Photodegradation of Poly(methacrylates), Poly(acrylates) and Polystyrene Derivatives by 146 nm Light

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Photodegradation of acrylate, methacrylate, and styrene type polymers was investigated under nitrogen using 146 nm light from Kr$_2$ excimer lamp. Photocrosslinking reactivity of poly(methacrylates) and poly(acrylates) was dependent on the structure of the ester units. Cleavage of ester units and formation of double bonds were observed. Decrease of film thickness due to ablation was observed. Poly(methacrylates) films irradiated at 146 nm were soluble in tetrahydrofuran (THF) but irradiated poly(acrylates) films were not soluble. Thickness decrease of styrene based polymer films did not occur on irradiation with 146 nm light. The irradiated polystyrene film was insoluble in THF but poly(α-methylstyrene) film was soluble in THF after irradiation. The irradiated poly(p-hydroxystyrene) and poly(p-hydroxy-α-methylstyrene) films were insoluble in THF. It was found that tertiary hydrogen atoms in the main chain and phenolic OH groups participated in crosslinking of the polymers.

Keywords: 146 nm light, poly(methacrylates), VUV resist, polystyrene, poly(α-methylstyrene), photodegradation, photocrosslinking

1. Introduction

Photolithography at 157 nm using F$_2$ excimer laser has been proposed as a promising technology for post ArF technology [1-3]. To develop matrix resins in 157 nm photoresist applications, it is important to investigate photoreactions of polymers by 157 nm light, because the photocrosslinking of the polymers is a serious problem for positive single-layer resists and the photodegradation of the polymers is also significant problem with respect to outgassing [4]. Photodegradation of poly(methyl methacrylate) [5-10], poly(acrylates) [11-13] or polystyrene [14-16] has been studied using UV light (λ > 254 nm) or VUV light at 185 nm. However, only few papers on photochemical reactions of polymers using F$_2$ excimer laser have been reported until now. Recently, Kishimura et al. have reported the photoreaction of conventional resists for ArF or KrF lithography with 146nm light and they found that undesirable photoreactions such as photocrosslinking and photodegradation, being different from irradiation at wavelengths longer than 185 nm [17,18].

In this paper we report the photodegradation of methacrylate, acrylate and styrene type polymers on irradiation under nitrogen with 146 nm light from Kr$_2$ excimer lamp. Effects of polymer structure on the photodegradation and photocrosslinking were studied using FT-IR and UV spectroscopies and gel permeation chromatography. Photodegradation and photocrosslinking mechanisms were discussed.

2. Experimental

2.1. Materials

Poly(methyl methacrylate) (PMMA), poly(isopropyl methacrylate) (PIPMA), poly(t-butyl methacrylate) (PTBMA), poly(isoboronyl methacrylate) (PIBOMA), poly(adamantyl methacrylate) (PADMA), poly(methyl acrylate) (PMA), poly(n-butyl acrylate) (PNBA) and polystyrene (PSt) were prepared by the conventional radical polymerization of corresponding monomers with azobis(isobutyronitrile) as initiator at 55-60 °C. The monomers were distilled before use. Poly(α-methylstyrene) (PMSI) was prepared by cationic polymerization of distilled α-methylstyrene with boron trifluoride etherate as initiator at...
(-50 °C). Poly(p-hydroxy-α-methylstyrene) (PHMSt) was synthesized as follows: poly(t-butoxycarbonyloxy-α-methylstyrene) (PtBocMSt) was prepared by cationic polymerization of corresponding monomers similar to the polymerization method for PMSt. Then, PtBocMSt was heated at 200 °C for 2 hr under nitrogen atmosphere. Decomposition of t-butoxycarbonyloxy units to OH was confirmed by disappearance of FT-IR absorbance due to the C=O groups. Poly(p-hydroxystyrene) (PHSt) was purchased from WAKO CHEMICALS. Characteristics and structures of the polymers are shown in Table 1 and Scheme 1, respectively.

