

CARBONIZATION MECHANISM OF PMDA-ODA-TYPE POLYOIMIDE

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Introduction

PMDA-ODA-type polyimide (PI) has been utilized as a precursor of synthetic graphite. Carbonization process of PMDA-ODA-type polyimide (**Figure 1**) synthesized from pyromellitic anhydride (PMDA) and 4,4'-diaminodiphenyl ether (ODA) has been studied for decades,¹ but various reaction mechanisms have been reported and it is still unclear. It is essential to understand the carbonized structure of PMDA-ODA-type polyimide to estimate the defect structure of graphite. In this work, the carbonization mechanism of polyimide film heated at 1273 K or lower was analyzed by X-ray photoelectron spectroscopy (XPS), infrared (IR) and Raman spectroscopy, elemental analysis, calculation of spectra, and molecular dynamic simulation with reactive force field (ReaxFF).

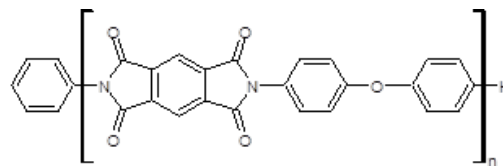


Figure 1. Molecular structure of PMDA-ODA-type PI.

Materials and Methods

PMDA-ODA was prepared by heat treatment at 773 K in air for 1 min. The film was further heated in nitrogen at 673-1273 K. These samples were analyzed by IR, Raman, XPS, elemental analyses, and NMR. Density functional theory (DFT) calculation was conducted to obtain IR and Raman spectra using b3lyp/6-31g(d) in Gaussian 09. PI was further analyzed computationally using ReaxFF.

Results and Discussion

Between 813 and 873 K, oxygen content decreased from 13 to 9 at.% as results of elemental analysis. The percentage of C=O decreased and C-O-C formed as results of IR and XPS. The decrement of a peak originating from C=O at 1714 cm⁻¹ and stretching vibration of C-N at 1376 cm⁻¹ were observed in IR spectra (**Figure 2**). On the other hand, increment of a peak originating from nitrile at 2228 cm⁻¹, amine at 3202-3446 cm⁻¹, and ether at 1200 cm⁻¹ were also observed in samples heated at 813, 833, and 833 K

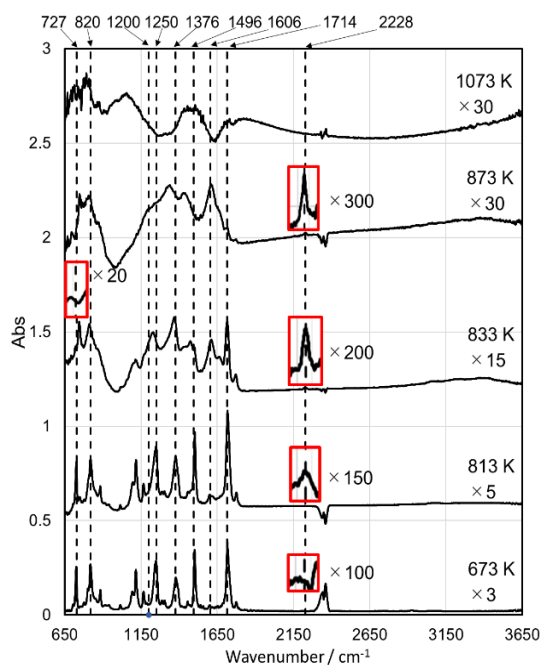


Figure 2. IR spectra of heat-treated PI.

using IR spectra, respectively. The formation of nitrile originates from the scission of C-N bonding in PDMA and the formation of ether originates from the crosslinking between molecules by C=O as being estimated by ReaxFF. G and D band of Raman spectra of PI appeared above 833 K or higher. Thus, the carbonization reaction proceeds above 833 K. Between 873 and 1073 K, the nitrogen content decreased from 19 to 14 at.% as results of elemental analysis. This decrement of nitrogen is caused by the formation of nitrogen-containing gas via the formation of isoimide as estimated by ReaxFF. Above 1073 K, C=O in PDMA was mostly disappeared and only cyclic-ether like functional groups and C-N bonding remained as results of ^{13}C -NMR (**Figure 3**) and N1s XPS spectra. **Figure 4** showed estimated carbonization mechanisms of PI based on the results of ReaxFF, XPS, IR and NMR. PI became isoimide form, and mainly three routes such as 1) nitrile, 2) quaternary nitrogen and amine, and 3) crosslinking via formation of ether were obtained.

