Cyclocopolymer of N-cyclohexyldimethacrylamide and Application to a Photoresist with Photo-Acid Generator

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The cyclized copolymers from N-cyclohexyldimethacrylamide (CHDMA) with t-butyl methacrylate (tBuMA) or tetrahydropyranyl methacrylate (THPMA) were synthesized. These copolymerizations occurred by general technique of radical polymerization and CHDMA mainly proceeded the cyclized reaction. The copolymers have high transmittance at 248 nm. These copolymers indicated high thermal property due to the cyclic structure in the main chain. The ester unit of the side chain was easily cleaved by baking with acid catalyst. The acid reaction was dependent on a number of methacrylate units and a kind of ester group. However, the cyclized unit from CHDMA was no changed on this process. We applied these copolymers to photoresist based on the chemically amplified system with PAG and obtained patterns of positive-tone image.

Keywords: cyclocopolymer, cyclized copolymerization, photoresist, N-substituted dimethacrylamide

1. Introduction

Photolithography using deep-UV region is a leading candidate for further microelectronics device manufacturing. These materials for photolithography were essentially transparent at the exposure wavelength and stable toward dryetching condition. While a high sensitive material was required for 248 nm, the chemically amplified resist was developed.[1] This system has mainly two component. One is a photo-acid generator, which produces acid catalyst when the light is irradiated. The other is polymeric material. This material has functional group which react under an acid catalyst. In the process, the polymeric material will be soluble in aqueous base.

For the photolithography using further short wavelength, the copolymer used of maleic anhydride has provided transparency and good imaging properties.[2] Furthermore, the copolymer shows good resistance to dry etching. However, the maleic anhydride was copolymerized with styrene or olefin derivative and the obtained polymer had alternating structure. In the case of terpolymerization of cycloolefin, maleic anhydride, and acrylate for deep-UV resist, the terpolymers with arbitrary unit ratio were obtained.[3-5] However, Ito and co-worker indicated that this copolymerization did not proceed homogeneously.[6] Thus, the composition in the terpolymer can not be controlled.

We study the cyclized copolymer to apply the photolithography.[7, 8] In this polymerization, the cyclic structures are introduced in the main chain of polymer when divinyl monomer is polymerized. For example, N-substituted dimethacrylamide was polymerized by radical initiator and the five-membered imide ring was formed.[9, 10] This monomer could be copolymerized with methacrylate monomer.[11] This copolymerization also proceeded on cyclized mechanism and the copolymer contained no side chain of vinyl group. The cyclized copolymer can archive high potential while the polymer have the high transparency for deep-UV and the good resistance of dry etching for cyclic structure.

In this paper, we synthesize the new type of cyclized copolymer from N-cyclohexyldi-
methacrylamide which contained no aromatic
groups and evaluate the properties as the
basepolymer to the chemical amplification
photoresist.

2. Experimental

2.1. Materials

The materials were purchased from Wako
Chemicals. Tetrahydrofuran (THF) and benzene
were distilled over sodium. Cyclohexylamine
was distilled over CaH₂ under reduced pressure.
tBuMA and methacrylic acid (MA) were distilled
under reduced pressure. Other material was used
without purification.

2.2. Preparation of CHDMA

To a solution of 49.6 g of cyclohexylamine in
150 ml of benzene was added dropwise 26.1 g of
methacryloyl chloride in 50 ml of benzene under
flowed N₂. The reaction was continued stirring
overnight. After the reaction was completed, 40 ml of water and 100 ml of benzene was added into the
reaction mixture. From this mixture, water layer
was separated and benzene layer was washed by 10% of Na₂CO₃
twice and water 3 times. This solution was dried
over Na₂SO₄ and removed benzene. The residue
was recrystallized from cyclohexane. Yield was
28.9 g (69%).

The three-necked flask was fitted with drop
funnel and reflux condenser and purged under
argon. In the flask, 5.6 g of magnesium turnings
for the Grignard reaction was placed and added 10
ml of dry THF. To the flask was first introduced
1 g of ethyl bromide. The Grignard reaction was
started at once 24.1 g of ethyl bromide in 90 ml of
THF was added. After the dropping, this solution
was refluxed for 1 hour. This Grignard regent
was cooled at room temperature and immediately
used to next step.

The flask, which was equipped with drop
funnel, was placed a solution of 25.1 g of N-
cyclohexylmethacrylamide in 90 ml of THF under
argon. In the flask, 1.2 equivalent of Et-MgBr in
THF solution was added dropwise for 1h. After
the dropping was completed, 15.9 g of
methacryloyl chloride in 60 ml of THF was added
dropwise to the reaction mixture and the mixture
was stirred for 3h at room temperature. After
the reaction was completed, the reaction mixture was
drained into 300 ml of 1N HCl solution which was
cooled with ice bath. This solution was extracted
by chloroform and washed by 10 wt% of Na₂CO₃
solution twice and by water third times. The
washed solution was dried by Na₂SO₄ and removed
solvent. The solid products were obtained. The
products was purified by column chromatography
(SiO₂; n-hexane/chloroform = 3/2) to give a white
solid. The yield was 23.4 g (66%).