### 2.2. Measurements

For FT-IR spectral measurements, films were prepared by spin-casting onto silicon wafers using a Mikasa spincoater 1H-D7. Casting solvent was cyclohexanone. The sample films were baked at 90 °C for 1 min on hot plate to remove the residual solvents. For UV spectral measurements, films were spin-cast on a quartz plate. Film thickness was adjusted to be 0.05-0.2 µm which was measured by interferometry using Nanospec/AFT. The sample films (0.05 µm thick) were transparent at 146 nm because it has been reported that transmittance at 146 nm for 0.1 µm thick film was 10-14 % [18].

Irradiation at 146 nm was carried out at room temperature under nitrogen using Kr2 excimer lamp (USHIO: UER20H-146V). The sample holder was placed in a chamber equipped with a MgF2 window for incident light. The distance between the sample and the lamp was 3 cm. Light intensity was about 3 mW/cm².

Molecular weights of the polymers were obtained by GPC using polystyrene standards. UV spectral changes were measured by the use of a Shimazu UV-2400PC. FT-IR measurements were carried out by the reflection absorption infrared spectroscopy method at accumulation of 100 scans using a JASCO FT-IR-7300 spectrophotometer equipped with PR-500. Polarizer was KRS-5 and the incident angle to the sample film was 85°.

Insoluble fraction of irradiated polymer films was calculated by measuring the thickness change before and after development in THF for 5 min.

Changes of number-average molecular weight (Mn) and dispersity of the irradiated polymer films were measured as follows: four pieces of irradiated film (3.5 × 2 cm, thickness 0.15 µm) were dissolved in distilled THF. Then, THF was evaporated after filtration (pore size 0.5 µm) to remove the gel fraction. The residual polymer was dissolved in 0.3 ml of THF and the THF solution was used as sample for GPC measurements.
3. Results and discussion

3.1. Photodegradation of poly(methacrylates) and poly(acrylates).

The mechanism for photodegradation of PMMA on irradiation with UV light (250-350 nm) has been reported as shown in Scheme 2 [6]. The photodegradation was reported to occur by main-chain scission and/or ester side chain scission followed by main-chain scission and depolymerization. It has been also reported that the ablative photodegradation of PMMA film occurs by 185 nm light [9,10].

Fig. 1 shows FT-IR spectral changes of PMMA film on irradiation at 146 nm. The absorption peaks at 1730 (vC=O) and around 1150 cm⁻¹ (vC-O-C) decreased, suggesting the cleavage of the pendant ester units. No significant changes were observed in the range from 2000 to 4500 cm⁻¹. Similar spectral changes were observed for other poly(methacrylates) and poly(acrylates) films. Fraction of decomposed ester units in the side chain was calculated as \( A/A_0 \), where \( A \) and \( A_0 \) are the absorbances at 1730 cm⁻¹ after and before irradiation, respectively. The rate of decomposition of ester units decreased in the order PTBMA > PIPMA > PMMA > PIBOMA > PADMA as shown in Fig. 2. This order was in agreement with the stability of alkyl radicals formed after cleavage of ester units (t-buty > isopropyl > methyl) except for PIBOMA and PADMA. This finding suggests that cleavage of ester units with 146 nm light depends on the stability of alkyl radical formed after irradiation. The rate of decomposition of ester units of PIBOMA and PADMA was lower than other methacrylate polymers because they had bulky alicyclic units. This may be due to the enhanced recombination of
Upon irradiation at 146 nm of poly(methacrylates) film, the decrease of film thickness was observed similar to the finding on irradiation at 185 nm [9,10]. Fig. 3 shows the decrease of thickness changes of poly(methacrylates) films on irradiation. The rate of thickness change decreased to the order PTBMA > PIPMA > PMMA > PIBOMA > PADMA and the order was in agreement with the order of the efficiency of photolysis of ester units.

When the PMMA film cast on quartz plate was irradiated at 146 nm, a new peak at 195 nm appeared as shown in Fig. 4. Similar spectral changes were observed for other methacrylate and acrylate polymer films. The new peak may be due to the formation of olefinic bonds generated by the main-chain scission. The absorbance at 195 nm was used as a measure of the number of main-chain scission and the amounts of the formation of olefinic bonds by 146 nm light. The absorbance at 195 nm was normalized by film thickness because thickness decreased remarkably after irradiation. The normalized changes in absorbance at 195 nm increased in the order PADMA < PIBOMA < PMMA < PIPMA < PTBMA as shown in Fig. 5. This order was in consistent with the order of the rate for the decomposition of the ester units observed by FT-IR spectroscopy. This means that main-chain scission of poly(methacrylates) by 146 nm light can be occurred by the cleavage of side chains rather than the direct main-chain scission.

