Synthesis and Lithographic Characterization of Poly(6-vinyluracil) Derivative

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Enol ether derivative of poly(6-vinyluracil) was synthesized. The polymer released completely the tert-butyl groups above 190°C and gave poly(6-vinyluracil) which was stable up to 350°C. The resist film as spin coated from chloroform solution containing photo-acid generator released completely the tert-butyl groups after UV light irradiation followed by post exposure baking. Solubility of the obtained polymer containing uracil unit was significantly different from the original polymer containing alkoxy units in both polar (TMAH aq) and nonpolar (anisole) solvents as developer. The resist film was found to have high sensitivity and high contrast as both positive and negative type deep-UV resist materials.

Keywords: poly(6-vinyluracil), tautomerism, deep-UV resist

1. Introduction

For recent years, we have studied photo-responsive materials using synthetic nucleic acid analogs. Thymine bases in DNA undergo [2+2] cycloaddition reaction by irradiation at $\lambda_{\text{max}}$ (270nm) of thymine base, and the photodimer readily reverse to monomer by UV light at shorter wavelength of 240 nm [1, 2]. We had reported that the synthesis of a variety of thymine derivatives and these reversible photodimerizations can be applied to photo recording systems [3-7] and photo resist materials [8-21].

Uracil, which is also one of pyrimidine bases in RNA, is known to show the structure in keto-enol tautomerism, and mostly exists in keto-form. Dialkoxypyrimidines, enol ether derivatives of uracil, therefore easily afford uracil by tautomerization with an acid catalyst (Figure 1). Previously, the polyethers containing pyrimidine and tert-alkyl units in the main chain were prepared, and the properties of these polymers were studied as chemically amplified deep-UV resists [22] (Figure 2). The polyether had high sensitivity and high contrast due to effective tautomerism by photo-acid generator. The ether bonds decomposed effectively by acid. Synthesis of the polyether by Williamson reaction, however, was difficult to yield high molecular weight polymer. In general, the polymerization of a vinyl compound is easier to control the molecular weight relative to a polycondensation such as the polyether synthesis.

In this paper, we report the synthesis and lithographic characterization of enol ether derivative of poly(6-vinyluracil). The polymer is proposed as a new strategy for a chemically amplified deep-UV resist material.
2. Experimental

2.1. Materials (Scheme 1)

6-Methyluracilyl triphenylphosphonium chloride (2)

Into a solution of 6-(chloromethyl)uracil (1) (32 g, 0.2 mol) in N,N-dimethylformamide (DMF, 200 ml), triphenylphosphine (80 g, 0.3 mol) was added. The mixture was stirred at 100°C for 3 h under nitrogen. The resulting mixture was cooled to room temperature, and deposited white solid was filtered and washed with diethyl ether. The product was recrystallized from ethanol to give 2 (88 g, 94% yield), containing 1 equivalent of ethanethol as co-crystal.

1H-NMR (270 MHz, DMSO-d6) 1.05 (d, 3H, CHCH2OH), 3.44 (q, 2H, CH3CH2OH), 4.39 (s, 1H, CH3CH2OH), 5.07 (s, 1H, 5-H), 5.14 (d, 2H, CH2), 7.76-8.10 (m, 15H, C6H5), 11.06 and 11.13 (s, 2H, 2NH).

6-Vinyluracil (3)

A mixture of the phosphonium chloride derivative 2 (2.1 g, 5.0 mmol, dried over P2O5 at 100°C for 20 h) and paraformaldehyde (0.75 g, 25 mmol, dried over P2O5 at 100°C for 20 h) was suspended in dry DMF (100 ml). To the stirred suspension was added dropwise under nitrogen a solution of sodium ethoxide (prepared from 0.5 g of sodium metal in 30 ml of absolute ethanol). After all the sodium ethoxide was added (30 min), the suspension was stirred at room temperature under nitrogen for 39 h and evaporated to dryness. Water (20 ml) was added into the residual solid, and insoluble solid (triphenylphosphine oxide) was removed by filtration. Hydrochloric acid (1 N) was added dropwise to the filtrate with stirring at 0°C for neutralization. The precipitated white solid was collected, and was washed with water and diethyl ether, and was recrystallized from acetic acid to give 3 (0.45 g, 65% yield).

1H-NMR (DMSO-d6) 5.64 (s, 1H, 5-H), 5.65 (d, 1H, =CH2 cis), 6.25 (d, 1H, =CH2 trans), 6.38 (q, 1H, RCH=C), 10.86, 11.03 (2s, 2H, 2NH), Jgem=0.7Hz, Jtrans=17.7Hz, Jcis=9.3Hz.

Anal. Calcd. for C6H6N2O2: C, 52.17; H, 4.38; N, 20.28%; Found: C, 51.57; H, 4.35; N, 20.18%.

