Cyclized Copolymer of Methacrylic Anhydride and an Application to Photoresist with Photo-Acid Generator

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The cyclized copolymerization of methacrylic anhydride with N-phenyldimethacrylamide and methacrylonitrile was carried out. The polymer consists of six-membered cyclic acid anhydride and five-membered imide ring. The cyclic acid anhydride was hydrolyzed by generated acid catalyst from photo-acid generator (PAG). The hydrolyzed copolymer is dissolved in an alkaline solution. We applied this copolymer with PAG to photoresist based on the chemical amplified system and obtained good patterns of positive-tone image.

Keywords: cyclopolymer, methacrylic anhydride, cyclized copolymerization, photoresist

1. Introduction

Acrylate and methacrylate polymers are easily able to have various functional groups as the ester moiety and are applied to many fields such as coatings, films, fibers, and other materials. In photolithography, the base polymers require low absorption at the wavelength of exposure. Consequently, acrylate and methacrylate polymers are available to the base polymer of the deep UV photoresist due to their main chains which have low absorption in the region.

In some advanced lithographic processes, resist polymers require to have high glass transition temperature (Tg). Acrylate and methacrylate polymers, however, have low Tg due to the linear main chain structure. Incorporation of cyclic structure units to a polymer main chain is an effective method to provide a high Tg.

On the other hand, methacrylic anhydride (MAAh) or N-substituted dimethacrylamide is polymerized with a radical initiator to give a cyclized polymer [1]. This cyclic polymer has high Tg because of its cyclic structure. The cyclopolymer from methacrylic anhydride contains six-membered ring of cyclic acid anhydride [2, 3] and the cyclopolymer from N-substituted dimethacrylamide has five-membered ring of imide structure [4-6].

The cyclic acid anhydrides can open their rings to produce corresponding two carboxylic acids using an acid catalyst under moisture conditions. It is known that poly(MAAh) including the cyclic acid anhydride can hydrolyze with an acid catalyst in a solution [7].

In this study, we designed a new type photoresists using cyclized copolymer of methacrylic anhydride with other vinyl monomers. This copolymer with photo acid generator (PAG) can be available for a new positive photoresist based on the chemical amplification concept. We discuss reactivity of cyclic acid anhydride in the film and evaluate property of photoresist.

2. Experimental

2.1 Synthesis of N-phenyldimethacrylamide (PhDMA)

This compound was prepared according to the literature [6]. The obtained solid was recrystallized twice from ether. The yield was 40 %.

\[ \text{H-NMR (400MHz, CDCl3)} \]

\[ \delta (ppm) 1.94 (6H, dd, J = 1.4, 1.0 Hz), 5.48 (2H, q, J = 1.4 Hz) 5.56 (2H, q, J = 1.0Hz), 7.12 (2H, ddd, J = 7.2, 1.4, 1.2 Hz), 7.33 (1H, ddd, J = 7.5, 7.2, 1.2 Hz), 7.41 (2H, 7.69}

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IR (KBr, disk) ν (cm⁻¹) 1701 (C(=O)-N-C(=O)), 1666 (C=O), 1625 (C=C), 1595 (Ar C-C), 1492 (C-H), 1454 (C-N).

2.2 Copolymerization

2.2 g of MAAh, 5.7 g of PhDMA, 1.5 g of methacrylonitrile (MAN), and 59.5 mg of N,N'-azobisisobutyronitrile (AIBN) were dissolved in 50 ml of cyclohexanone. This solution was purged oxygen gas by argon bubbling with supersonic. The polymerization was carried out in an oil bath kept at 60 °C for 6 hrs. After heating, the reaction solution was poured into a large amount of n-hexane. The precipitate was isolated by filtration and dried under reduced pressure. The obtained polymer was purified once by reprecipitation in THE/n-hexane. The yield was 1.6 g. Number-average molecular weight (Mn) was 1.7 × 10⁴ and molecular weight distribution (Mw/Mn) was 1.5.

FT-IR (KBr, DISK) ν (cm⁻¹) 2235, 1805, 1758, 1712, 1598, 1151, 1020.

2.3 Apparatus

IR spectra were recorded on a Horiba FT-200 Fourier transform infrared spectrometer. 'H-NMR spectra were obtained on a JEOL GSX-400. The molecular weight of polymer was determined by gel permeation chromatography using a TOSO HLC-802UR high speed liquid chromatograph system through three TSK-GEL H-type columns (styrene gel column) in THF with polystyrene standards. TG/DTA curves were recorded on a Seiko Instrument Inc. TG/DTA 200 with Al₂O₃ as a reference. DSC were measured by a Seiko Instrument Inc. DSC22C. UV spectra were obtained on a Hitachi U-3000 spectrophotometer. The resist film thicknesses were measured by a Tencor Alphastep 200.