Upon irradiation, molecular weights of the polymers decreased and molecular weight distribution increased except PMSt as shown in Table 2. The number-average molecular weight of PMMA (Mn=5.23 × 10^4, Mw/Mn=2.0) became 9.5 × 10^3 (Mw/Mn=5.0) after irradiation for 30 sec. The efficiency of main-chain scission increased in the order PMMA < PIPMA < PTBMA and was consistent with the order of the amounts of olefinic bonds and of the rate of decomposition of ester units. It has been reported that the photolysis of PMMA results in a random scission of the polymer chain.
Photodegradation process of methacrylate polymer by 146 nm seems to be similar to that reported.

Solubility changes of the irradiated poly(methacrylates) and poly(acrylates) films in THF were studied. Fig. 6 shows the relationship between insoluble fraction and irradiation time. All poly(methacrylates) films irradiated at 146 nm were soluble in THF but irradiated PMA and PNBA films were insoluble in THF. This finding means that tertiary hydrogen atoms in the main chain of the polymer strongly induce the insolubilization. The insolubilization efficiency for PNBA was higher than PMA. The lower Tg value for PNBA can enhance the motion of the polymer chain, which increases the efficiency of the photocrosslinking.

3.2. Photoreaction of polystyrene derivatives.

When PHSt films were irradiated at 146 nm, the absorbance at around 195 nm decreased and the absorbance at wavelengths longer than 203 nm increased (Fig. 7). Similar results were obtained for other PST derivatives. The peaks at 1230 (v C-O), 1455, 1515 and 1610 (v aromatic C=C) and broad peak at 3100-3600 cm⁻¹ (v O-H) decreased a little (Fig. 8). Fig. 9 shows the photo-induced insolubilization of styrene based polymers. The efficiency of photo-induced insolubilization was strongly dependent on the polymer structure and decreased in the order PHS > PHMSt > PSt. PMSt was not photocrosslinkable. This result suggests that tertiary hydrogen atoms in the main chain and phenolic OH group in the polymers strongly induce the photocrosslinking. It has been reported that the most important photodegradation step of polystyrene in vacuum on irradiation at 254 nm is the scission of tertiary C-H bond in the polymer backbone [19]. When the resulting two macroradicals are close each other, crosslinking may occur as shown in Scheme 3. A septet line ESR spectrum has been reported as a direct evidence for the formation of polymer alkyl radicals [20,21]. It has been also reported that when PHSt film was irradiated at 254 nm in vacuum, PHSt gives a...
of 254 nm irradiation.

Photodegradation of PMSt was studied. Mn of the irradiated PMSt decreased and Mw/Mn also decreased as shown in Table 2. It has been reported that molecular weight of PMSt irradiated at 250-280 nm rapidly decreased and led to monomer formation [23]. Therefore, this result may be due to the decrease of the number of detectable molecules for GPC measurement because PMSt which has low ceiling temperature at 0 °C in THF solution in vacuum [24] was converted into monomers after 146 nm irradiation (Scheme 4).

4. Conclusion

Photodegradation of methacrylate and styrene based polymers was studied. poly(methacrylates) and poly(α-methylstyrene) were photodegradable and poly(acrylates), poly(p-hydroxystyrene) and poly(p-hydroxy-α-methylstyrene) were photocrosslinkable when irradiated at 146 nm. Tertiary hydrogen atoms in the main chain and phenolic OH groups of the polymers participated in the photocrosslinking.

Fig. 8 FTIR spectral changes of PHSt film on irradiation at 146 nm. Film thickness: 0.05 μm.

Fig. 9 Insoluble fraction of irradiated styrene based polymer films. (O) PSt, (△) PHSt, (□) PMSt, (○) PPHSt. Film thickness: 0.05 μm.
References