Conformational Analysis of Polyimides Derived from *s*BPDA Dianhydride Based on Far-IR Absorption Spectroscopy and DFT Calculations

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Introduction

Absorption peaks in Far-infrared (Far-IR) spectra of polymers are sometimes significantly displaced depending on their local conformations of main chains rather than bond lengths and bond angles. In this study, local conformations of the main chain, represented as dihedral angles, in semi-crystalline and amorphous polyimides (PIs) derived from *s*BPDA dianhydride were analyzed by combining Far-IR spectroscopy and the density functional theory (DFT) calculations. In addition, correlations between the distribution of local conformations and the optical properties of PIs were examined based on the conformation-dependence of calculated Far-IR spectra.

Experimental

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

Results and Discussion

The calculated Far-IR spectra of an imide, *s*BPDA-An (Fig.1a), with variable dihedral angles 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 as expressed by two dihedral angles, ϕ (Fig.2b) and ω (Fig.2c). As is consistent with X-ray diffraction study [1], the experimental peaks coincide well with the peaks calculated for $\phi =180°$. Moreover, the spectrum calculated for $\phi =0°$ obviously differs from that for $\phi =180°$, which enables to distinguish these two planar biphenyl structures. Wave numbers of the two peaks, calculated at 550 cm^{-1} and 360 cm^{-1}, enable to analyze the conformations of PIs derived from *s*BPDA because these peaks are assigned to the local vibration of *s*BPDA moiety (Fig.3). The peak positions of the characteristic peaks for the PI films from *s*BPDA (Fig.4b) are close to that for $\phi =180°$, but different from $\phi =0°$. The dihedral angle ω of PIs can also be estimated as shown in Fig.4c. For *s*BPDA-DMDB and *s*BPDA-ODA, peaks are observed around 360 cm^{-1}, which corresponds to twisted forms with $\omega =40-60°$ from the comparison with the calculated spectra. Although *s*BPDA-PDA shows a peak at ca. 345 cm^{-1}, it also corresponds to a twisted form because the phenylene group is too small to generate cooperative vibrational motions between neighboring phthalimide rings. Based on the calculated spectra for another model (Fig.4c, bottom), the ω can also be estimated as $40-60°$. As a consequence, the local conformations of these three PIs were estimated as $\phi \approx180°$ and $\omega \approx30-60°$. In addition, we focus on different spectral shapes of the peaks at 550 cm^{-1} among the PIs. The sharp peak observed for *s*BPDA-PDA is indicative of a narrow distribution of ϕ with highly ordered molecular structure. In order to clarify the relation between the spectral shapes and physical property, refractive indices (RIs) and the Far-IR spectra of *s*BPDA-PDA films cured at different heating rates are shown in Figs.5 and 6, respectively. The RIs of the films increased with increasing heating rate because residual solvent enhances densification of aggregation structures during imidization [2]. In addition, the spectral shapes at 550 cm^{-1} are sharpened with increasing heating rate, which corresponds to more ordered local conformation at ϕ. These facts indicate that spectral shapes of characteristic Far-IR peaks are sensitive to the ordering of molecular structures of PIs as well as their aggregation structures.

Conclusions

We have successfully developed a facile and versatile method for analyzing the local conformations of aromatic polymers based on Far-IR absorption spectroscopy and DFT Calculations. For the PIs derived from *s*BPDA, the absorption peaks around 550 cm^{-1} agree well with anti-coplanar conformation at biphenyl moiety ($\phi =180°$) with highly ordered and well packed aggregation structure. Moreover, the peaks around 360 cm^{-1} agree well with the twisted conformation at imide-phenyl moiety ($\omega \approx30$ to $60°$). Since the aggregation structure of PIs has significant influences on their refractive indices and fluorescent properties [3], Far-IR spectra could be utilized to correlate the conformations and aggregation structure of aromatic polymers with their physical properties.

Reference

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2. L. Vladimirov, M. Hasegawa, R. Yokota, *High Perform. Polym.*, **19**, 18 (1998).
3. J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, *J. Phys. Chem. B*, **113**, 15212 (2009).
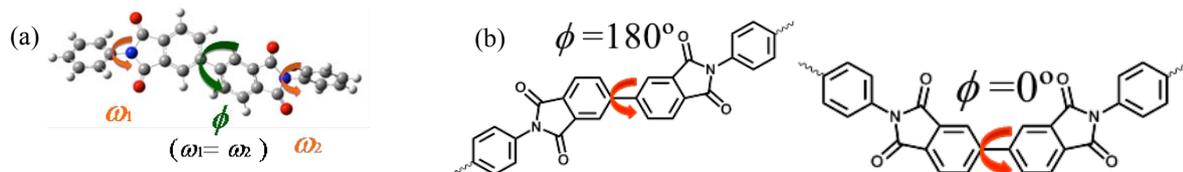
Figure 1. (a) Structure of *s*NPDA-An (b) Two conformational isomers at *s*BPDA moiety ϕ =180º and ϕ =0º.
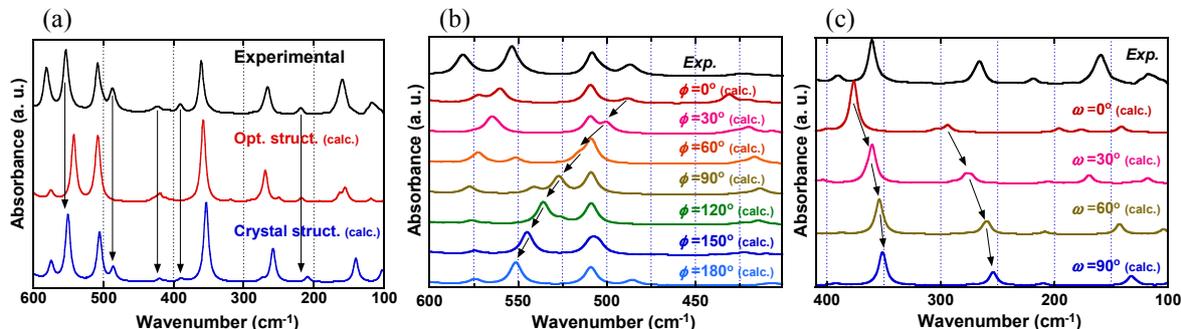