3. Results and discussion

3.1 Copolymerization of MAAh

The copolymerization of MAAh with PhDMA was carried out by radical polymerization with AIBN as a radical initiator. The structure of this copolymer was identified by FT-IR spectrum. We found the absorption due to cyclic structure units on which were 1700 and 1760 cm⁻¹ from imide ring and 1760 and 1800 cm⁻¹ from cyclic acid anhydride. The absorption of vinyl group, however, was not observed. This result indicates that the cyclized propagation reaction mainly proceeded in this copolymerization.

The obtained copolymer was insoluble into organic solvents, because the main chain of this copolymer was very rigid due to cyclic structures. Accordingly, we designed the new copolymer which was introduced other mono-vinyl monomer for good solubility in organic solvents. G. Smets and co-workers reported that the intramolecular cyclization of a MAAh radical competes with the addition to other vinyl monomer in the propagation reaction [8]. Moreover, it reported that the copolymer of MAAh with a vinyl monomer that has high reactivity to a radical included cyclic structure and pendent vinyl group [9]. Thus, we used MAN that has a low reactivity to a MAAh radical. This copolymerization is illustrated as following scheme. The obtained copolymer 1 has imide rings, cyclic acid hydrides and nitrile groups, but vinyl group was not found from IR spectrum. This result indicates that this copolymerization mainly proceeded to cyclization. Furthermore, this copolymer had high Tg at 132 °C and decomposed at 379 °C. This is the first report to synthesis of cyclized copolymer containing two different types of ring structures.

3.2 Thermal reaction with acid catalyst

It is well-known that acid anhydride can be hydrolyzed to produce corresponding two carboxylic acids in the presence of a acid catalyst. Poly(MAAh) can also open the rings in the solution under acid catalyst [7]. Thus, we performed the hydrolysis of copolymer 1 in the film.

Figure 1 shows the DSC curves of copolymer 1. Without acid catalyst, we found only the Tg of the polymer at 130 °C. On the other hand, when p-toluenesulfonic acid (TosOH) was used as a catalyst, this copolymer 1 revealed an exothermic
peak from 70 °C. From these results, it was found that the hydrolyses of cyclic acid anhydride was occurred in the solid states.

The hydrolysis of copolymer 1 was performed with diphenyliodonium trifluoromethanesulfonate (DPI-OTf) as a PAG in the film. The IR spectra of copolymer 1 film with PAG are shown in figure 2. Without post exposure baking (PEB), the IR spectrum was not changed after irradiation of sufficient exposure energy. After PEB at 150 °C, the IR spectra were shifted. The absorptions of 1760, 1800, and 1020 cm⁻¹ from cyclic acid anhydride structure are decreased. As the same time, the absorption of 1750 cm⁻¹ from carboxylic acid is increased. From these results, we decide that this copolymer 1 was hydrolyzed by generated acid from PAG in the film.

3.3 Application to a photoresist

The copolymer 1 has good film-forming properties. In the film, this copolymer with 5 wt.% of DPI-OTf has a little absorption in the deep UV region, because the transmittance of 0.95 μm film thickness was about 60% at 254 nm. This formed film was insoluble in an alkaline solution. After the hydrolysis of cyclic acid anhydride, the solubility of copolymer 1 was changed and the polymer could be soluble into an aqueous basic solution. This copolymer 1 with DPI-OTf can be used to the photolithography in the deep UV region.

The characteristic curves of the copolymer 1 with PAG are shown in Figure 3. These samples were irradiated by a low pressure Hg lamp and developed in 2.38 wt.% of tetramethylammonium aqueous solution with 10 wt.% of 2-propanol for 1 minute after PEB. These characteristic curves depend on the PEB temperature and time. When the irradiated samples were treated at high temperature and for a long time on PEB, the sensitivity show higher than that treated at low temperature and for a short time. These results indicate that this reaction was carried out by the chemical amplified mechanism. In very high PEB temperature such as 190 °C, the film thickness was decreased in the development process without irradiation. The loss of this film thickness is explained that a little amount of DPI-OTf was pyrolyzed at this temperature and the generated acid reacted as a catalyst.

The positive-tone images were successfully obtained from the copolymer 1 film with 5 wt.% of DPI-OTf irradiated about 790 mJ/cm² by a low pressure Hg lamp in the contact mode. SEM photographs of this result are shown in Figure 5. The good patterns were obtained.

4. Conclusion

It is found for the first time that the MAAh with PhDMA and MAN was mainly polymerized by cyclized propagation reaction. The obtained copolymer consists of six-membered rings of cyclic acid anhydride and five-membered imide rings. This cyclic acid anhydride can hydrolyze and produce two carboxylic acids in the presence of an acid catalyst in the film. This copolymer containing PAG showed good properties for photoresist and gave good positive patterns.

References
Figure 3. Sensitivity curves of copolymer 1 with 5 wt% of DPI-OTf irradiated by a low pressure Hg lamp in various conditions of post-exposure baking (PEB).
   a) Baking time: 5 min., b) Baking temperature: 170 °C

Figure 4. SEM photographs of positive pattern on the copolymer 1 with 5 wt% of DPI-OTf.
   Pre-baking: 100 °C, 5 min., Exposure energy: 790 mJ/cm², PEB: 170 °C, 5 min.