

XAFS study of structural changes of PMMA by the soft X-ray exposure

Hiroyuki Ikeda

Abstract

By C and O K-edge XAFS measurements, I studied the PMMA's decomposition under X-ray exposure. It showed that the PMMA's side structure was destroyed widely. Concretely the side structure in PMMA (ester structure) changed to the ketone one. But according to the main chain cutting, the clear evidence was not found. Assumed that "C=C" generation is to cut the main chain, the main cutting number is much smaller than the side structure decomposition.

SR center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

Introduction

The LIGA process consists of lithography, plating and mold technology. The first step is X-ray lithography and development technology, in which PMMA (poly methyl metacrylate) is used popularly as a resist material. The PMMA's polymer is decomposed by X-ray irradiation in the molecular level, and can be dissolved in a solvent easily. The polymer structure's decomposition causes the changes of the physical properties. The knowledge of PMMA's physical property change by X-ray exposure is very important to make a fine pattern. However, the decomposition process of PMMA by X-ray irradiation has not been studied in any detail so far.

In this note, C and O K-edge XAFS measurements were used to study the PMMA's structural change by X-ray exposure in the molecular level.

Experiments

(1) The preparation of samples and the exposure

PMMA dissolved in anisole was coated on a Si wafer by spin coating. Then, it was annealed at 160 °C for 2 hr to evaporate anisole entirely. The thin PMMA film whose thickness is about 3 μ m was obtained. This sample was divided into half and half. One was exposed under soft X-rays in He 1atm atmosphere. Another was kept for the reference of XAFS measurements. The BL-6 of the Ritsumeikan SR center was used for X-ray irradiation equipment. The BL-6 has a thin Be foil (200 μ m) to separate the chamber from the SR ring in ultra high vacuum. Photons with the energy of 1 ~ 7(keV) were filtered out to expose the sample.

The PMMA film on Si was set in the chamber, and exposed for 1 hr. The X-ray dose was about 0.1(Ah/cm), where the dose is expressed as a value of the accumulation current of SR ring multiplied by the exposed time.

(2) XAFS measurements

The XAFS measurements were done at the BL-8, in which a grazing incidence monochromator with a varied line spacing grating is equipped. C and O K-edge NEXAFS spectra were obtained with the partial electron yield method. Both of exposed and no exposed sample were set on the same holder, and measured sequentially to minimize the experimental error in the XAFS measurements.

Results and Discussion

The C K-edge and O K-edge XAFS spectra were shown in Fig.1 and.2, respectively. Spectra from non-exposed sample were also shown as references.

(1) Side chain breaking

C K-edge XAFS of organic molecules have been extensively studied and it is known that each C atom in a specific functional group gives a feature at a characteristic energy. (reference): C of C=C double bond gives a feature at 285.1 eV ①, C of C=O gives a feature at 286.5 eV ②, C of C-H gives around at 287.7 eV ③, and C of ester type structure (O-C=O) appears at 288.5 eV ④.

From the observed C K-edge XAFS spectra, the feature ④ in Fig.1 shows a drastic decrease by X-ray exposure. Instead, a new feature appeared at ②. This clearly indicates that ester group is destroyed and ketone group is generated.

On the other hand, the feature marked as ③, which is caused to the “C-H” bonding, significantly decreased by X-ray exposure. It is, however, difficult to discriminate which C-H bonds are cleaved, since there are many kinds of “C-H” bonds in PMMA.

