Structural modification of poly(methyl methacrylate) by proton irradiation


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Received 5 August 1999; accepted 19 January 2000

Abstract

A general survey is presented on the structural modification of poly(methyl methacrylate) (PMMA) by proton implantation. The implanted PMMA films were characterized by FT-IR attenuated total reflection (FT-IR ATR), Raman, Rutherford backscattering spectroscopy (RBS), gel permeation chromatography (GPC) and surface profiling. The ion fluence of 350 keV protons ranged from $2 \times 10^{14}$ to $1 \times 10^{15}$ ions/cm$^2$. The IR and Raman spectra showed the reduction of peaks from the pendant group of PMMA. The change of absorption and composition was observed by UV–VIS and RBS, respectively. These results showed that the pendant group is readily decomposed and eliminated by proton irradiation. The change of molecular weight distribution was also measured by GPC and $G$-value of scission was estimated to be 0.67. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: PMMA; Proton irradiation; IR; Raman; MWD; RBS; Compaction

1. Introduction

Bond scission and cross-linking are the main result of high energy ion irradiation on polymer surfaces. These reactions induce structural modification and change of physical properties [1–5]. Bond scission prevails in poly(methyl methacrylate) at low fluence irradiation with hydrogen ions. With this characteristic, PMMA can be used as a positive resist for lithography [1,6,7]. Proton irradiation also affects the refractive index and it can be used for manufacturing passive waveguides [8,9]. To understand the process of structural modification, FT-IR attenuated total reflection (FT-IR ATR), Raman, Rutherford backscattering spectroscopy (RBS), UV–VIS, gel permeation chromatography (GPC) and surface profiling method were used in this study.

The change of functional groups of PMMA with irradiation was studied by the analysis of FT-IR and Raman spectra, and the change of composition of elements on PMMA surface was measured by RBS analysis. To determine the degree of scission directly, molecular weight distribution (MWD) was measured by GPC. The change of light absorption in UV–VIS range was characterized by a UV–VIS spectrometer, and to understand the degree of compaction, the surface profile method was applied.

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PII: S0169-4332(00)00699-1
2. Experimental

2.1. Sample and irradiation

For FT-IR, Raman, RBS, UV–VIS analyses and surface profiling, PMMA sheet with 1 mm thickness (ME307901, Goodfellow) was used. For GPC analysis, the PMMA with polydispersivity of 1.1 and peak maximum molecular weight of 185,000 Da (Polymer Lab.) was spincoated on silicon wafer for a thickness of about 2.5 μm.

The ion implantation was performed in the implantation chamber at KIGAM with hydrogen ions at an energy of 350 keV. The homogeneity of the ion beam irradiation was maintained with a raster scanner.

The PMMA sheets for FT-IR, Raman, RBS, UV–VIS analysis and surface profiling were irradiated with the ion fluences in the range from $2 \times 10^{14}$ to $1 \times 10^{15}$ ions/cm$^2$, and the spincoated PMMA films for GPC were irradiated at the fluences from $7 \times 10^{12}$ to $3 \times 10^{14}$ ions/cm$^2$.

2.2. Analysis of modified properties

Infrared measurements (FTS175, Bio-Rad) were performed in ATR geometry to be sensitive to the surface layer which was modified by irradiation. Raman measurements (NR1100, Jasco) were carried out to confirm the result of IR.

To analyze the carbon and oxygen ratio, RBS measurement was performed with KIGAM system. To monitor the dose of irradiation, the sample and sample holder were insulated and used as a Faraday cup. He$^{2+}$ ion beam of 2.4 MeV with 10 nA was used. The sample surface was coated with 300 Å gold to eliminate the effect of sample charging.

Molecular weight distribution (MWD) were measured by GPC (Waters2698, Waters) equipped with a refractive index detector, and with two KF806M and one KF801 Shodex columns connected in series. Such column arrangement covers the molecular weight range of $10^2$–$10^6$ Da. The flow rate of THF solution was 1.0 ml/min, and the operation temperature was 40°C.

UV–VIS (UV–VIS 849353, Hewlett Packard) was used to measure the change of light absorbance in the ultraviolet and visible range (200–800 nm). Proton irradiation in PMMA induces compaction, and the degree of compaction was measured with the Alpha Step (KLA Tencor).

3. Results

3.1. Infrared spectroscopy and Raman spectroscopy

Fig. 1 shows the IR spectra of PMMA samples modified by proton irradiation. At 1720 cm$^{-1}$, a peak is seen which is identified as C=O vibrations in the pendant group (–COOCH$_3$) of PMMA. This peak decreases with the fluence of irradiation. An absorption band in the range of 1500–700 cm$^{-1}$ comes from the C–O stretching vibration (1270–990 cm$^{-1}$), C–H bending vibration (1450–1350 cm$^{-1}$) and CH$_2$ rocking vibration (810 and 750 cm$^{-1}$). These peaks decrease also with the fluence. This shows that the C–O, C=O bonds and CH$_2$, CH$_3$ groups diminish with proton irradiation.