Figure 2. Far-IR spectra of imide model compound (a) *top*; experimental, *middle*; calculated with optimized structure, *bottom*; calculated by assuming crystal structure, and calculated Far-IR spectra of *s*BPDA-An with variable dihedral angles (b) ϕ and (c) ω.
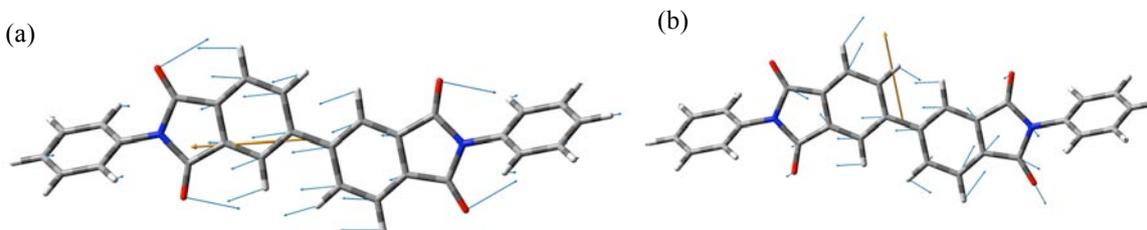

Figure 3. Vibrational modes of imide model compound calculated at (a) 360 cm^{-1} and (b) 550 cm^{-1}.
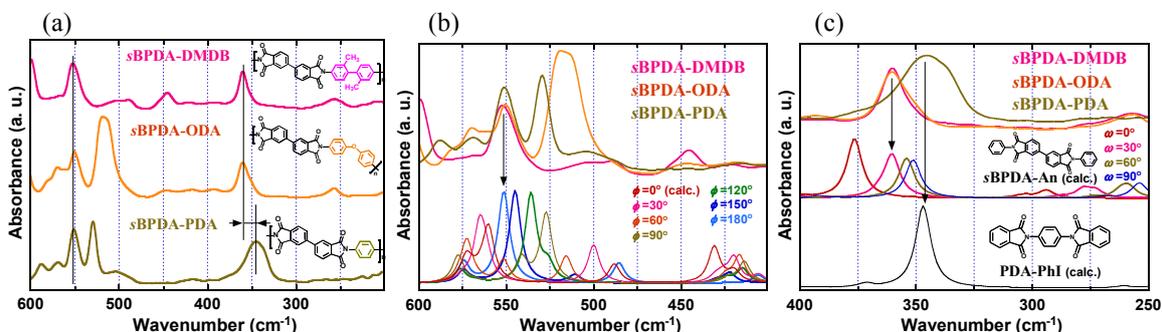
Figure 4. Far-IR spectra of PIs (a) *top*; *s*BPDA-DMDB *middle*; *s*BPDA-ODA, *bottom*; *s*BPDA-PDA (b) *top*; experimental spectra of PIs, *bottom*; calculated with varying dihedral angle ϕ (c) *top*; experimental spectra of PIs, *middle*; calculated with varying dihedral angle ω, *bottom*; calculated spectra of PDA-PhI.
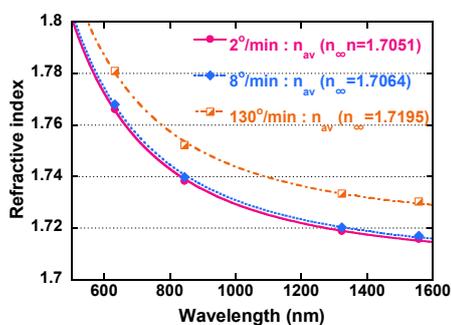
Figure 5. Refractive indices of *s*BPDA-PDA PI films cured at different heating rates during imidization.
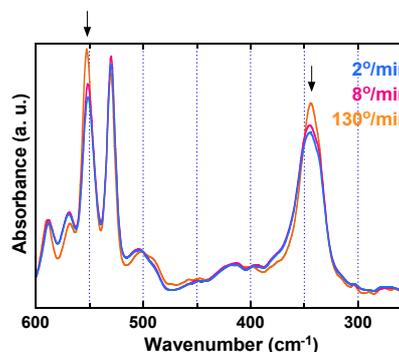
Figure 6. Experimental Far-IR spectra of *s*BPDA-PDA PI films cured at different heating rates during imidization.