Fragments from PMMA exposed to soft X-ray; a study by liquid chromatography

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Abstract

By using a liquid chromatography method, PMMA's fragmentation induced by X-ray exposure was studied. The PMMA molecule was decomposed by X-ray irradiation. The molar weights of fragments decrease with the increase of X-ray dose. This can be related with the fragmentation caused by breaking of bonds in the molecular main chain. However, a detailed study at high dose suggested fragmentation at other part of the PMMA molecule, possibly side chain decomposition, and also the generation of new materials that cannot be decomposed easily by the X-ray irradiation.

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Introduction

The LIGA process consists of lithography, plating and mold technology. The first step, X-ray lithography and development technology are important, in which the PMMA has been used popularly as a resist. The PMMA's polymer structure is decomposed by X-ray on the molecular level and the decomposed PMMA becomes easier to be dissolved in a solvent. The polymer structure's decomposition causes change in its physical property. The knowledge of PMMA's behavior toward X-ray exposure is very important to improve the LIGA technology of fine pattern formation.

In this report, the liquid chromatography method was used to study the PMMA's structure change in the molecular level by the X-ray irradiation.

Experiments

(1) The preparation of samples and the exposure

The PMMA dissolved in anisole was dripped on glass plates. They were then annealed at 160℃ for 2 hr in order to vaporize anisole completely. The PMMA films on the glass plates were exposed to soft X-ray in He gas at 1 atm. The BL-6 of Ritsumeikan SR center was used for X-ray irradiation experiment. The BL-6 has a thin Be foil (200 μm) which isolates the irradiation chamber from the SR ring. Low energy lights are absorbed by the Be foil and thus 1 ~ 7 keV lights are used for the irradiation to the samples.

The PMMA samples on glass plates were set in the BL6 chamber and exposed for prearranged periods of time. The X-ray dose value is defined as the accumulation current of the SR ring multiplied by the exposure time.

(2) The liquid chromatography measurement

First of all, standard materials for molecular weight were used to calibrate the retention time of the liquid chromatography. The relation between the molar weight and the retention time was linear. Next the PMMA samples dissolved in chloroform after the X-ray exposure were studied by using the same column.

Results and Discussion

The PMMA's liquid chromatography signals were shown in Fig.1. The samples were exposed to different doses of X-ray. The horizontal axis indicates molar weight. The vertical scale for each sample is normalized at its maximum. The following things can be realized clearly. The PMMA's molar weight decreases as the dose increases. Non exposed PMMA's liquid chromatography signal has a beautiful shape (dose:0.0 in Fig.1) for the molar weight distribution curve. But at high doses, the signal shapes are distorted and a shoulder structure becomes apparent. This indicates that new materials are generated during the X-ray exposure. And some of them don't changed easily by X-ray.

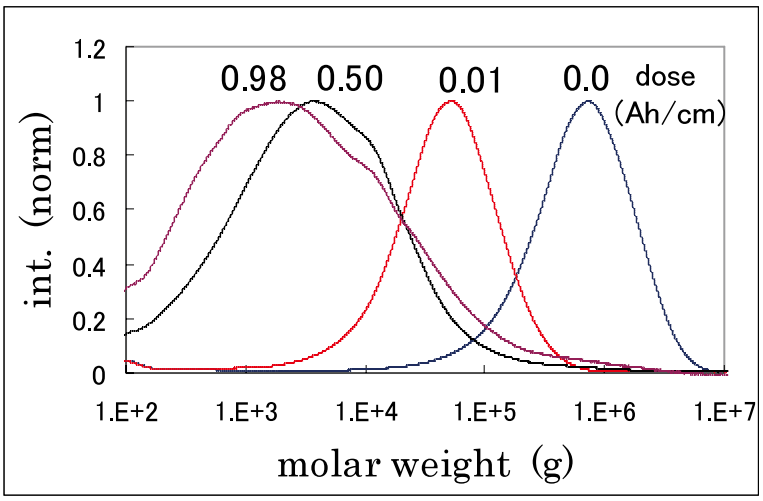

Fig.1. Liquid chromatography signals

The relation between the X-ray dose and the maximum in the molar weight distribution curve is shown in Fig.2. The molar weight decreases as the dose increases. The decreasing rate in the molar weight at low dose is larger than that at high dose. This phenomenon can be understood using a simple model that the X-rays break the PMMA's main chain only.

Simulation was performed using this model. The results are shown in Fig.2 for the cases of 0.4 and 0.7 cuts at the molecular chain per 1 mAhr/cm dose. At low doses the simulation results for 0.7 cuts fit well, while at high doses those for 0.4 cuts fit well. This result suggests that other PMMA decomposition processes except the main chain cutting must be considered also. There are two possibilities. One is that the side structures break widely at low doses. Second is that the generated materials don't decomposed easily by the X-ray.

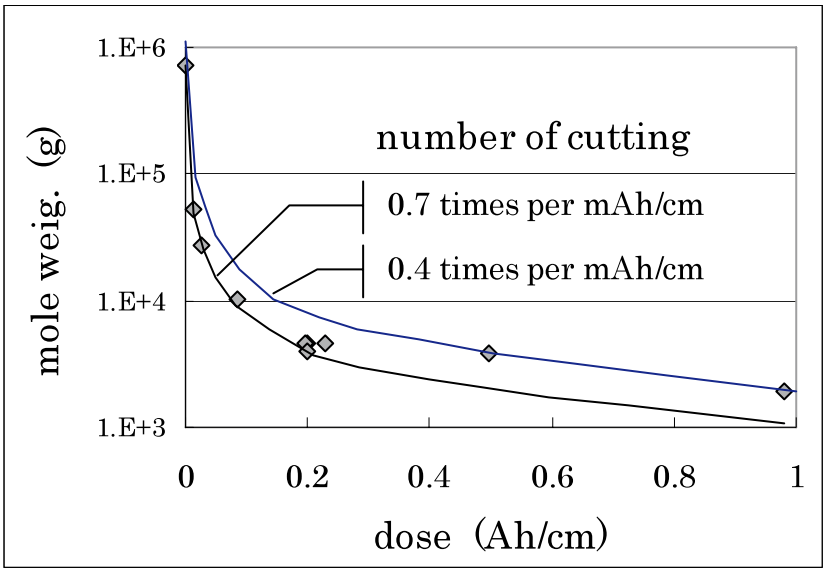

Fig.2. The PMMA's molar weight v.s. dose

Summary

By liquid chromatography measurements, the PMMA's decomposition on the molecular level under X-ray exposure was studied. It was shown that the PMMA's molar weight decreases as the dose increases. At low doses the shapes of molar weight distribution curve did not change so much, but at high doses those shapes were distorted and a shoulder appeared. It is considered that some of the generated materials do not easily broken by X-ray.

A simple model that the molar weight decrease is mainly caused by the cutting of the PMMA's main chain seems to be appropriate. And this cutting number per unit irradiation amount (1mAh/cm) is seemed from 0.4 to 0.7. However, the fact that the decomposition rate per dose at low dose is not the same as that at high dose proposes the presence of different decomposition mechanisms also. There are two mechanisms can be considered. The first one is a side structure's decomposition and the second is new material's formation which can not be decomposed easily by the X-ray.