Fig. 2 shows the Raman spectra of PMMA samples and similar result as the IR measurements is found in the spectra. An absorption band appears in the range of 3100–2800 cm$^{-1}$. This band is identified as C–H stretching vibrations of CH$_2$ and CH$_3$. The peaks at 1720 cm$^{-1}$ (C=O stretching), 1460 cm$^{-1}$ (C–H bending), 1270–990 cm$^{-1}$ (C–O stretching) and 816 cm$^{-1}$ (CH$_3$ rocking) appear similar to FT-IR. These peaks decrease with the increase of fluence, too. By the very similar result of IR and Raman, the decomposition of pendant group is confirmed.

3.2. Rutherford backscattering spectroscopy

Since He ions damage three times more than hydrogen ions at a same fluence, the irradiation of 4 μC for RBS analysis produces the same damage with 350 keV H$^+$ irradiation at a fluence of $1 \times 10^{14}$ ions/cm$^2$. To consider the influence of additional He damage, the RBS data were collected separately in the range of beam charge from 1 to 5 μC and the result was extrapolated to zero charge. Fig. 3 shows the relative yields of carbon and oxygen at the fluence between 0 and $1 \times 10^{15}$ ions/cm$^2$. Since oxygen is included only in the pendant group, the decrease of oxygen means the decomposition of pendant group. The apparent increase of carbon seems to be mainly due to the decrease of oxygen. This result agrees well with the results of IR and Raman.
3.3. Molecular weight distribution

We have studied the change of MWD of PMMA samples before and after the bombardment with 350 keV H⁺, in a fluence range from $7 \times 10^{12}$ to $3 \times 10^{14}$ ions/cm². Fig. 4 shows the MWD of these samples. At lower fluence than $5 \times 10^{13}$ ions/cm², all the polymer mass is soluble and the MWD represents the information on all the irradiated sample. At the fluence of $3 \times 10^{14}$ ions/cm², however, the polymer matrix is partly in gelled phase which is made by cross-linking of polymer. At high fluence, cross-linking increases and it makes macromolecules which is insoluble in THF. So the gel–sol solution had to be filtered with 0.2 µm pore PTFE filter, and therefore the MWD represents only the sol phase.

![Fig. 1. Infrared spectra of PMMA irradiated with hydrogen ion. The ion fluences range from 0 to $1 \times 10^{15}$ ions/cm².](image1)

![Fig. 2. Raman spectra of PMMA irradiated with hydrogen ion. The ion fluences range from 0 to $1 \times 10^{15}$ ions/cm².](image2)

![Fig. 3. Change of relative contents of carbon and oxygen with the fluence of 350 keV H⁺ irradiation.](image3)
From the MWD spectra, on going towards higher fluence the distribution of the scission products moves lower mass. With the change of the MWD, $G$-value for scission can be found directly, which was calculated from the next equation [1]

$$\frac{1}{M_n(D)} = \frac{1}{M_n(0)} + 1.04 \times 10^{-10} G_s D,$$

(1)

where $M_n$ is the number-average molecular weight and $D$ is the adsorbed dose (in Gy). From MWD of the PMMA which was irradiated with $7 \times 10^{12}$ ions/cm$^2$, $M_n(D)$ (18,154 Da), $M_n(0)$ (105,874 Da) and $D$ (6.6 × $10^5$ Gy) were obtained. In this case, $G$-value for scission is calculated as 0.67.

3.4. Ultraviolet and visible absorption

Fig. 5 shows the change of the UV–VIS absorption of PMMA with the increase of ion fluence. There is an absorption band in the range of 270–350 nm in the spectrum of pristine. With the increase of fluence, the absorption at the high edge of the absorption band increase, and the threshold of absorption goes higher up to 500 nm. No more absorption is found at the wavelength higher than 500 nm in this range of fluence.

3.5. Compaction measurement

Fig. 6 shows the subsided depth of PMMA versus ion fluence. It shows that the compaction increases with fluence. In the case of $1 \times 10^{15}$ ions/cm$^2$, the subsided depth is measured to be 2.4 μm. The total depth accessed with 350 keV hydrogen ion is 4.2 μm. It means that the modified layer shrinks to more than half in depth. The degree of compaction is unexpectedly large.

4. Conclusion

The infrared, Raman, RBS measurements give evidence for the ion induced structural changes of the PMMA. The infrared and Raman measurements show the decrease of the C=O and C–O bondings and the RBS measurements show the decrease of oxygen content. This means that the pendant group
(COOCH₃) is readily decomposed and eliminated by outgassing with proton irradiation.

The degree of scission was measured with MWD by GPC. The scission was confirmed by the decrease of the average molecular weight with the increase of fluence, and the G-value for scission was calculated as 0.67. But in the case of high fluence, cross-linking is not negligible and it makes insoluble macromolecules. To study the phenomena of cross-linking and threshold of gel phase in PMMA in detail, a further research at various fluences should be followed.

The characteristics of UV–VIS absorption with hydrogen irradiation were studied, and the absorption in the range of 350–400 nm was found to increase with fluence. The shrink depth of PMMA irradiated with 350 keV hydrogen ion at 1 × 10¹⁵ ions/cm² is 2.4 µm when the total thickness of modified layer is 4.2 µm. The compaction of PMMA by irradiation is unexpectedly high.

The results of these analyses may be useful for the design of polymeric optical devices and lithography with proton implantation. The fabrication of polymeric waveguides by proton implantation on PMMA will be published in this proceeding [10].

Acknowledgements

The authors would like to thank S.S. Kang and S.U. Kim (Hankook Tire R&D Center) for the assistance of measurement of FT-IR ATR.

References