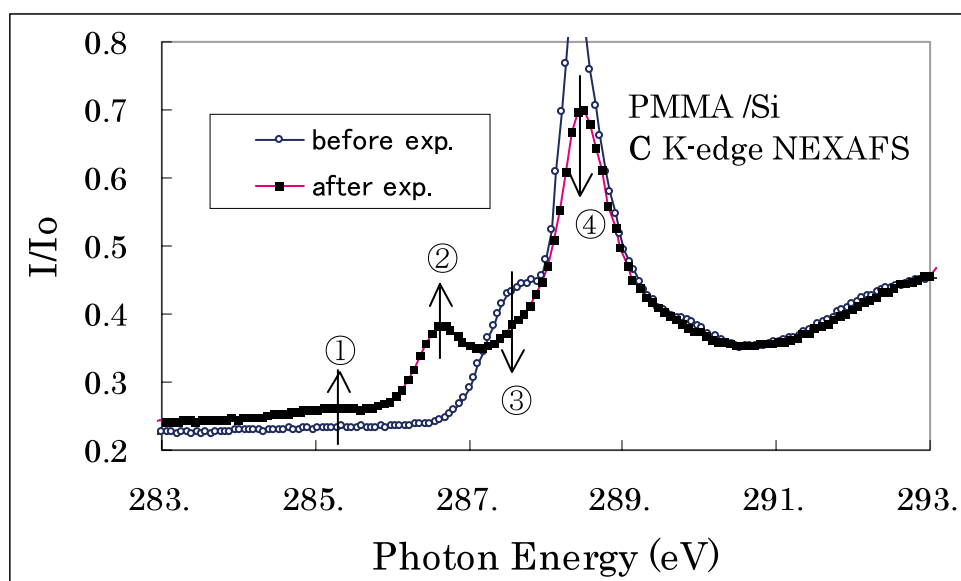


Fig.1 C K-edge XAFS

In the O K-edge XAFS spectra of organic molecules, it is known that the features B and D in Fig.2 are associated with the ester structure, and the feature A with the ketone group. By X-ray exposure, the B and D decreased and the feature A appears, although the features A and B were not well-resolved. O K-edge XAFS spectra exhibit same tendency as C K-edge ones. The ketone structure is stable under X-ray exposure, because the signal of ketone structure is observed even after a long X-ray exposure.

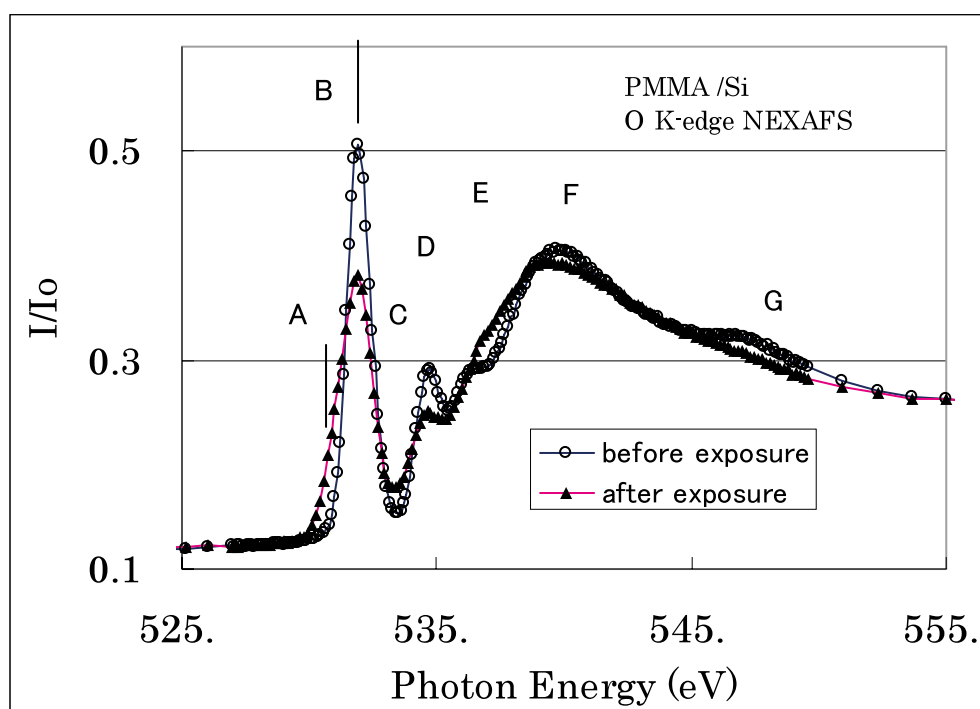


Fig.2 O K-edge XAFS

The molecular structure of PMMA is shown in Fig.3 (a), in which the ester functional group surround by a dashed line. The ketone groups are generated by decomposition of the ester, as shown in Fig.3 (b). The present experiments indicate clearly that X-rays attack side chain and decompose the side structure mainly.

