Study on Electron-beam-induced Reactions of Methyl α-Allyloxymethyl Acrylic Polymer

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α-Allyloxymethyl acrylic (AMA) polymers are radical-curable resins that contain tetrahydrofuran (THF) rings in their main chain and acrylic units in their side chains. AMA polymers are generally cured by ultraviolet light with photopolymerization initiators and are used as adhesive agents, sealants, inks, and resist materials owing to its high adhesiveness, transparency, and thermal tolerance. In this study, the applicability of methyl AMA polymer (PMeAMA) as an electron beam (EB) resist was investigated. PMeAMA performs as a negative-tone resist upon EB irradiation, and the sensitivity of PMeAMA was determined to be 300–400 μC/cm² for a 55 kV EB. This value is comparable to those of poly(methyl methacrylate) (PMMA) and hydrogen silsesquioxane. The radiation-induced early reactions of PMeAMA in nanosecond time scale were studied by using nanosecond pulse radiolysis. The electron scavenging capability of PMeAMA was confirmed, and its electron scavenging rate constant was comparable to that of PMMA. The reactivity of PMeAMA with solvent radical cations was observed in dichloromethane solution.

Keywords: α-Allyloxymethyl acrylic polymer, Poly(methyl methacrylate), Electron beam resist, Pulse radiolysis, Tetrahydrofuran

1. Introduction

α-Allyloxymethyl acrylic (AMA) polymers are radical-curable resins that contain tetrahydrofuran (THF) rings in their main chain and acrylic units in their side chains. The chemical structure of AMA polymers is shown in Fig. 1. AMA polymers can be used as adhesive agents, sealants, inks, and resist materials because of their excellent properties: high adhesiveness, transparency, and thermal tolerance [1–3]. These features are attributed to the THF rings in the main chain and the methylene groups next to the THF rings.

The most noticeable usages of AMA polymers are as colorant dispersion compositions. Since AMA polymers facilitate the dispersion stability of colorants, AMA polymers can be used as excellent color filter resists [1,2]. Moreover, AMA monomers are also useful as reactive diluents [4], and AMA...
polymers turn into an alkali-soluble resins by introducing an acid group such as a carboxyl group in their structure [2].

Generally, AMA polymers are cured using photopolymerization initiators under ultraviolet light. However, the curing of AMA polymers using ionizing radiations has not been sufficiently investigated.

In this study, we investigated a methyl AMA polymer (PMeAMA) as an electron beam (EB) curable resin for the future potential application to a negative-tone resist material. The characteristics of PMeAMA solid films after the EB exposure and development were also investigated.

In contrast to ultraviolet irradiation, ionizing radiation generates charged active species in addition to neutral radicals. Therefore, the EB-induced early reactions of PMeAMA with these charged active species in nanosecond time scale were also investigated using nanosecond pulse radiolysis in solution.

2. Experimental

2.1. EB exposure and development

PMeAMA (Nippon Shokubai Co., Ltd.) (Mw: 30,000) was used in the experiments. PMeAMA was soluble in organic solvents because acid groups were absent in its structure. A PMeAMA sample was dissolved in THF at 1.5 w/v%, spin-coated on Si wafers at 2500 rpm, and baked at 80 °C for 10 minutes. A baking temperature lower than 170 °C was required to prevent the thermal crosslinking of PMeAMA (data not shown). The obtained PMeAMA solid films were approximately 90 nm in thickness.

The films were exposed to a 55 kV-accelerated EB in air by using a table-top accelerator (IWASAKI). The beam energy at the target surface was decreased by scatterings by a thin Ti film and air. Therefore, the maximum energy of the irradiated EB, which was calculated by using a general Monte-Carlo simulation code (EGS5) [5], was approximately 46 keV. The dose rate of the present experimental setup was 0.33 MGy/s.

The exposed films were developed with 4-methyl-2-pentanone (MIBK: methyl isobutyl ketone) for 60 s at room temperature and rinsed with 2-propanol (isopropyl alcohol) first and with water subsequently. The residual resist thicknesses after development were measured using an AFM5300E atomic force microscope (Hitachi High-Technologies Corporation).

2.2. Pulse radiolysis study on PMeAMA

Kinetic traces and transient absorption spectra were obtained using nanosecond pulse radiolysis. A pulsed EB by L-band linac in the Institute of Scientific and Industrial Research (ISIR) at Osaka University [6,7] was used in the experiments. The EB pulse width was 8 ns, and the time resolution of the system was ~10 ns. The energy of the pulsed EB was 26 MeV. The deposition dose per pulse was calculated to be ~200 Gy. A Xe flash lamp was used as white probe light. The probe light was absorbed by the radiation-induced active species in the samples, dispersed by a monochromator, and detected by photodiode detectors.

PMeAMA and poly(methyl methacrylate) (PMMA, Mw: 25,000) were dissolved in THF, N,N-dimethylformamide (DMF), or dichloromethane (DCM) and sealed with screw caps in quartz cells with an optical length of 1.0 cm. The samples were deoxidized by Ar bubbling for 10 min.

