The Effects of Rotational Barrier on β Relaxation Behaviors Among the Isomeric Polyimides

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Abstract

The effect of structural isomerism on the local relaxation process of polyimide (PI) main chain were examined. Not 180º but several degree of π-flip rotation is activated during β relaxation. According to the energy calculations, *m*-phenylene and symmetric diphenyldiimide linkage have higher rotational barrier. Not only molecular packing, but also isomeric structure crucially effect on thermal expansion behavior and relaxation process of polymer.

Introduction

Recently, particular interests have been directed to technologies for Carbon Dioxide Capture and Storage (CCS). The use of polymer membrane is one of the candidates for CO_2 gas separation technology. Polyimides (PIs) are representative high-performance engineering plastics exhibiting outstanding physical and chemical properties. They are expected to be applied to H_2/CO or CO_2/N_2 separation membrane. However, polymer membrane is not suitable for use in a wide temperature range because the key steps for gas permeation are solubility and diffusion of penetrant molecules. In most cases, selectivity for gas separation is decreased at elevated temperatures because penetrant molecular diffuse much faster owing to thermal expansion of polymers. Thereby it is important to investigate the thermal expansion mechanism of polymers to control the gas permeation properties in a wide temperature range. In addition, expansion of intermolecular free volume, which is 'unoccupied volume' among polymers (see Fig. 1), and activation energy for local motion of polymers play important roles in gas selectivity [1]. As shown in Fig. 2, the local molecular motions, which lead to dynamical relaxations, and free volume among polymers are directly related to thermal expansion behaviors of polymers. Although aromatic polyimides (PIs) had been analyzed in multifaceted approach, their local relaxation process is not clarified clearly. Especially, relaxation process of main chain is uncertain because of its complexes. In this study, we investigated thermal expansion behavior, dynamic relaxation and conformational energy of isomeric PIs (Fig. 3) to clarify their local relaxation mechanism.

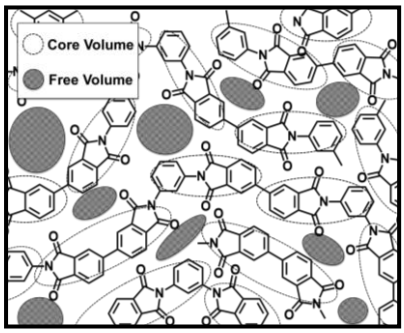

Fig. 1 Schematic image of PI chains and free volume.

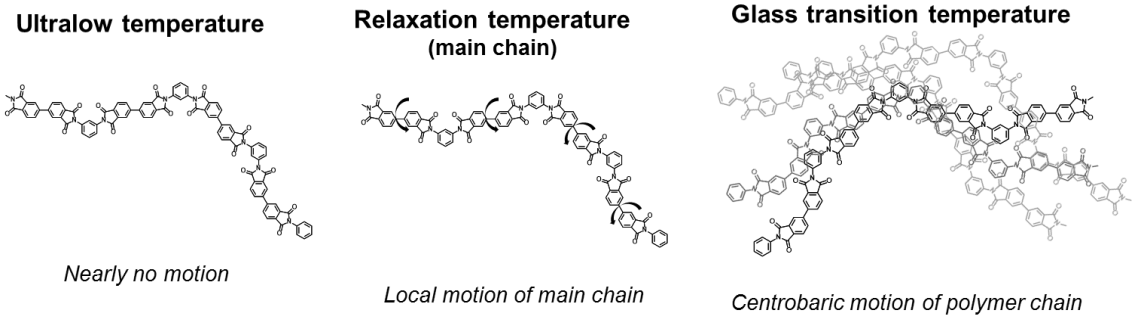

Fig. 2 Schematic images of molecular motions in polymers below and above T_g.

Experimental

Precursors of PIs, poly(amic acid)s (PAAs), were prepared by mixing equimolar amounts of dianhydride and diamine dissolved in DMAc. The PAA solutions were spin-coated onto Si substrates, followed by soft baking at 70 ºC for 1h and subsequent thermal imidization at 350 ºC for 1.5h on a hot plate. The packing coefficients of PI films were calculated from their refractive indices and density functional theory (DFT) calculations [2]. In-plane thermal expansion coefficients ($CTE_{//}$) were

measured by thermo-mechanical analyses (TMA) with a Shimazu TMA-60, and out-of-plane expansion coefficients (CTE⊥) were estimated by optical interferometry [3]. Dynamic mechanical analyses (DMA) were conducted with a Seiko DMS-7100.