2,4-Dichloro-6-vinylpyrimidine (4)

To 6-vinyluracil 3 (2.1 g, 5.0 mmol) was added phosphorus oxychloride (20 ml, 220 mmol) and N,N-diethylaniline (2.4 ml, 15 mmol). The mixture was refluxed for 1 h under nitrogen, and the volatile components were removed under diminished pressure. The residual brown fluid was poured into crushed ice-water. Ether extract was washed with cooled water 3 times, dried on MgSO4, and ether was removed to give crude 4 (light yellowish oil, 1.5 g, 86% yield). Because the compound decomposed slowly in air, the compound was used for the following reaction without further purification.

1H-NMR (CDCl3) 5.84 (q, 1H, =CH2 cis), 6.58 (q, 1H, =CH2 trans), 6.68 (q, 1H, RCH=C), 7.23 (s, 1H, 5-H), Jgem=2.0Hz, Jtrans=17.1Hz, Jcis=9.3Hz.

Poly(6-vinylpyrimidine) derivative (6)

The compound 4 (1.5 g, 8.6 mmol) was dissolved in dry THF (50 ml), and potassium tert-butoxide (1.0 M THF solution, 0.18 ml) was added to the solution at -78°C with stirring. After the solution was stirred for 3 h at -78°C, potassium tert-butoxide (1.0 M THF solution, 50 ml) was added. The temperature of the mixture was raised slowly to room temperature, and stirred for 1 week. After the solvent was removed, cooled water (ca. 100 ml) was added to the residue, and insoluble brown solid was collected and washed with water. The brown solid was dissolved in a small amount of chloroform and washed with water 3 times. After the solution was dried on MgSO4 and evaporated, the brown solid was dissolved in methanol, and the solution was poured into 10% aqueous methanol. The precipitated solid was collected and reprecipitated repeatedly until monomer and potassium chloride were removed completely to give the polymer 6 (1.6 g).

IR (cm⁻¹): 2962, 2925, 1675, 1585, 1560, 1480, 1460, 1435, 1410, 1400, 1380, 1255, and 1175.

Anal. Calcd. for 25% chloride units remaining: C, 61.31; H, 7.38; N, 12.28%; Found: C, 61.00; H, 7.32; N, 12.18%.

2.2. Preparation of resist film

The polymer 6 (90 mg) and a photo-acid generator (triphenylsulfonium triflate: TPS, 10 mg) were dissolved in chloroform (1.0 ml), and the solution was spin coated on a HMDS-treated silicon wafer presented by Shin-Etsu Chemical Co. Ltd., and prebaked at 150°C for 10 sec to give a 1 µm thickness of resist film.

2.3. Lithographic Evaluation

The resist film was irradiated by deep-UV light at 250 nm. After the irradiated resist film was post baked, the film was developed with 3.0 wt% of TMAH (tetramethylammonium hydroxide) aqueous solution or anisole for 1 min. The remaining film thickness was calculated from the absorbance of IR spectra related with measurement by SEM.

2.4. Apparatus

The molecular weight determination of the polymer 6 was made by gel permeation chromatography (GPC) using a Showa Denko Shodex A-80M col-
umns at 40°C in tetrahydrofuran. Thermal analyses were performed on a SEIKO SSC/580 thermal analyzer at a heating rate of 5°C/min for TGA and 10°C/min for DSC under inert atmosphere. The 1H-NMR spectra (270 MHz) were measured on a JOEL GSX FT NMR spectrometer using tetramethylsilane as internal standard. The elemental analyses were performed by the Analytical Center of Osaka University. The IR spectra were measured on a Nicolet SDXC FT-IR spectrometer. The irradiation of deep-UV light at 250 nm to the resist film was carried out a JASCO CRM-FA Spectro Irradiator.

3. Results and Discussion
3.1. Synthesis of Enol Ether Derivative of Poly(6-vinyluracil)
Enol ether derivative (6) of poly(6-vinyluracil) was prepared according to Scheme 1. Wittig reaction of 6-(chloromethyl)uracil (1) gave 6-vinyluracil (3). The reaction of 6-vinyluracil with phosphorus oxychloride afforded 2,4-dichloro-6-vinylpyrimidine (4). Anionic polymerization of the monomer 4 was carried out by catalytic amount of potassium tert-butoxide at -78°C for 3 h to give the polymer 5. Finally, Williamson reaction of the polymer 5 with excess potassium tert-butoxide gave the polymer 6. The polymer 6 was found to have still about 25% chloride units from elementary analysis, and molecular weight of 36,000 (polystyrene-equivalent) from GPC measurement.

3.2. Thermal Analysis
DSC measurement of polymer 6 was achieved (Figure 3). In the first run, the sample of polymer 6 was measured in the range of room temperature to 250°C. In the second run, the cooled sample was measured again from room temperature to 500°C. In the first measurement, a sharp endothermic peak was observed around 193°C. However, there was no peak in the second measurement. The fact suggests that the endothermic peak would not be due to a change of the higher structure or a phase transition, but a change of the chemical structure or a decomposition.