IR (KBr, disk) ν (cm⁻¹) 1703, 1655, 1626, 1448
¹H-NMR (400 MHz, CDCl₃) δ (ppm) 5.33 (2H, q,
J = 0.76 Hz), 5.18 (2H, q, J = 0.72 Hz), 4.30 (1H,
tt, J = 12.3, 3.7 Hz), 2.06-1.96 (2H, m), 1.84-1.79
(8H, m), 1.72-1.65 (3H, m), 1.39-1.29 (2H, m),
1.24-1.13 (1H, m)

2.3. Copolymerization

In the copolymerization method, the monomers
and initiator were dissolved into the solvent. The
solution was degassed and purged under argon.
After heating in an oil bath at 65 °C for the
appropriate time, the solution was poured into a
large amount of methanol/water mixture (5/1)
when copolymerized with tBuMA, or n-hexane
when copolymerized with MA. The precipitated
solid was filtered and dried in vacuo. This
polymer was purified by reprecipitation twice.
These conditions of copolymerization were
described in Table 1.

2.4. Protection of carboxylic acid group by
tetrahydropyranyl ester in poly(CHDMA-co-MA)

To a dispersion of 1 g of poly(CHDMA-co-
MA) in 10 ml of ethyl acetate and 20 mg of p-
toluenesulfonic acid as a catalyst was added 2 g of
3,4-hydro-2H-pyran with ice bath. After stirring
for 2h, ice bath was removed and the reaction solution was stirred at room temperature for 1 day. After reaction was completed, the solution was poured into a large amount of methanol/water (1/1). The mixture was filtered and dried under reduced pressure. Yield was 1.07 g.

2.5. Measurements

IR spectra were recorded on a Horiba FT-200 Fourier transform infrared spectrometer. \(^1\)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 curves 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. Polymerization

The cyclized polymerization has been studied since A. Crawshaw and G. B. Butler reported. [13]
The copolymerization proceeded to form the cyclic structure in the main chain. This polymerization was high reactivity to radical initiator and the cyclized polymer was easily obtained. Thus, we designed a new type of base polymer for chemical amplification resist including cyclic structure by this polymerization. These base polymers were composed of two types of units. One was cyclized unit in the main chain, which gave the thermal and dry-etching resistance. The other unit was reacted by acid catalyst and changed solubility into the developer. This overall process for the preparation of monomer and their polymerization is outlined in Scheme 1 and 2. N-phenyl, N-propyl, and N-methyldimethacrylamide have been prepared by literature. However, the preparation of CHDMA have never been reported. We developed the preparation of CHDMA which used to Grignard reagent. The obtained CHDMA was identified by $^1$H-NMR and IR. The copolymerization was occurred with 2,2'-azobisisobutyronitrile (AIBN) as a radical initiator. These conditions were summarized in Table 1. These polymers had five-membered ring of imide structure which was observed 1770 cm$^{-1}$ and 1700 cm$^{-1}$ on the IR spectrum. However, vinyl group and carbonyl group from CHDMA was not found on IR and $^1$H-NMR spectrum. Thus, this copolymerization with CHDMA mainly proceeded to cyclize reaction. While the copolymerization of CHDMA with MA or tBuMA was carried out, the CHDMA unit ratio in the copolymer was less than the feed ratio of CHDMA ratio. These results suggested that the monomer reactivity to propagation radical of CHDMA was lower than that of MA or tBuMA.

The protection of carboxylic acid in CM-55 by tetrahydropyranyl group was easily carried out. The protection was confirmed by IR spectrum, where the absorption of 3500 cm$^{-1}$ for OH group was disappeared and the broad absorption of 1700 cm$^{-1}$ for carbonyl group was shifted to 1730 cm$^{-1}$.

3.2. Polymer properties

These polymers have a transparency at deep UV region because the copolymers were not contained aromatic structures. In Table 2, the optical density at 248 nm was shown. The O.D. was less than 0.2 / µm in the film. This result was important to use as the base polymer for the deep UV photosist.

These copolymers have high T$_g$ (> 110 °C) by DSC due to cyclic structure. On the TG curve, these polymers showed two weight loss steps. One was deprotection of $t$-butyl or tetrahydropyranyl ester. The $t$-butyl ester was decomposed at about 200 °C and the tetrahydropyranyl ester was deprotected at 140 °C, respectively. The other of weight loss step was thermolysis of the main chain. These polymers have higher T$_g$ than general methaclylate polymers. This result was explained by the introduction of the cyclic structure into the main chain.

