Polymers with Acid-amplifying Side Chains as Positive-type Photoresists

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Novel polymers substituted with acid-amplifying units in their side chain are described, aiming at developing photoresist materials exhibiting both of the suppression of the mobility of generated acids and the enhancement of photosensitivity. The thermal decomposition of pinanediol monosulfonate groups tethered covalently to polymer backbones derived from 2-hydroxypropylnyl-3 p-styrenesulfonate proceeds non-linearly and involves the autocatalytic process to generate sulfonic acid groups in the side chains. Photoresists comprised of the homopolymer or a copolymer of a high loading (62%) of the acid-amplifying unit and a photosensitive generator exhibited no alkaline developability probably because of a dissolution inhibitory effect of rearranged product(s) from the acid-amplifying unit. On the other hand, copolymers of the acid-amplifying monomer of 10% and 42% loadings with tert-butyl methacrylate gave positive-tone photoresists developable with an aqueous alkali to display high photosensitivity.

Keywords: acid amplifier, side chains, photosensitivity enhancement

1. Introduction

We proposed the way to enhancing photosensitivity of chemically amplified photoresists (CAP) by the involvement of acid proliferation reactions, which is the autocatalytic decomposition of acid amplifying molecules triggered by photogenerated acidic molecules.[1] Since the concentration of acidic species increases markedly as a result of the decomposition of acid amplifiers, an acidoletic deprotection of acid-sensitive side chains of polymers is accelerated upon post-exposure baking (PEB) to result in the improvement of photosensitivity of CAP.[2] We developed various kinds of acid amplifiers such as acetacetate derivatives,[1a,b] β-sulfonyloxyketals,[3] monosulfonates of cyclic 1,2-diols[2a], disulfonates of cyclohexan-1,4-diols[4], a trioxane derivative[5] and benzyl sulfonates.[6] The addition of the acid amplifiers to CAPs resulted in the enhancement of photosensitivity of polymers with acid-labile ester side chains as positive-working photoresists developable with alkaline solutions.[1-6] Consequently, the concept of acid amplification to improve photosensitivity characteristics has been applied to sensitivity enhancement of 193 nm-resists[2a,e] and a ketal-type resistant sensitive to DUV at 254 nm and electron beam.[7]

The demand for resists with higher sensitivity has been boosted more and more to ensure sufficient throughput in the next generation nanolithography so that resists loaded with acid amplifiers may play a critical role. Generally speaking, the improvement of sensitivity of photopolymers results in reducing their resolution power, because the translational movement of acidic molecules in a resist film is necessary to catalyze the deprotection of acid-labile side chains. We suggested previously[8] that the acid amplification diffusion of strongly acidic
molecules in a polymer solid film subjected to PEB occurs in the following three steps; the migration within the so-called reactive spheres leading the acidolytic reaction,[9], the diffusional escape from the reactive spheres to result in acidolytic transformation of excess amounts of side chains and the evaporation from a polymer surface into the air.[10] The first process takes place quickly and may determine the resolution power of the resist, whereas the second requires longer baking time to deteriorate the resolution. Concerning the acid proliferation reactions in polymer films, the movement of acid amplifier molecules has to be also taken into consideration, since excessive levels of diffusion of acid amplifier molecules including evaporation from a polymer surface leads to deteriorating pattern profiles. In this respect, we described the synthesis and properties of polymers substituted with 3-alkanesulfonyloxy-2-pyranil side chains (1) to fix acid-amplifying units.[11] But this type of polymers liberate low molecular weight sulfonic acids as a result of acid proliferation reaction so that their diffusion in polymer films may not sufficiently retarded. Consequently, we had an idea to fix acid-amplifying molecules to backbones of a resist polymer in such a way that sulfonic acid residues after the reaction are tethered to polymer backbones to suppress the excessive translational motion of acidic species, as described in our preliminary report.[12]

It has been recently indicated that our concept is applicable to F2 photoresists exhibiting reasonable sensitivity and resolution.[13] In this context, we report here in more detail that the acid proliferation reaction occurs in polymer films even when acid-amplifying groups are attached covalently to polymer backbones to give sulfonic acid side chains. 2-Hydroxypropyl-3-p-styrenesulfonate was employed again here as the acid-amplifying monomer to be copolymerized with tert-butyl methacrylate to provide positive-type photoresists.

