Liquid-crystalline precursor for uniaxially oriented cross-linkable polyimide toward low thermal expansion material

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Introduction

Polyimides (PIs) have been used as a heat-resistant insulating material owing to the excellent thermal stability, mechanical strength, and electrical insulation. However, polymer materials containing PIs have larger coefficients of volumetric thermal expansion (CVE) compared with inorganic materials (Si, Cu, Al, and ceramics) as substrates and wiring. The large difference in CVE may cause defects leading to peeling and cracking. Polymer materials generally exhibit small coefficient of thermal expansion (CTE) along the main chain direction ($\alpha_{//}$) due to covalent bonds, while the CTEs along the directions perpendicular to the molecular chain ($\alpha_{\perp}$) are significantly large because of the weak non-covalent interactions [1]. We have reported that the $\alpha_{\perp}$ can be effectively reduced by introducing diphenylacetylene (tolan) group (Ph−C≡C−Ph) into the main chain of a PI which forms cross-linking between PI chains by thermal curing above 350 °C [2]. Recently, we developed novel precursors of PI, poly(amic ester)s (PAEs), which have semi-rigid structures and exhibit smectic (Sm) liquid crystalline behaviors in concentrated NMP solution [3]. In the Sm phase, the polymer chains can form 'layer by layer' structure, and cross-linking reaction can occur more effectively than in the amorphous state. Thereby, new materials with very low CVEs can be expected from the PAEs having Sm layer structure. On the basis of this concept, we designed a new liquid crystalline PAE in **Fig. 1** and investigated the molecular orientation behaviors of the PAEs.

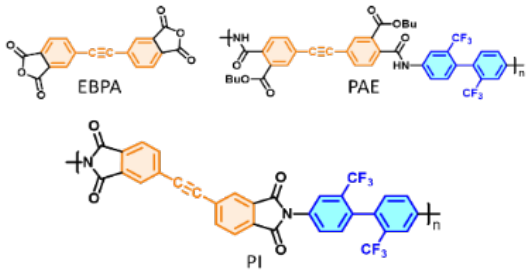

Fig. 1 Chemical structures of PAE and PI.

Experiment

PAE was synthesized from TFDB diamine and a half ester derivative of acid dianhydride with tolan group (EBDA) which is thermally cross-linkable, and thus PI was obtained by heating of the PAE (**Fig. 1**). The uniaxially oriented PAE film was obtained by shearing a concentrated NMP solution of the PAE on hydrophilic glass substrate at room temperature. The refractive index in each axial direction of the PAE film was measured at four wavelengths by using a prism coupling method. The uniaxial orientation order parameter, $S = (3\langle\cos^2\theta\rangle - 1)/2)$, of PAE film near the substrate side was evaluated by ATR-FTIR method, in which θ is the angle between the shear direction and the molecular long axis, and $\langle\ldots\rangle$ represents statistical average.

Results and Discussion

From polarized optical microscopy, a 50 wt% NMP solution of the PAE showed liquid crystalline phase at room temperature. A uniaxially oriented PAE film was prepared from this 50 wt% solution. The wavelength dispersions of the refractive index along each axis measured by prism-coupling method are shown in **Fig. 2** (x, y, z are the shear, width, and film thickness directions respectively, and n_j is defined as the refractive index in j-direction). A large refractive index (n_x = 1.75) was observed along the shear flow direction, and the birefringence (Δn) defined as $n_x - n_y$ or $n_x - n_z$ (n_y = 1.56, n_z = 1.52) is about 0.2, which indicates that the molecular chains are highly oriented along the shear direction (x). The infrared extinction spectra of the PAE film in the x and y directions (k_x, k_y) were measured using ATR-FTIR (**Fig. 3**). In these spectra, a characteristic band was observed at 1490 cm^{-1}, which was assigned to the aromatic C=C stretching vibration mode whose transition moment is parallel to the main chain. The S value was calculated from the dichroic ratio of the band. Considering the relationship between Δn and S ($\Delta n = \Delta n^0 \cdot S$), the intrinsic birefringence (Δn^0) of the PAE was estimated as 0.32, which is comparable to the value of a fluorinated aromatic PI having a rigid-rod structure (PMDA-TFDB). Therefore, much higher birefringence is expected for the PI prepared from this uniaxially oriented PAE films. According to the thermogravimetric analysis (TGA), it was confirmed that non-oriented powder sample of the PAE was converted into PI in the range of 200 and 250 °C. Since the thermal cross-linking reaction proceeds above 300 °C [2], the effect of introducing intermolecular cross-linking can be quantitatively discussed by comparing the thermal properties (thermal expansion rate, thermal dispersion rate) before and after thermal cross-linking.

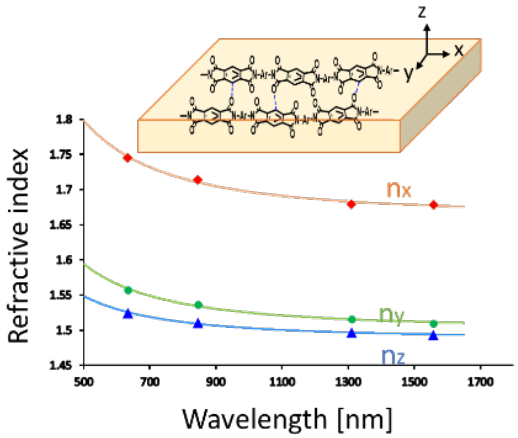

Fig. 2 Wavelength dispersion of refractive index along each axis of the PAE film (x, y, z are shear, width, and film thickness directions respectively).

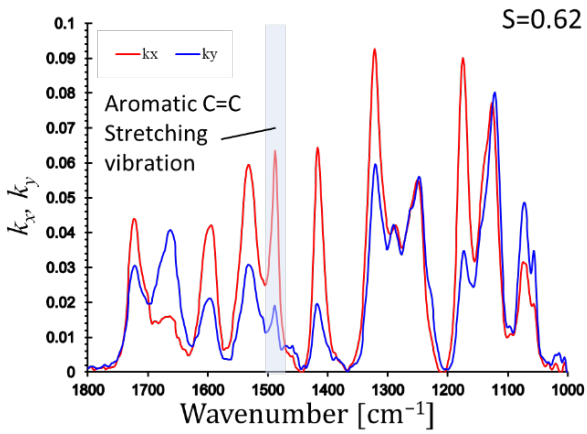

Fig. 3 Extinction coefficient spectra from polarized ATR-FTIR of the PAE film (substrate side).

References

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[2] S. Ando, M. Harada, T. Okada, R Ishige, *Polymer*, **10**, 761-774 (2018).

[3] K Tanaka, S. Ando, R Ishige, *Macromolecules*, **52**, 5054-5066 (2019).