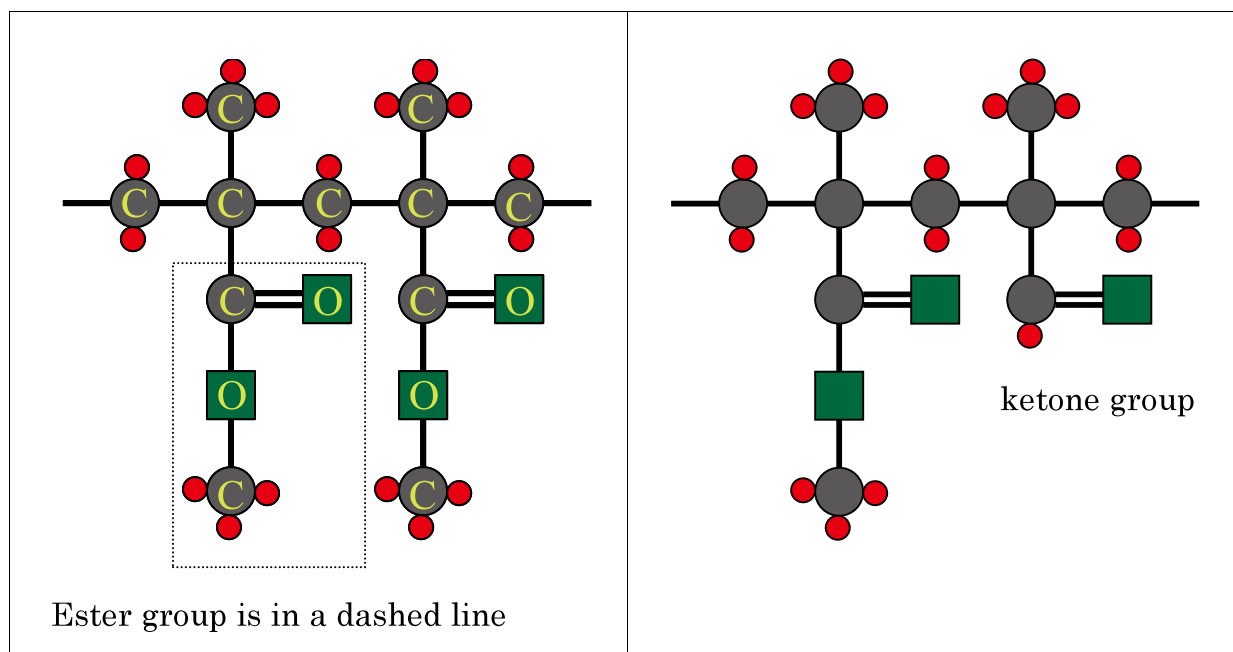


Fig.3 (a) PMMA structure

Fig.3 (b) PMMA structure :decomposition

(2) Main chain breaking

It was seen the side structure decomposition obviously, but there was no information about main chain breaking. It is natural to generate “C=C” double bonds, when the main chain is broken as shown in Fig. 4. The resonance of “C=C” is observed at 285.1(eV) in C K-edge XAFS. A little growth of the feature ① was observed in Fig. 1. The growth of the feature ① might be a good probe to indicate how much the main chains are broken. If it is collect our results show that the main chain breaking is much less than that the side chain decomposition.

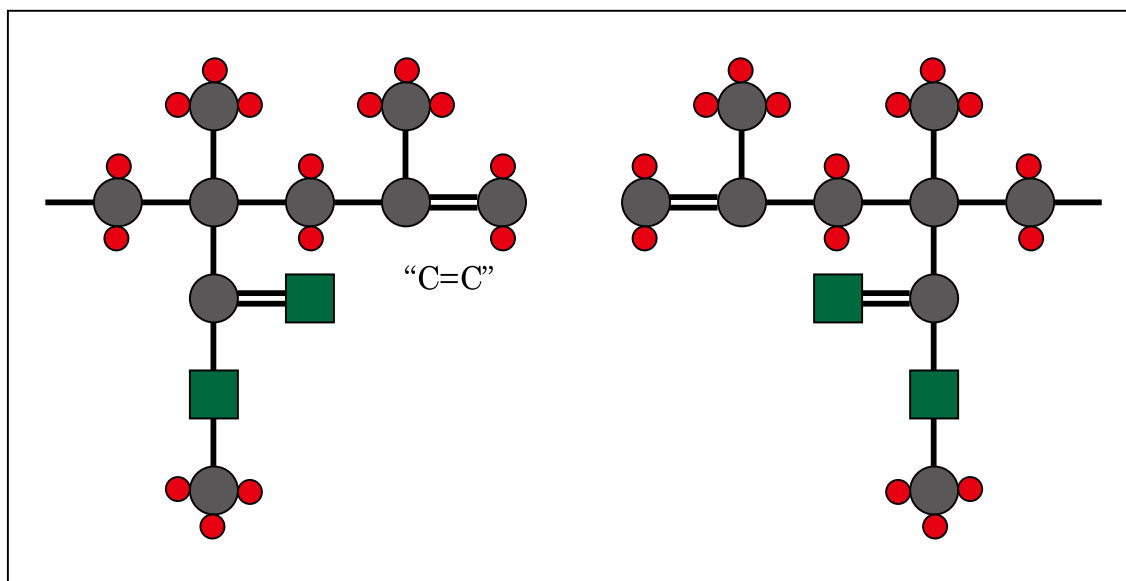


Fig.4 “C=C” generation : the main chain cutting

Summary

By the XAFS measurement of C and O K-edge, the PMMA's decomposition under X-ray exposure was seen very clearly. It showed that the ester structure in PMMA changed to the ketone one widely. The decomposed process is not clear but the ketone structure is stable, because its signal was big and still seen.

And according to the main chain cutting, the clear evidence was not found. Assumed that “C=C” generation is to cut main chain, the main cutting number is very smaller than the side structure decomposition. The PMMA's physical properties change by X-ray exposure must be considered both the decomposition of side structure and the main chain cutting. The side structure decomposition might be important more than thinking.