As shown in TGA curve of polymer 6 (Figure 4), the polymer was stable to about 150°C. The great decrease of the weight was observed around 190°C. The weight loss at 190°C was in fair agreement with the calculated value of tert-butyl group. The IR spectra of the polymer 6 before and after heating at 200°C for 3 min are shown in Figure 5. After heating, the absorbances of tert-butyl group (2962 and 1365 cm⁻¹) disappeared, and new peaks of carbonyl group (1720 cm⁻¹) and N-H (3200 cm⁻¹) appeared. These facts suggest that the polymer 6 released tert-butyl group by heating above 190°C and tautomerized to poly(6-vinyluracil) that was stable to 350°C.
3.3. Sensitivity to Photo-Acid

The polymer 6 and the acid generator (triphenylsulfonium triflate) were dissolved in chloroform, and the mixture was casted on HMDS-treated silicon wafer to obtain resist film. Photosensitivity of the resist film was investigated by deep-UV light irradiation at 250 nm. After UV irradiation and PEB at 150°C for 3 min, absorbances of tert-butyl group (2962 and 1365 cm⁻¹) and pyrimidine (1580 cm⁻¹) disappeared, and new peaks of uracil (3200 and 1720 cm⁻¹) appeared (Figure 6). It is similarly to the case of heating at 200°C without an acid generator. This fact suggests that the generated acid by UV irradiation promoted releasing of tert-butyl group and the structure changed from enol ether form to keto form as shown in Figure 7, because of the polymer 6 was stable to 190°C without an acid generator.

Polymer 6 is insoluble in water, but the polymer 7 containing uracil unit is soluble in aqueous alkaline solution, because pKa value of uracil is around 8. Therefore, the solubility of the polymer 7 after irradiation should be significantly different from that of the polymer 6 before irradiation in both polar (TMAHaq) and nonpolar (anisole) solvents.

3.4. Positive Type Photoresist

The resist film should be serve for a positive type photoresist using TMAH aq as a developper. The post exposure baking (PEB) condition of the resist film was investigated for a positive type development. After UV light irradiation (250 nm, 50 mJ/cm²), PEB, and development with 3.0 wt% TMAH aq, the remaining film thickness was measured (Figure 8). No irradiated film (dot line) was insoluble until 3 min PEB at 150°C, and after that, the solubility of the film slightly increased. Irradiated (250 nm, 50 mJ/
cm²) film (solid line), however, became slightly soluble even after PEB at 100°C and soluble completely under the condition of PEB at 150°C for 3 min. So the PEB (150°C for 3 min) condition must result in the highest sensitive resist for a positive type photoresist.

Figure 9 shows the normalized remaining film thickness against irradiated energy using the PEB condition. The sensitivity of the positive type resist using 3.0 wt% TMAH as a developer was 50 mJ/cm², and the contrast (γ) was 4.3. The gentle decreasing of film thickness at the lower exposing energy would be due to the weight decrease by releasing of tert-butyl group.

3.5. Negative Type Photoresist

The resist film should be serve for a negative type photoresist using anisole as a developer. The PEB condition of the resist film was investigated for a negative type development. After UV light irradiation (250 nm, 50 mJ/cm²), PEB (140 or 150°C), and development with anisole, the remaining film thickness was measured (Figure 10). No irradiated film (dotted line) was soluble completely until 5 min under the condition of PEB at 140°C, and after that, the film became slightly insoluble (Figure 10a). Irradiated film (250 nm, 50 mJ/cm²), however, became insoluble completely under the condition of PEB at 140°C for 2 min (Figure 10a). Under the condition...
of PEB at 150°C (Figure 10b), on the other hand, no irradiated film (dotted line) became insoluble even for 1 min PEB. So the PEB condition of 140°C for 2 min must result in the highest sensitive resist for a negative type.

Figure 11 shows the normalized remaining film thickness against irradiation energy using the PEB condition (140°C, 2 min). The sensitivity of the negative type resist using anisole as a developer was 35 mJ/cm², and the contrast (γ) was 8.0.

4. Conclusion

It was revealed that the enol ether derivative (polymer 6) of poly(6-vinyluracil) (polymer 7) was synthesized. The polymer released completely tert-butyl groups above 190°C and gave poly(6-vinyluracil) which was stable to 350°C. The resist film as spin coated from chloroform solution containing photo-acid generator released completely the tert-butyl groups after UV light irradiation and following post exposure baking. The solubility of polymer 6 after UV irradiation was significantly different from the original polymer in both polar (TMAH aq) and non-polar (anisole) solvents. The resist film of polymer 6 was found to have high sensitivity and high contrast as both positive and negative type deep-UV resist materials.

5. References