Ablation of Poly(methacrylates) Film Using 185-nm Light

Masamitsu Shirai, Takeshi Yamamoto and Masahiro Tsunooka

Department of Applied Chemistry, College of Engineering,
Osaka Prefecture University, Sakai, Osaka 593, Japan

Keywords: photodegradation, poly(methacrylates), ablation

Although photodegradation of poly(methyl methacrylate) and its homologs has been studied by many workers [1], most studies have been limited to wavelengths longer than 250 nm [2-4], probably because far-UV radiation forms a negligible component of terrestrial sunlight and so there is little practical concern. Studies on the far-UV degradation of polymers are important subjects relating to development of materials for far-UV lithography [5]. Photoinduced degradation of waste polymers is also a significant subject. In this paper we report the degradation of poly(methacrylates) using 185-nm light. Effect of the structure of pendant ester units of the polymers on the photodegradation efficiency was studied. Photoinduced ablation of the polymer films was observed, if irradiated at elevated temperatures (50-130 °C), depending on the polymer structure.

Poly(methyl methacrylate) (PMMA), poly(n-butyl methacrylate) (PNBMA), poly(t-butyl methacrylate) (PTBMA) and poly(isopropyl methacrylate) (PIPMA) were prepared by the conventional radical polymerization of corresponding monomers with azobis(isobutyronitrile) as an initiator at 55 °C. Characteristics of the polymers are shown in Table 1. Irradiation at 185 nm was carried out with a low-pressure Hg lamp (6W) under high vacuum (< 0.03 Torr) in the range of 30-130 °C. The distance between the lamp and sample films was 5 cm.

A laboratory-constructed piezoelectric apparatus was used to measure the changes in mass of polymer films during irradiation. The AT-cut quartz crystal with gold electrodes showing a resonance frequency of 10.000 MHz was used. With this crystal, a frequency shift of 1 Hz corresponds to a mass change of about 1 ng. Polymers (600-1200 ng) were deposited onto the quartz crystal (8 mm diameter) by casting from chloroform solution. The quartz crystal was placed in the irradiation apparatus. The frequency changes during irradiation were monitored. The frequency change, ΔF(Hz), is linearly related to the mass on the quartz crystal plate according to the equation [7]:

ΔF = - 2.26 X 10^6 F^2 Δm/A

where F (MHz) is the initial frequency of the quartz crystal used, Δm (g) is the mass on the quartz crystal plate, and A (cm²) is the area of the crystal surface occupied by the polymer film.

Table 1. Characteristics of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R</th>
<th>Mn (10^-5)</th>
<th>Mw/Mn</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNBMA</td>
<td>(CH₂)₃CH₃</td>
<td>1.03</td>
<td>1.7</td>
<td>20 (b)</td>
</tr>
<tr>
<td>PIPMA</td>
<td>CH(CH₃)₂</td>
<td>1.15</td>
<td>1.4</td>
<td>105</td>
</tr>
<tr>
<td>PMMA</td>
<td>CH₃</td>
<td>1.36</td>
<td>1.6</td>
<td>116</td>
</tr>
<tr>
<td>PTBMA</td>
<td>C(CH₃)₃</td>
<td>2.02</td>
<td>1.5</td>
<td>126</td>
</tr>
</tbody>
</table>

a) Glass transition temperature from DSC.
b) Cited from reference No. 6.
Main-chain scission numbers (Ns) were obtained as $N_s = (M_{n0}/M_n) - 1$, where $M_{n0}$ and $M_n$ are the number-average molecular weights before and after irradiation, respectively. Molecular weights were obtained by GPC using polystyrene standards.

The selected polymers used in this study showed an absorption peak at about 215 nm. The absorbance of 1 µm thick film of PMMA was 0.19 at 215 nm. When the PMMA film casted on quartz plate was irradiated at 185 nm, a new peak at 195 nm appeared as shown in Fig. 1. Similar spectral changes were observed for polymers other than PMMA. The rate for the appearance of the absorbance at 195 nm upon irradiation increased in the order PTBMA < PNBMA < PIPMA < PMMA. As will be discussed later, the new peak may be due to the formation of olefinic bonds by the main-chain scission. A low-pressure Hg lamp mainly emits lights at 185 and 254 nm. If polymer films were irradiated using a glass filter (Toshiba UV-25) which can eliminate the light at wavelengths shorter than 250 nm, no changes in absorption spectrum were observed. This means that the photochemical reaction occurred by 185-nm light in the present experimental conditions.