3. Results and discussion

3.1. EB exposure and development

The thicknesses of the PMeAMA solid films after the EB exposure and development are shown in Fig. 2. The shown thicknesses are relative values with respect to that before the exposure.

As shown in Fig. 2, the PMeAMA films were entirely removed after the development when the absorbed dose was lower than or equal to 0.66 MGy. For higher doses, the thickness of the PMeAMA film after the development increased with the absorbed dose. This confirms that PMeAMA performs as a negative-tone resist upon EB irradiation.

The sensitivity of negative-tone resist is defined as the dose at which the developed thickness is equal to half of the thickness before exposure.

![Fig. 2. Sensitivity curve of PMeAMA. The PMeAMA film was exposed to a 55 kV-accelerated EB in air and developed with MIBK for 60 s.](image-url)
(developed thickness = 0.5 (Fig. 2)). Therefore, the sensitivity of PMeAMA as a negative-tone resist was determined to be 2.4 MGy for a 55 kV EB irradiation in air. The sensitivity in terms of charge per unit area was calculated to be 300–400 μC/cm².

This value is comparable to those reported for typical non-chemically-amplified resists, such as hydrogen silsesquioxane (negative-tone) and PMMA (positive-tone), which are in the range 200–400 μC/cm² for ~50 keV [8,9].

PMeAMA contains ethylene groups, which are categorized into vinyl type groups, in the main chain and can be considered as an alternating copolymer of the vinyl type group and the other group. The sensitivity of PMeAMA is higher than that of polystyrene (~1000 μC/cm² for 50 keV [10]), another vinyl polymer.

This experiment confirmed that PMeAMA can be employed as a negative-tone EB resist. Its sensitivity can be improved by optimizing development conditions such as a developer and temperature.

3.2. Pulse radiolysis study on PMeAMA

3.2.1. Transient absorption spectrum in THF

The EB-induced early reactions of PMeAMA in solution in nanosecond time scale were also investigated using nanosecond pulse radiolysis. The transient absorption spectra of neat THF and 0.5 M PMeAMA solution in THF are shown in Fig. 3. PMeAMA concentration refers to the molar concentration of the repetitive monomers, and optical density denotes the common logarithm of the ratio of the incident to the transmitted intensity of the probe light.

A broad transient absorption band of solvated electrons was observed in neat THF in the near IR and visible regions (Fig. 3(a)). Its absorption maximum is known to be at wavelengths longer than 2000 nm [11,12]. This absorption band decreased by dissolving 0.5 M PMeAMA in THF, as shown in Fig. 3(b). This indicates that solvated electrons were scavenged and short-lived by PMeAMA; thus, they could not be measured using nanosecond pulse radiolysis. The process can be represented as follows:

\[
\text{THF} \leftrightarrow \text{THF}^+ + e^- \quad (1)
\]
\[e^- \rightarrow e^-_{\text{sol}} \quad (2)\]
\[e^-_{\text{sol}} + \text{PMeAMA} \rightarrow \text{PMeAMA}^{-} \quad (3)\]

A transient absorption band was observed in the 0.5 M PMeAMA solution at wavelengths shorter than 700 nm (Fig. 3(b)). Because the lifetime of the absorption band is longer than that of the solvated electron, the absorption band can be found more clearly in the spectrum obtained at \( t = 50 \) ns.

To identify this absorption band, the transient absorption spectra of 0.5 M PMeAMA solutions with triethylamine (TEA) or DCM in THF were also measured using pulse radiolysis. TEA and DCM are a cation and an electron scavenger, respectively. These transient absorption spectra (\( t = 50 \) ns) are shown in Fig. 4. The absorption band at wavelengths shorter than 700 nm decreased by adding DCM, although it was not changed by adding TEA. In the absence of DCM, the free electrons generated by the EB irradiation in polar THF were mainly scavenged by PMeAMA and turned into PMeAMA radical anions (Eq. (3)). On the other hand, in the presence of DCM, the free electrons in the PMeAMA solution were mainly scavenged by DCM, and the PMeAMA radical anions were hardly generated. Since DCM contains chlorine atoms, it shows higher electron scavenging...
The spectral shape at 400–700 nm obtained for the PMeAMA solution (Fig. 4) is similar to the weak broad absorption band reported for PMMA radical anions [13–15]. Moreover, it was reported that the weak absorption band around 440 nm is attributed to a transition of the PMMA anion (n-π* transition) by means of a molecular orbital (MO) calculation [16]. We supplementally calculated the spin density of the methyl AMA monomer radical anion by means of MO calculation using the Firefly 8.2.0 package [17], which is partially based on the GAMESS (US) source code [18]. The theory level used was UHF/6-31+G(d,p). The spin density of the methyl AMA monomer radical anion was high around the acrylic side chains (-COOCH₃) that are also contained in PMMA. Therefore, we conclude that the electron scavenging capability of PMeAMA is due to the side chains (-COOCH₃), and that the absorption band at wavelengths shorter than 700 nm can be attributed to the PMeAMA radical anions.