2. Experimental
2.1 Materials
(1S, 2S, 3R, 5S)-(+) pinanediol and p-styrenesulfonyl chloride were purchased from Aldrich Co., Ltd. and used without further purification. tert-Butyl methacrylate (BMA) was obtained from Tokyo Kasei Co., Ltd. Diphenyl-(4-phenylthiophenyl)sulfonium hexafluoroantimonate (DPS) was gifted by Midori Chemical Co., Ltd. 2,2'-Azobisobutyronitrile (AIBN) received from the Kanto Chemical Co., Ltd. was used without further purification.

2.2 2-Hydroxypropyl-3-p-styrenesulfonate (2)
To a cold solution of (1S, 2S, 3R, 5S)-(+) pinanediol (22.9 g, 134 mmol) and 16.3 g (161 mmol) of triethylamine and 4.02 g of 4-dimethylaminopropidine in dichloromethane (258 ml) was added slowly p-styrenesulfonyl chloride (30.0 g, 148 mmol) dissolved in dichloromethane (110 ml). After the addition was completed, the reaction mixture was stirred at room temperature for 24 h, neutralized with dilute HCl. An organic layer was washed with a saturated NaHCO3 solution and a saturated brine and dried over MgSO4. Evaporation under a reduced pressure gave a residue, which was purified by flash chromatography on silica gel using chloroform as an eluent to give 21.6 g (48 %) of 2 as a yellowish syrup. 1H NMR (CDCl3): δ (ppm) = 0.93 (s, 3H, CO-CH3), 1.20-2.50 (m, 13H, (CH)2, (CH3)2, C(CH3) and OH), 4.89 (dd, J = 6.1, 9.6 Hz, 1H, O-CH), 5.50 (d, J = 10.9 Hz, 1H, H-C=C), 5.90 (t, J = 17.6 Hz, 1H, H-C=C), 6.77 (dd, J = 10.9, 17.6 Hz, 1H, CH=), 7.57-7.91 (m, 4H, aryl-H). IR (NaCl): ν (cm-1) = 3537 (O-H), 2925 (C-H), 1632 (C=C), 1455 (CH3), and 1359, 1181 (S=O). C18H12SO4 (336.44): Calc. C 64.29 H 7.14 S 9.52%, Found C 64.06 H 7.20 S 9.65%.

2.3 Polymerization
Poly(2-hydroxypropyl-3-p-styrenesulfonate) (P100/0) was synthesized by radical polymerization of 2 in dry THF at 67°C using 2,2'-azobisobutyronitrile (AIBN) as an initiator. A homopolymer was isolated by precipitation in petroleum ether and dried under reduced pressure. Copolymerization of 2 with BMA was undertaken in a similar way in dry THF containing AIBN at 70°C, followed by precipitation in hexane and drying under a reduced pressure to give acid-amplifying polymers.
Table 1 Properties of acid-amplifying polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer ratio</th>
<th>Copolymer ratio</th>
<th>Mw (Mw/Mn)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P100/0</td>
<td>100/0</td>
<td>100/0</td>
<td>1.8x10⁴</td>
<td>5.9</td>
</tr>
<tr>
<td>P62/38</td>
<td>84/16</td>
<td>62/58</td>
<td>1.0x10⁴</td>
<td>6.2</td>
</tr>
<tr>
<td>P42/58</td>
<td>50/50</td>
<td>42/58</td>
<td>2.1x10⁴</td>
<td>5.8</td>
</tr>
<tr>
<td>P10/90</td>
<td>16/84</td>
<td>10/90</td>
<td>4.7x10⁴</td>
<td>5.4</td>
</tr>
</tbody>
</table>

2.4 Physical Measurements

$^1$H NMR spectra were recorded on a Bruker AC-200 spectrometer. FT-IR spectra were obtained by using a JASCO FT/IR-300 spectrometer. Differential scanning calorimeter (DSC) data were taken on a Seiko Instrument DSC-200 thermal analysis system at a heating rate of 10°C/min. Molecular weights and molecular weight distributions were obtained from GPC on a JASCO Intelligent UV detector by using a calibration curve for a polystyrene standard. Film thickness of photoresists was measured on a DEKTAK3 ST (ULVAC Co., Japan).

2.5 Thermal Decomposition in Solution

PSS was dissolved in chloroform-$d_1$ containing a small amount of tetramethylsilane. The solution placed in a sealed NMR tube was heated at 100°C in an oven to be subjected to intermittent NMR measurements to monitor time courses of the consumption of PSS. The reaction was followed by monitoring the decrease of peak heights of a signal due to methine proton at δ = 4.89 ppm.

