# Thermal Imidization Reaction of PMDA-ODA Polyimide Studied by NEXAFS Spectroscopy

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## 1. Introduction

Nowadays, various types of polyimide (PI) have been synthesized and practically used for various purposes. PI is usually synthesized by a two-step reaction as illustrated in Fig. 1. In the present study, the thermal imidization reaction (the second step in Fig. 1) of Poly[4,4'-oxydiphenylene-pyromellitimide] (PMDA-ODA) PI (Kapton®) was studied by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. NEXAFS spectroscopy is suitable for studying the chemical reaction of polymers, since NEXAFS spectra reflect the local chemical structure around the core-excited site, and the polarization dependence of the spectra gives the information of molecular orientation.

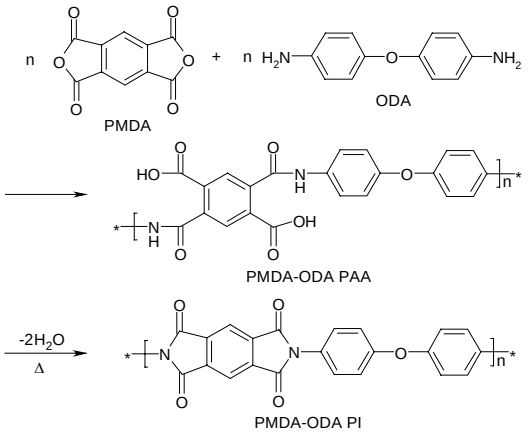


Fig. 1. Two-step reaction scheme to synthesize PMDA-ODA PI.

## 2. Experimental

A γ-butyllactone solution of PMDA-ODA PAA was spin-coated onto an ITO (indium tin oxide)–coated glass substrate, and the substrate was pre-baked at 80ºC for 1 min to evaporate the solvent. Then the PAA-coated substrates were post-baked for 20 min at various different temperatures, forming the films of about 60 nm. NEXAFS measurements were performed at the BL-8 of SR Center at Ritsumeikan University, equipped with a grazing incidence monochromator with a varied-line-spacing plane grating. Carbon K-edge NEXAFS spectra of the samples were measured in partial electron yield by a micro-channel plate detector with retarding grids. The retarding voltage was set to –150 V.

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## 3. Results and discussion

Figure 2 shows the C K-edge NEXAFS spectra of the samples post-baked at various temperatures. The spectrum of sample before post-baking mostly comes from PMDA-ODA PAA. At 100-250ºC, the shape of the spectrum changes significantly, indicating the thermal imidization reaction proceeds at this temperature range. The peak-E decreases in intensity and cannot be distinguished above 200ºC. On the other hand, new peaks A, D, and F appear at about 175ºC, and grow gradually up to 250ºC. Tentatively, we assign peaks A and D to $C_{\bullet}1s\rightarrow\pi^*(C=C)$ and $C_{\circ}1s\rightarrow\pi^*(C=O)$ transitions in PMDA-ODA PI, respectively, and peak E to $C_{\square}1s\rightarrow\pi^*(C=O)$ transition in PAA (symbols □, ●, ○ correspond the C atoms indicated in Fig. 2(b)). The spectra post-baked at 250ºC and 300ºC are similar to that of PMDA-ODA PI reported by Weiss *et al.*[1], suggesting that the films above 250ºC are almost fully imidized.

To estimate the ratio of imidization in the film, we fitted the spectra $I = (1-p)I_{\text{no-bake}} + pI_{440^\circ\text{C}}$ to the observed spectra for each baking temperature (100−400ºC), assuming that the spectrum of partially imidized film can be approximately described by the linear combination of the spectra of pure PAA and PI, and that the observed spectra of the sample that was not post-baked ($I_{\text{no-bake}}$) and the sample baked at 440ºC ($I_{440^\circ\text{C}}$) can be regarded as the spectra of pure PAA and PI, respectively. The best-fitted value of $p$ (= imidization ratio) is plotted in Fig. 3. From this figure, to achieve >90% imidization ratio, post-baking temparature of >250ºC is necessary for the present baking condition (20 min).

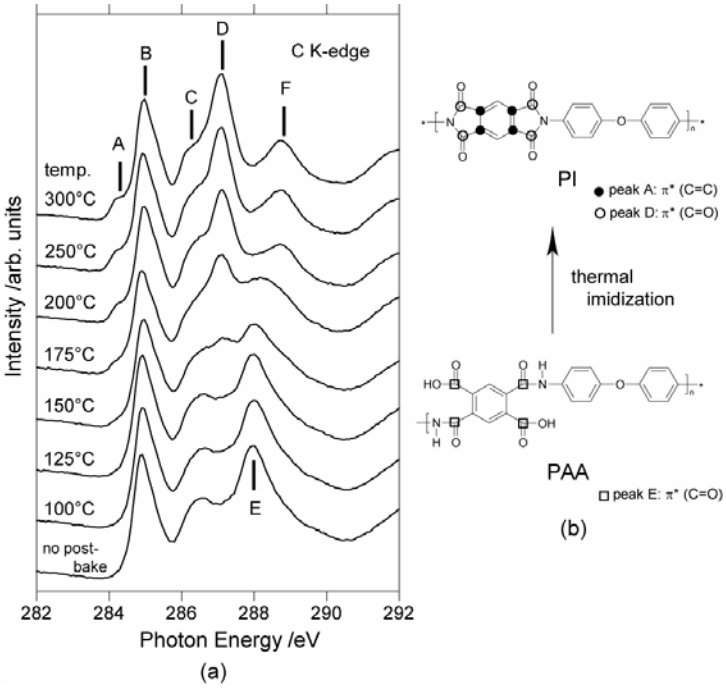


Fig. 2. (a) C K-edge NEXAFS spectra of the samples post-baked at various temperatures. (b) Carbon atoms for the core-excitations corresponding to peaks A, D, and F.

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**Reference**

[1] K. Weiss *et al.*, Macromolecules **31** (1998) 1930.

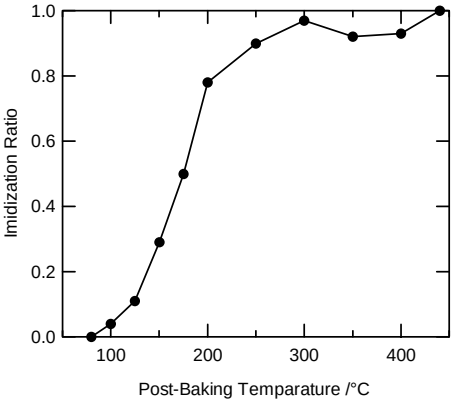


Fig. 3. Estimated imidization ratio.