Extended Abstract

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

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I. INTRODUCTION

Polyimides (PIs) have been widely used in electronics and microelectrics applications because of their high thermal stability, good chemical resistance, and mechanical properties. For these applications, control of coefficients of linear thermal expansion (CTE) is crucial in terms of the dimensional stability of polymeric insulating layers in integrated components.

Relating to thermal expansion of polymers, it has been understood that the expansion of 'free volume' composed of Brownian motion, local rotation, and local vibration play important roles [1]. Below the glass transition temperatures (T_g), local rotation and vibration play more important roles in thermal expansion. We have recently clarified the relationship between the far infrared (Far-IR) spectra and the conformation of polymer chain based on the density functional theory (DFT) calculations [2]. Far-IR spectra of PIs exhibit obvious changes reflecting their dihedral angles. In this study, we tried to estimate the local conformations in the main chains of aromatic PI powders at elevated temperatures using variable temperature (VT) Far-IR spectra with the aid of DFT calculations.

II. EXPERIMENTAL

The molecular structures of PIs used in this study are shown in Fig. 1. Far-IR spectra were measured with JASCO FT/IR-6100 in the temperature range of 40–280°C. DFT calculations were performed for imide model compounds (Fig. 1c).

III. RESULT AND DISCUSSION

VT-Far-IR spectra of *s*BPDA-DMDB and *s*BPDA-DATP PIs are shown in Fig. 2. As indicated by circles, the peaks at 555-554 cm^{-1} were gradually shifted to lower wavenumbers with elevating temperatures. The calculated spectra of model compounds with variable dihedral angle φ are shown in Fig. 3. The peak shifts by elevating temperatures correspond to the shifts in the calculated spectra with reduced dihedral angle φ from 180° to 170°. It can be considered that the dihedral angle φ varied to more twisted conformations at elevated temperatures. Althgough the optimized conformation of the imide model compound assumes a twisted structure (φ =140°), PI chains in solid films have a coplanar structure (φ =180°) [2]. Because PI main chains undergo vigorous molecular motions at higher temperatures than lower temperatures, the average dihedral angle approaches to more stable conformation with smaller φ for PI single chain.

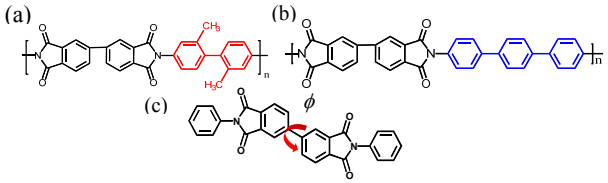

Fig.1 Molecular structure of (a) *s*BPDA-DMDB, (b) *s*BPDA-DATP and (c) imide model compound

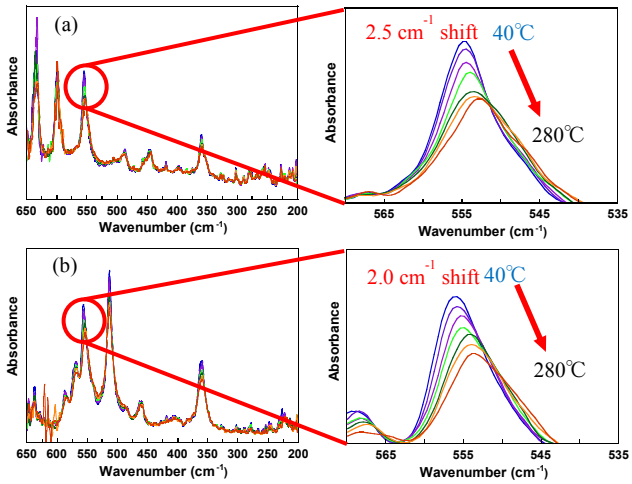

Fig.2 VT-Far-IR spectra of (a) *s*BPDA-DMDB and (b) *s*BPDA-DATP

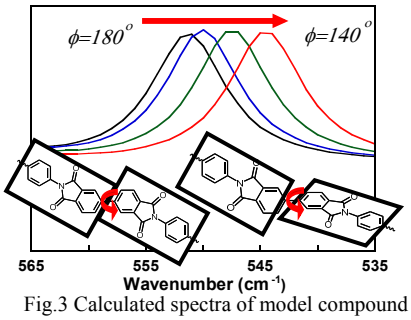

Fig.3 Calculated spectra of model compound with variable dihedral angle

References

[1] K. Hagiwara, T. Ougizawa, T. Inoue, K. Hirata, Y. Kobayashi "Studies on the free volume and the volume expansion behavior of amorphous polymers," *Rad. Phys. Chem.* pp. 525 June 2000.

[2] T. Okada, S. Ando, "Conformational Analysis of Polyamide Acid and Polyimide Films Based on Variable Temperature Far-Infrared Absorption Spectroscopy," *Polym. Prep. Japan*, pp. 842 May 2013