Sample films casted on a Si wafer were irradiated and changes in FT-IR spectrum were studied. Upon irradiation, the absorption peaks at 1730 (C=O) and around 1200 cm⁻¹ (C-O-C) decreased, suggesting the cleavage of the ester moiety. The rate for the disappearance of the ester peak increased in the order PTBMA < PIPMA ≈ PMMA < PNBMA.

Changes in mass due to the cleavage of ester moiety upon irradiation were measured using a quartz crystal microbalance. As shown in Fig. 2 the mass linearly decreased with irradiation time and the rate of decrease of mass increased in the order PTBMA < PMMA < PIPMA < PNBMA.

Fig. 1. Spectral changes of PMMA film upon irradiation at 185 nm. Film thickness: 0.57 µm.

Fig. 2. Changes in mass of poly(methacrylates) film with irradiation. Polymer: (□) PNBMA; (○) PIPMA; (△) PMMA; (●) PTBMA. Sample mass: 596-1200 ng.

Fig. 3. Changes in number of main-chain scission with irradiation. Polymer: (□) PNBMA; (○) PIPMA; (△) PMMA; (●) PTBMA.
Upon irradiation molecular weights of the polymers decreased and molecular weight distribution increased. Numbers of photoinduced main-chain scission of the polymer films at room temperature are plotted as a function of irradiation time (Fig. 3). The rate of the main-chain scission increased in the order PTBMA < PMMA < PIPMA < PNBMA. The polymer with low T_g showed effective main-chain scission. Fig. 4 shows the effect of irradiation temperature on the main-chain scission of PMMA and PTBMA. Irradiation time was kept constant (30 sec). Efficiency of the scission was accelerated above the temperature at 75 °C for PMMA and at 90 °C for PTBMA. The motion of polymer chain can be enhanced near or above T_g, which increase the main-chain scission efficiency. It has been known that the photodegradation of ketone polymers in the solid state can be enhanced at temperatures above T_g. The N_g/M_0 value for PMMA at 130 °C was lower than that at 110 °C. The photoinduced ablation of PMMA film occurred, if irradiated at 130 °C. The N_g/M_0 value observed was for the residual polymer film on the plate after ablation.

Depolymerization reactions took place during the ablation, which was confirmed by the formation of methyl methacrylate detected by gas chromatography. The corresponding monomers was detected during the photoinduced ablation of all polymers used. Fig. 5 shows the change in thickness of PMMA film upon irradiation at 130 °C. The film thickness measured by interferometry decreased with irradiation time. In the present experimental conditions, the rate of ablation
was 0.042 µm/min for PMMA film. When the film was heated at 130 °C after irradiation at room temperature, no changes in film thickness were observed. Effect of irradiation temperature on the decrease of film thickness is shown in Fig. 6. The ablation rate can be divided into two different regions that occur in sequence, except PNBMA film: initial slow rate region and rapid rate region. At the rapid rate region, the ablation rates for PMMA, PIPMA and PTBMA were almost the same. The critical temperatures where the acceleration of ablation rate for these polymers began were dependent on polymer structure and the temperatures were about 20 °C lower than Tg of the corresponding polymers. The ablation of PNBMA film which had low Tg was observed at 50 °C. Although the effect of molecular weight of PMMA (Mn = 20,000 - 100,000) on the ablation rate was studied, a distinct difference between the rates was not observed. From a SEM micrograph, the film surface after ablation was found to be smooth as well as the surface before ablation.

The mechanism for the photoinduced degradation of poly(methyl methacrylate) in the solid state upon irradiation with UV-light (250 - 350 nm) has been reported [2-4]. Considering the results obtained in this study, photodegradation of poly(methacrylates) using 185-nm light seems to occur by a similar mechanism as shown in Scheme 1. The photodegradation occurs by direct main-chain scission and/or ester side-chain scission followed by main-chain scission. Efficiency of the degradation of poly(methacrylates) by 185-nm light in the solid state was higher than that reported for irradiation with UV-light (λ > 250 nm).

References