Conformational Analysis of Aromatic Polyimides at High Temperatures Using Fourier Transform Far-IR Spectroscopy

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Polyimides (PIs) have been widely used in electric and electronic applications. In these applications, control of linear and volumetoric thermal expansion of PI films is crucial in terms of dimensional stability and reduction in thermal expansion mismatch. It has been understood that the thermal expansion of free volume induced by localized vibration and conformational motions plays an important role. [1]. In this study, we tried to estimate the variations in local conformations of PI main chains at elevated temperatures using variable temperature (VT) Fourier transform far-infrared (Far-IR) spectroscopy with the aid of density functional theory (DFT) calculations.

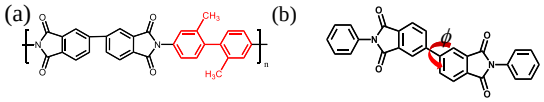

Fig.1 Molecular structure of (a) *s*BPDA-DMDB and (b) imide model compound

The VT-Far-IR spectra of sBPDA-DMDB (Fig.1(a)) are shown in Fig. 2. The absorption peak observed at 555 cm^{-1} was gradually shifted to lower wavenumbers with increasing temperatures. The far-IR spectra calculated for a model compound (Fig.1(b)) with variable dihedral angle φ are shown in Fig. 3. The peak shifts observed at elevated temperatures correspond to those with reduced φ from 180° to 170° as seen in Fig.3, which indicates that the biphenyl moiety was gradually changed to 'twisted conformations' upon heating. PI chains take a coplanar structure (φ =180°) in solid films, although a twisted conformation (φ =140°) is the optimal for the model in calculation, [2]. Because PI main chains undergo vigorous molecular motions at elevated temperatures, the average dihedral angle gradually approaches to more stable conformations with reduced φ for PI single chain.

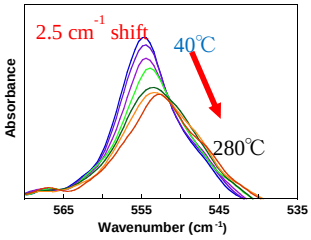

Fig.2 VT-Far-IR spectra of *s*BPDA-DMDB

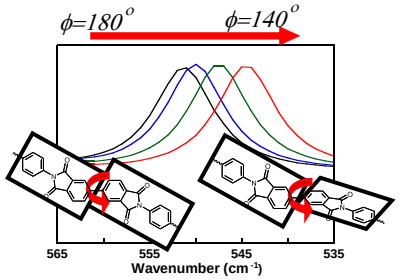

Fig.3 Calculated spectra of model conpound with variable dihedral angle

References

[1] K. Hagiwara, T. Ougizawa, T. Inoue, K. Hirata, Y. Kobayashi, *Rad. Phys. Chem.*, **2000**,*58* 525. [2] T. Okada, S. Ando, *Polym. Prep. Japan*, **2013**, 842.