasonication. d By contact-type thickness analyzer. e At unirradiated area.
developer containing only the nucleophile and water. In our previous work [8], RDP for PAr films with 10–15 µm needed addition of NMP to developer and also showed lower sensitivity (E_0 ~ 600 mJ/cm^2) and contrast (γ = 0.83) than RDP for PAr-A(11)/Si. As a consequence, introducing the silicone moiety could improve the RDP process for PAr.

The RDP procedure using EA/water developer was also applied to PAr-A(23)/Si and PAr. PAr-A(23)/Si was also afforded a clear fine pattern from the dry film (entry 2 in Table 1, Fig. 2b). As compared with PAr-A(11)/Si, PAr-A(23)/Si showed low dissolution rate of the exposed area (78.7 nm/s for PAr-A(11)/Si and 47.2 nm/s for PAr-A(23)/Si). In contrast, the dry film of PAr (U-100) containing PC-5 dissolved little in the EA/water developer regardless of photo-irradiation (entry 4 in Table 1, Fig. 2d), although U-100 film containing PC-5 and NMP (41%, determined by 1H NMR) was able to give a positive-tone pattern by RDP with EA/water developer (entry 3 in Table 1, Fig. 2c). The patterning results about PAr-A(11)/Si, PAr-A(23)/Si and U-100 indicated that dissolution rate of the photo-irradiated areas into the EA/water developer increased as the content of the silicone unit increased. The flexible silicone moiety may act as a substitute of residual solvent in the photosensitive films, which promotes permeation of the RDP developers [5], leading to fast cleavage of the main-chain and dissolution.

4. Conclusion
Multi-block copolymers between polyarylate and polydimethylsiloxane (Par-A/Sis) were synthesized by polycondensation using Bis-A and KF-2200 as diol monomers. Par-A/Sis gave positive-tone pattern by RDP with developer containing only ethanolamine as a nucleophile and water. The silicone unit hybridized with PAr contributed not only to high photosensitivity but also to high dissolution rate at the photo-irradiated area. As a result, introduction of the silicone unit realized pattern formation of the dry PAr films by RDP process.

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References