Structural Evolution in Polyimide Precursor Films during Thermal Curing Process Observed by Synchrotron X-ray Diffraction Method

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Abstract: Aromatic polyimides (PIs) film are widely used in industrial field, such as; insulating layers in electronic circuits, thermal protection coatings on artificial satellites, alignment layer in liquid-crystalline (LC) displays, owing to their high thermal and chemical stability and mechanical toughness. Although molecular orientation of PI chain are not intentionally controlled in usual film-formation processes, highly oriented PI films are attractive for optical retardation plate, rubbing-free alignment layer for LC display, and so on. Recently, we focused lyotropic LC phase to control the chain orientation of PIs, inspired by previous work of Neuber *et al*[1], and successfully developed lyotropic LC PI-precursor solution at ambient temperature from linear poly(amic ester)s (PAEs) with long alkylene side chains. In this study, we analyzed structural evolution in the PAE films by in-situ measurements based on synchrotron radiation wide-angle X-ray diffraction (SR-WAXD), conventional Fourier-transform polarized infrared absorption spectroscopy (pFT-IR), and new method, *p-polarized multi-angle incidence resolution spectroscopy* (pMAIRS)[2] in the mid-IR region, which was developed to analyze in-plane/out-of-plane anisotropy in thin films. Thick films (~5 μm) prepared by shearing of concentrated PAE solution in the LC phase and thin films (~300 nm) prepared by spin-coating of the diluted PAE isotropic solution, were compared and the effect of the LC orientation field was discussed.

Experimental: The monomers and the PAEs were synthesized according to previous papers (**Fig. 1**)[1, 3]. In-situ SR-WAXD measurements were conducted at BL-10C or BL-6A in Photon Factory (PF) of High Energy Accelerator Energy Source, Tsukuba, Japan (Proposal No. 2015G587, 2016G544, and 2017G693). The wavelength of X-ray was 0.89 and 1.5 Å at BL-10C and BL-6A respectively. FT-IR measurements were conducted with FT/IR-6100FF (JASCO), which was equipped with AM-4000 rotation stage and home-made heating system[4].

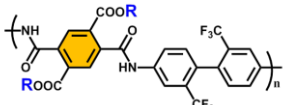

Fig. 1 Chemical structure of PAE (R is alkylene chain).

Results and discussion: In SR-WAXD patterns, a thick PAE solution film sheared in the LC phase showed typical uniaxially oriented smectic structure, in which the main chains and the layer normal were aligned in the shear direction and the uniaxial orientation order parameter, *S*, reached 0.8. The SR-WAXD and pFT-IR methods gave same *S* values, indicating the LC phase was homogeneous. During the thermal imidization process, the *S* value of PI segments was enhanced to reach 0.9, whereas that of PAE was once decreased and then recovered in the early and late stages of imidization, respectively, as presented in **Fig. 2**. This phenomenon can be explained by a model that PI segments with much longer persistence length than PAE were spontaneously aligned along the initial orientation direction of the PAE matrix. On the other hand, a thin spin-coated film of the PAE and corresponding PI showed relatively low planar orientation; *S* was about −0.1 and −0.2 for PAE and PI films respectively. Furthermore, the *S* value estimated by SR-WAXD was larger than that by pMAIRS for the PAE thin film but same as that by pMAIRS for the PI thin film. This results implies that a heterogeneous structure containing non-oriented region was generated in the initial PAE film, because the PAE chains have shorter persistence lengths in diluted solution, and then quenched during fast evaporation process of spin-coating. The heterogeneous structure was then converted into a homogeneous structure, following an increase in the persistence length during thermal imidization.

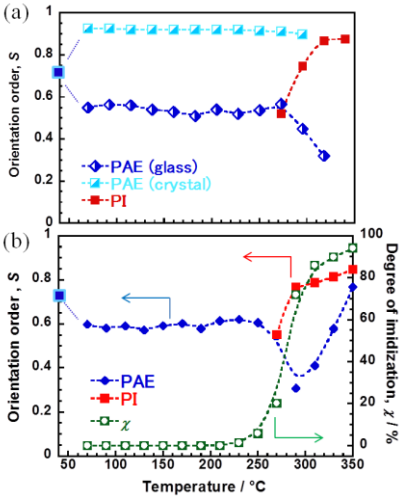

Fig. 2 Temperature dependence of *S* for PAE (blue) and PI (red) by (a) SR-WAXD, (b) FT-IR method and degree of imidization, χ (green in panel b).

References [1] C. Neuber, R. Giesa, H-W. Schmidt, *Macromol. Chem. Phys.* **203**, 598–604 (2002) [2] T. Hasegawa, *J. Phys. Chem. B*, **106**, 4112–4115 (2002) [3] B. W. Harkness, J. Watanabe, *Macromolecules*, **24**, 6759–6763 (1991) [4] R. Ishige, K. Tanaka, S. Ando, *Macromol. Chem. Phys.* **219**, 1700370 (2017)