4th Multidisciplinary International Student Workshop (MISW2012)
August 9-10, 2012, Tokyo Institute of Technology, Tokyo, Japan

Extended Abstract

Conformational Analysis of Polyimides Films Based on Far-infrared Spectroscopy

T. Okada, S. Ando
Department of Chemistry and Materials Science
e-mail: tokada@polymer.titech.ac.jp

I. INTRODUCTION

Polyimides (PIs) have been widely used in microelectronics and aerospace applications because of their high thermal stability, *i.e.* thermal degradation and glass transition temperatures, excellent mechanical strength, and good solvent resistance. We have recently clarified molecular aggregation structures of fully aromatic and semi-aliphatic PI films using grazing incidence (GI) WAXD technique [1]. Meanwhile, local conformation could be correlated with aggregation structures in polymers, though WAXD is not suitable for estimating local conformation of amorphous polymers. In contrast, Far-infrared (far-IR) IR spectroscopy (400~10 cm^{-1}) could be a better probe to estimate the local conformation because Far-IR peaks are less unaffected by bond length and strength than Mid-IR. In this study, we tried to estimate dihedral angles of the main chains in aromatic PI films using Far-IR spectra with the aid of density functional theory (DFT) calculations.

II. EXPERIMENTAL

PI films were prepared by spin coating of DMAc solutions of poly (amic acid), precursor of PI, onto Si substrates (Fig.3 (a)), followed by thermal curing under nitrogen at 350°C for 90 min. Far-IR spectra were measured with JASCO FT/IR-6100 spectrometer equipped with an evacuable chamber.

III. RESULTS AND DISCUSSION

The calculated Far-IR spectra of *s*BPDA-An (Fig.1a) with variable dihedral angle are shown in Fig.2. As indicated by the arrows, three characteristic peaks are displaced by ca. 25−70 cm^{-1} depending on the local conformation expressed by two dihedral angles, ϕ (Fig.2a) and ω (Fig.2b). The wave numbers of these peaks enable to analyze conformations of the PIs derived from *s*BPDA because these peaks are assigned to the local vibration of *s*BPDA moiety. As is consistent with X-ray diffraction study [2], the experimental peaks coincide well with the peaks calculated for ϕ =180º. Moreover, the spectrum calculated for ϕ =180º obviously differs from that for ϕ =0º, which enables to distinguish these two planar biphenyl structures. The characteristic peaks observed for PI films derived from *s*BPDA (Fig.3) are also close to those for ϕ =180º, but not similar to ϕ =0º. The dihedral angle, ω, of PIs can be also estimated from Fig.3a. *s*BPDA-DMDB and *s*BPDA-ODA show peaks around 360 cm^{-1}, which indicates twisted imide structures with ω =40~60º from the comparison with the calculated spectra (Fig.2b). Although *s*BPDA-PDA shows a peak at ca. 345 cm^{-1}, it indicates a twisted structure with ω =40~60º as well because its phenyl group is small enough to generate cooperative vibrational motions between neighboring phthalimide rings. In conclusion, Far-IR spectroscopy is a useful and versatile tool to estimate the local conformations of aromatic polymers.

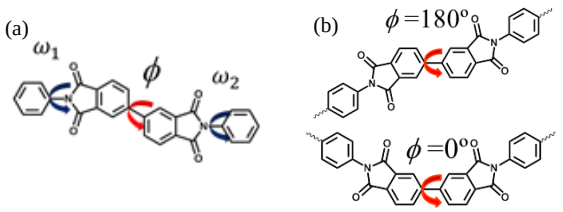

Fig.1 (a) Structure of model compound (*s*BPDA-An), (b) Schematic conformational difference between ϕ =180º and ϕ =0º.

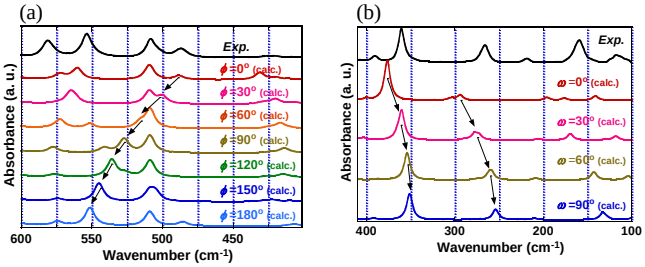

Fig.2 Calculated Far-IR spectra of *s*BPDA-An with variable dihedral angles (a) ϕ and (b) ω.

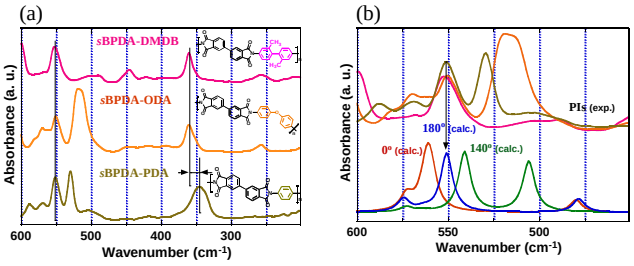

Fig.3 (a) Experimental Far-IR spectra of PIs. (b) Comparison between dihedral angle dependence of calculated Far-IR spectra of *s*BPDA-An.

REFERENCES

[1] J. Wakita, S. Jin, T.-J. Shin, M. Ree,, S. Ando, "*Analysis of Molecular Aggregation Structures of Fully Aromatic and Semialiphatic Polyimide Films with Synchrotron Grazing Incidence Wide-Angle X-ray Scattering*", *Macromolecules*, **43**, 1930-1941, 2010.

[2] K. Okuyama, I. Rozhanskii, K. Goto, "*Bilayered structure of N, N' –diphenyl-4, 4' -biphtalimide*", *Acta Cryst*. **C55**, 424-425, 1999.