Table 1 Packing coefficients, in-plane CTE, out-of-plane CTE, CVE, and β-relaxation temperatures; T_β for PIs.

Polyimide	Packing coefficient	CTE$_{//}$* (in-plane)	CTE⊥* (out-of-plane)	CVE* (volumetric)	T_β
*s*BPDA/PPD	0.648	5.4 ppm/K	120 ppm/K	130 ppm/K	≈ 190 ºC
*s*BPDA/MPD	0.603	38.5 ppm/K	41 ppm/K	118 ppm/K	≈ 180 ºC
*a*BPDA/PPD	0.600	51.2 ppm/K	46 ppm/K	148 ppm/K	≈ 130 ºC
*a*BPDA/MPD	0.596	45.0 ppm/K	48 ppm/K	138 ppm/K	≈ 120 ºC

*; in the temperature range between 80 and 280 ºC

Result & Discussion

As listed in Table 1, *s*BPDA/PPD exhibits much larger packing coefficient (corresponds to dense molecular packing) and smaller CTE$_{//}$ than the other PIs. The semi-crystalline nature of this PI probably promotes molecular chain orientation in the in-plane direction of film. Except for *s*BPDA/PPD, CTE$_{//}$s of the PI films are comparable to their CTE⊥s. This is explainable by nearly isotropic orientation of PI chains with their amorphous nature. For both of *s*BPDA- and *a*BPDA-PIs, the CVEs of PIs derived from MPD are smaller than those from PPD. In addition, for both of the PPD- and MPD-PIs, *a*BPDA-PIs exhibit larger CVEs than *s*BPDA-PIs. To explain the thermal expansion behaviors of these PIs, DMA analyses were performed to investigate their relaxation behaviors. The peak hallows corresponds to β relaxations are observed in the range of temperature between 100 and 200 ºC, and their peak temperature are indicated in Table 1. These relaxations could be closely related to their volumetric thermal expansion behaviors. The β relaxations of *s*BPDA- and *a*BPDA-PIs were attributed to the rotational relaxation at the 4,4'-diphthalimide and 3,4'-diphthalimide moieties, respectively [4]. However, *s*BPDA/PPD and *s*BPDA/MPD exhibit different CVEs despite their same dianhydride structures. Fig. 4 shows the variations of conformational energies between phenylene and phthalimide rings, which indicates that the rotational barriers of PPD-PIs are lower than those of MPD-PIs. Thereby, the β relaxations could be also related to the rotational motions between the phenylene and phthalimide rings. Kochi et al. [4] have reported that *a*BPDA-PIs exhibited lower β relaxation temperatures with smaller activation energies compared with *s*BPDA-PIs. The lower β relaxation temperatures lead to vigorous molecular motion and increase in CVEs for *a*BPDA-PIs compared to *s*BPDA-PIs. As a consequence, a combination of 4,4'-diphthalimide and *m*-phenylene linkages in the repeating unit of PI can effectively reduce the CVE than those for PIs containing 3,4'-diphthalimide and/or *p*-phenylene linkages.

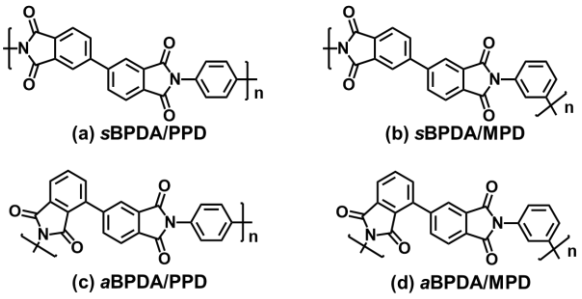

Fig. 3 Chemical structures of PIs.

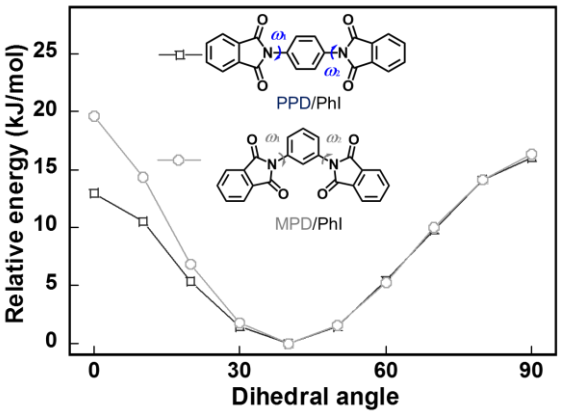

Fig. 4 Calculated conformational energy of model compounds.

Reference

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