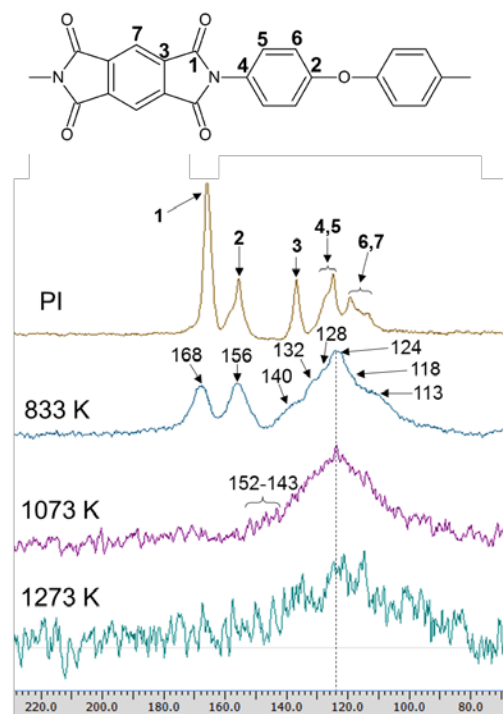


Figure 3. ^{13}C -NMR TOSS spectra of PI and PI heated at various temperature.

Conclusions

Structural change of PDMA-ODA type PI proceeded above 813 K. Nitrile formed above 813 K because of the scission of C-N bonding in PDMA as confirmed by IR and ReaxFF. PI was carbonized at 833 K because of the formation of G and D band. Ether formed at 833 K because of the formation of crosslinking via consumption of C=O as confirmed by IR, NMR, and ReaxFF. Formation of nitrile, amine, and crosslinking by formation of ether has not been reported elsewhere.

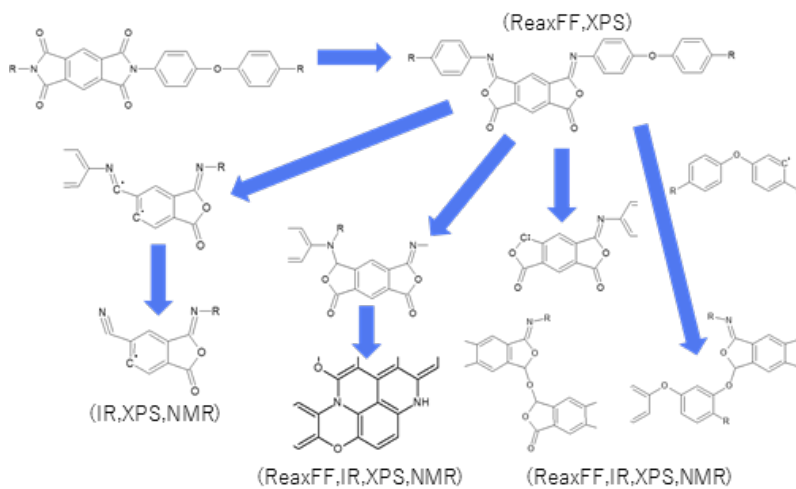


Figure 4. Estimated carbonization mechanism of PI.

References

1. Hatori H., Yamada Y., Shiraishi M., Yoshihara M., Kimura T. (1996) The mechanism of polyimide pyrolysis in the early stage. *Carbon* 34, 201-208
2. Fuente E., Menendez J. A., Diez M. A., Suarez D., Montes-Moran M. A. (2003) Infrared Spectroscopy of Carbon Materials: A Quantum Chemical Study of Model Compounds. *J. Phys. Chem. B* 107, 6350-6359