3.2.2. Rate constants of electron scavenging

The rate constants for electron scavenging by PMeAMA and PMMA were measured. PMMA was used for comparison because it also contains the acrylic units (-COOCH₃). DMF was used as solvent because the lifetime of solvated electrons in THF was quite short and, therefore, accurate lifetime measurements in THF by using nanosecond pulse radiolysis were difficult as described above (Fig. 3(b)). Since the maximum absorption wavelength of the solvated electron in DMF is 1600 nm [19], the lifetimes of the solvated electrons of the PMeAMA and PMMA solutions in DMF were measured at 1600 nm. Figure 5 shows the results.

The measured lifetimes of solvated electrons in the PMeAMA and PMMA solutions were almost equal. The rate constants of repetitive monomer units were calculated by linear fittings to the data obtained (Fig. 5) and determined to be 1.7 × 10⁸ M⁻¹ s⁻¹ and 1.8 × 10⁸ M⁻¹ s⁻¹ for the PMeAMA and PMMA solutions, respectively. Since almost the same rate constants were obtained for these solutions, the electron scavenging capability of PMeAMA, in common with that of PMMA, can be attributed to the acrylic side chains (-COOCH₃), as already concluded in the previous section.

3.2.3. Transient absorption spectrum in DCM

The transient absorption spectrum of 1.0 M PMeAMA solution in DCM was measured to investigate the radical cation of PMeAMA and the reactivity of PMeAMA with cationic active species. Since DCM is a chlorine-containing strong electron capture reagent, the transient absorption spectra of neat DCM (black ■), DCM with 1.0 M THF (red ●), and 1.0 M PMeAMA solution in DCM (blue ▲) (t = 0 ns) are shown in Fig. 6.
scavenger, the radiation-induced electrons are rapidly scavenged by DCM through the so-called dissociative electron attachment. The transient absorption spectra of neat DCM, DCM with 1.0 M THF, and 1.0 M PMeAMA solution in DCM ($t = 0$ ns) are shown in Fig. 6.

The spectrum obtained for neat DCM is in good agreement with a previous study [20]. The related radiation-induced reactions in neat DCM can be represented as:

$$\text{DCM} \rightleftharpoons \text{DCM}^+ + e^- \quad (4)$$

$$\text{DCM}^+ \rightarrow \text{DCM}(-\text{Cl})^+ + \text{Cl}^- \quad (5)$$

$$\text{DCM} + e^- \rightarrow \text{DCM}(-\text{Cl})^- + \text{Cl}^- \quad (6)$$

$$\text{DCM}(-\text{Cl})^+ + \text{Cl}^- \rightarrow (\text{DCM}(-\text{Cl})^+\text{Cl}^-)_{\text{sol}} \quad (7)$$

The broad absorption band observed in the spectrum of neat DCM was previously attributed to the radiation-induced solvated ion pairs (Eq. (7)) [20]. This absorption band decreased by adding both THF and PMeAMA. Because the dissociative electron attachment (Eq. (6)) occurs very rapidly, the generation of chlorine ions is hardly affected by adding PMeAMA and THF. Therefore, it is considered that the DCM radical cations, before their decomposition (Eq. (5)), were scavenged by both THF and PMeAMA.

Because the absorption intensity for PMeAMA solution in DCM was lower than that for DCM with THF, any absorption band attributed to radical cations of PMeAMA could not be observed in this experiment. It is considered that radical cations of PMeAMA disappear immediately or exhibit no absorption band in this wavelength range.

4. Conclusion

It was confirmed that PMeAMA, which has many excellent characteristics such as high adhesiveness, performs as a negative-tone resist upon EB irradiation. The sensitivity of PMeAMA was determined to be 300–400 $\mu$C/cm$^2$ for a 55 kV EB irradiation in air. This value is comparable to that of typical non-chemically-amplified resists such as PMMA. It is reported that the radical curing of AMA is hardly affected by the presence of oxygen owing to the oxygen scavenging capability of the tetrahydrofurfuryl groups in AMA [1,2]. Although the EB writing is generally performed under vacuum, we found that PMeAMA can be used as a negative-tone EB resist in air because of its oxygen scavenging capability.

The radiation-induced chemical reactivity of PMeAMA with solvated electrons and radical cations was investigated by means of pulse radiolysis.

The absorption band at wavelengths shorter than 700 nm in a PMeAMA solution in THF is attributed to the PMeAMA radical anions. The rate constants of electron scavenging were determined to be $1.7 \times 10^8$ M$^{-1}$ s$^{-1}$ and $1.8 \times 10^8$ M$^{-1}$ s$^{-1}$ in PMeAMA and in PMMA solutions in DMF, respectively. Since very similar rate constants were obtained, it was confirmed that the electron scavenging capability of PMeAMA can be attributed to its acrylic side chains (-COOCH$_3$).

The absorption band observed in the spectrum of neat DCM decreased by the addition of both THF and PMeAMA. It appears that DCM radical cations are rapidly scavenged by both THF and PMeAMA.

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