2.6 Acid-Catalyzed Deprotection

Films spin-cast from cyclohexanone solutions of resists were prebaked at 100°C for 60 s to remove the residual solvent and exposed to produce a photoacid, followed by heating at 100°C on a hot plate and FT-IR measurements at intervals.

2.7 Photosensitivity Determination

Resist solutions were prepared by dissolving acid-amplifying polymers and 5 wt.% of DPS in cyclohexanone, spin-coated on a silicon wafers and prebaked at 100°C to remove the residual solvent. Spin-cast films were exposed to 313 nm light at 10 ml/cm² from a 200W Hg-Xe lamp through a band-pass filter, followed by post-exposure baking (PEB) at 100°C for 90 s on a hot plate. After the PEB, the wafers were dipped in a 2.5 wt.% tetramethylammonium hydroxide (TMAH) solution and rinsed with water for 20 s, followed by thickness measurements.

3. Results and Discussion

3.1 Polymer Design and Synthesis

Among various acid amplifiers developed so far, we selected a pinanediol-1,2 monosulphonate as a acid amplifying unit because of its excellent reactivity and thermoreversibility.[2g] In this context, 2-hydroxypinanyl-3 $p$-styrenesulphonate (2) was designed as an acid-amplifying monomer to give polymers with pendant acid-amplifying residues in the side chains, generating sulfo groups in the side chains after the acidolysis reaction. The preparation of 2 was achieved by the one-step esterification of

Fig. 1 Decomposition of 2 in chloroform-$d_1$ at 100°C.

Fig. 2 FT-IR spectral changes of a film of P100/0 containing 5 wt.% of DTS (a) before and (b) after exposure to 313 nm and (c) after PEB at 100°C for 300 s.
(1S, 2R, 3R, 5S)-(−) pinanediol by p-styrene-sulfonyl chloride (Fig. 1).

The autocatalytic acidolysis of 2 was followed by 1H NMR spectra in chloroform-d$_6$ solutions at 100°C. The quartet peak due to the methine proton of the 2-hydroxypinanyl units at δ = 4.89 ppm decreased upon heating, while new peaks at 2.1-2.3 ppm probably due to ketone derivative(s) appeared. Fig. 1 shows the sigmoidal time course of the consumption of 2, indicating that the acidolysis occurs autocatalytically to result in the proliferation of the acid. The formation of the ketonic product(s) was confirmed by FT-IR spectroscopy to monitor the appearance of ν$_{C=O}$ at around 1700 cm$^{-1}$.

The radical polymerization of 2 was carried out in THF to give a homopolymer (P100/0) and copolymers of 2 with BMA (Fig. 1). Table 1 summarizes the properties of acid-amplifying polymers. Compositions of the copolymers were estimated by means of 1H NMR spectral measurements.

3.2 Acid-Catalyzed Deprotection in Polymer Film

The acid-catalyzed cleavage of the 2-hydroxypinanyl side chains was followed by FT-IR spectral measurements of a film of P100/0 doped with DPS as a photoacid generator. The film was exposed to 313 nm light and baked subsequently at 100°C. Before the exposure, the absorption bands at 1362 and 1177 cm$^{-1}$ due to ν$_{S=O}$ asymmetric bands of the sulfonate were observable (Fig. 2a). After the exposure, no marked spectral change was induced (Fig. 2b), whereas PEB results in the disappearance of the ν$_{S=O}$ band at 1362 cm$^{-1}$ and the appearance of two sharp peaks at 1034 and 1006 cm$^{-1}$ corresponding to the ν$_{S=O}$ symmetric bands of the sulfo groups (Fig. 2c). Fig. 3 shows changes in band intensities of the sulfonate and the sulfo groups as a function of PEB periods. Sigmoidal curves support that P100/0 displays the non-linear chemistry based on the acid proliferation reaction even in a film.

3.3 Photosensitivity Characteristics

Spin-cast films of P100/0 containing 10 wt-% of DPS were exposed to 313 nm light, followed by PEB at 100°C for 90 s to evaluate photosensitivity characteristics. It was observed that exposed areas of a film of P100/0 is not removed by rinsing with a 2.5 wt-% of TMAH solution even though sulfo residues are generated, as described above. P62/38 with the highest loading of 2 among the copolymers showed also no developability in the

Fig. 3 Time conversion curves for the disappearance of the ν$_{S=O}$ band of the sulfonate at 1360 cm$^{-1}$ (σ) and the appearance of that due to the sulfonic acid residue at 1006 cm$^{-1}$ (●) of a film of P100/0 containing 5 wt-% of DTS as a function of PEB period at 100°C after exposure to 313 nm light of a 10 mJ/cm$^2$ dose.