With acid catalyst, the ester groups of these copolymers were easily cleaved at lower temperature than without acid catalyst. This reaction was observed on IR spectrum. In the case of CB-37 with 3 wt% of diphenyliodonium...
trifluoromethanesulfonate (DPI-OTf) as a PAG, the absorption from CB-37 before and after irradiation was not changed. However, the alteration of this sample was observed while the sample was treated by post-exposure baking (PEB). This alteration was shown in Figure 1 by IR diffraction spectrum. The absorption of 1722 cm\(^{-1}\) was sifted to 1698 cm\(^{-1}\) and 1740 cm\(^{-1}\). The absorption of 2935, 2975, and 1140 cm\(^{-1}\) was decreased. The absorption of 1722 cm\(^{-1}\) was derived from the carbonyl group in \(t\)-butyl ester group and the absorption of 1740 and 1693 cm\(^{-1}\) was defined from carbonyl groups in carboxylic acid group, respectively. The absorption of 1139 cm\(^{-1}\) was assigned to C-O linkage in ester group. The other absorption, 2931 and 2976 cm\(^{-1}\), were confirmed to \(t\)-butyl group of ester group.

In the case of CP-55 with 3 wt% of DPI-OTf, the different spectrum from CB-37 was found. The absorption of 1730 cm\(^{-1}\) and 1700 cm\(^{-1}\) was increase and the absorption of 2950 cm\(^{-1}\) and 2870 cm\(^{-1}\) was decrease, respectively. When tetrahydropyranyl ester is cleaved with acid catalyst, the oxocarbenium ion is produced. This oxocarbenium ion can then react with water from the air to give in first instance 2-hydroxytetrahydropyran or it can lose a proton to give 3,4-dihydropyran. The 2-hydroxytetrahydropyran is a hemiacetal and is in equilibrium with 5-hydroxypentanal.[14] The absorption of 1730 cm\(^{-1}\) was defined as carbonyl group from 5-hydroxypentanal. The other absorption of 1700 cm\(^{-1}\) was identified as carbonyl group from carboxylic acid, which produced by deprotection from tetrahydropyranyl ester.

However, the cyclic structure from CHDMA
unit in these samples was not changed. This result was exhibited that this cyclized unit was outstanding for thermostability and acidstability.

3.3. Applied to photoresist

These copolymers except CM-55 were easily dissolved in THF, acetone, cyclohexanone, and aprotic solvents. From cyclohexanone solution, the good thin film was formed. CB-55, CB-37, and CP-55 were evaluated for basepolymer due to chemically amplified photoresist. These formed films were insoluble into 2.38 wt% of TMAH solution as a developer. Moreover, when ester unit was cleaved and the carboxylic acid was produced, these polymer films can be easily soluble into the developer. The cleavage of ester group was previously identified by IR spectrum.

These copolymers with 3 wt% of DPI-OTf as a PAG were evaluated for as a photoresist. These characteristic curves were shown in Figure 2 and 3. These films were exposed with a low pressure Hg lamp. CB-37 could be developed by 2.38 wt% of TMAH solution, when the film was irradiated about 80 mJ/cm². However, CB-55 exposed sufficient energy could not be developed by the same condition. This result was considered that the CB-55 was not produced enough carboxylic acid to dissolve into the developer, when the film was treated by PEB. Because the number of t-butyl units in the polymer were less than that of CB-37 and the deprotection of t-butyl ester was difficult to proceed in the polymer. CP-55 could be developed easily by 1 wt% of TMAH solution. Moreover, the amount of exposure energy was about 50 mJ/cm² which was less than CB-37. The sensitivity curves were strongly dependent on PEB temperature. At 140 °C, no exposure area was also dissolved into the developer. This phenomenon was indicated that the thermolysis of tetrahydropyranyl ester could occur in this polymer at about 140 °C.

The positive-tone images were successfully obtained from CP-55 film with 3 wt.% of DPI-OTf exposed to 60 mJ/cm² with a low pressure Hg lamp. The SEM photographs of the pattern are shown in Figure 4.

4. Conclusion

The cyclized copolymers from N-cyclohexyldimethacrylamide with metacrylate monomers were synthesized. This cyclized copolymerization was easily occurred and the obtained copolymer was mainly proceeded to cyclized propagation reaction. These copolymers have high transparency at deep-UV region and thermal properties. We applied these copolymers to the photoresist for chemically amplified system. The properties of these copolymers were satisfactory for the photoresist in the deep-UV region. The good images were successfully obtained from these components.

References