Fig. 4 Photosensitivity curves of films of P62/28 (●) and pBMA (○) containing 5 wt-% of DTS under development with a 75:25 (v/v) mixture of toluene and THF.
Fig. 5 Photosensitivity curves of pBMA (●), P10/90 (○), P42/58 (△) and P62/28 (○), respectively, containing 5 wt-% of DTS after alkaline development.

acidolysis product(s) act as a dissolution inhibitor to suppress the alkaline dissolution of polymers with sulfo side chains. In order to confirm this situation, photosensitivity determination of P62/38 was undertaken by using a less polar solvent of a 75:25 (v/v) mixture of toluene and THF, which dissolves the copolymer and may also remove the low-mass rearranged products. The results are shown in Fig. 4. As expected, the copolymer acted as a negative-working resist, displaying higher photosensitivity when compared with a BMA homopolymer (pBMA) doped with DTS as a reference.

It was found that the copolymers with moderate and lower loadings with the acid-amplifying unit demonstrate alkaline developability after PEB treatment. The photosensitivity curves for P10/90 and P42/58 are shown in Fig. 5. Note that the homopolymer P100/0 is not developable with an alkaline solution, as stated above. The results show that P10/90 exhibits the highest photosensitivity of slightly less than 2 mJ/cm² whereas P42/58 becomes alkaline soluble at a 2.5 mJ/cm² exposure dose. The photosensitivity of P10/90 is thus about twofold higher than that of the pMBA systems. The photosensitivity enhancement may come from the following two possibilities. The first relies on the acid proliferation process, whereas the second involves the accelerated deprotection of t-BOC groups catalyzed by neighboring sulfo residues generated from the acid-amplifying side chains. On account of a relatively low content of the acid-amplifying unit in P10/90, the first possibility seems to be rather unfeasible because the acid proliferation exhibits a significant concentration effect. Consequently, the second possibility may be acceptable, though further studies are needed.

In order to assist the acid proliferation of the side chains, a low-mass acid amplifier was added to the copolymers. cis-3-(p-Toluenesulfonyloxy)-2-pinanol (3)[2g] was used here as the acid

Fig. 6 Photosensitivity curves of P10/90 containing 5 wt-% of DTS in the absence of (●) and in the presence of 5 wt-% (○), 10 wt-% (△) and 20 wt-% (○) of the low-mass acid amplifier, respectively.

Fig. 7 Photosensitivity curves of P42/58 containing 5 wt-% of DTS in the absence of (●) and in the presence of 5 wt-% (○), 10 wt-% (△) and 20 wt-% (○) of the low-mass acid amplifier, respectively.
amplifier to formulate acid proliferation type photoresists. Figs. 6 and 7 shows the effect of 3 on the photosensitivity characteristics of P10/90 and P42/58, respectively. Both of the copolymers exhibited about 8 and 6 times higher photosensitivity when 20 wt-% of 4 was added.

Conclusion

A homopolymer of 2 displays the acidolytic cleavage of 2-hydroxypropinyl-3 side chains in a non-linear manner to generate sulfo side chains in the presence of a photogenerated acid, revealing that the acid proliferation takes place even though the sulfonic acid residues generated from the acid-amplifying units are covalently tethered to polymer backbones. Though the polymer side chains was converted into sulfonic acid residues after UV irradiation and PEB, the alkaline development was not performed probably because of the dissolution inhibitory effect of acidolysis product(s) of the 2-hydroxypropinyl side chains. The dissolution inhibitory effect was confirmed by the development with a less polar organic solvent to afford a negative-type photoresist. On the other hand, copolymers with tert-butyl methacrylate of loadings of less than 42 wt-% of 2 were alkaline developable to exhibit improved photosensitivity when compared with a homopolymer of BMA.

This type of the copolymers is one of the candidates for resist material exhibiting improved photosensitivity though studies on optimizing chemical structures of the polymers is necessary. Copolymers incorporating acid-amplifying monomer unit, 2-hydroxypropinyl-3 2-propene-sulfonate, with high transparent to DUV have been developed[15] and will be reported elsewhere.

References