Structural Analysis Based on pMAIRS and GI-WAXD Methods for Thin Film Aromatic Polyimide Prepared from Liquid Crystalline Precursor *(invited)*

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Recently, we synthesized a series of linear poly(amic ester)s (PAEs, **Fig. 1**), which is one of the precursors of aromatic polyimide (PI) and exhibits lyotropic liquid crystalline (LC) phase in a concentrated solution above 50 wt%. In this study, thin film structure of these PAEs and resultant PI were investigated by grazing-incidence wide-angle X-ray diffraction (GI-WAXD) using synchrotron X-ray source, and new spectroscopic method, variable temperature p-polarized multi-angle incidence resolution spectroscopy (VT-pMAIRS)[1] in the mid-infrared region, which provides in-plane and out-of-plane spectra separately at the same time in the same absorbance scale, and enables easy and precise molecular-orientation analysis for thin films.

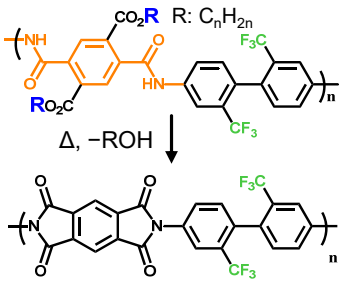

Fig. 1 Chemical structure of target PAE and resultant PI.

Thin films of PAEs synthesized according to previous report[2] were spin-coated on Si wafers from diluted solutions. GI-WAXD measurements were conducted at BL-6A in Photon Factory (PF), High Energy Accelerator Energy Source (KEK), Tsukuba, Japan (Proposal No. 2015G587, 2016G544, and 2017G693). VT-pMAIRS measurements were conducted with FT/IR-6100FF (JASCO), which was equipped with AM-4000 rotation stage and home-made heating system.

The thin film of the PAE and resultant PI exhibited low planar orientation; uniaxial orientation order parameter, $S = (3\langle\cos^2\theta\rangle - 1)/2$, where θ is the angle between molecular axis and averaged orientation direction, was about −0.1 and −0.2 for the PAE and PI films respectively. In the case of spin-coated films, S values −0.5, 0, and 1 correspond to perfect planar, random, and perfect perpendicular orientations, respectively. Furthermore, the values of |S| estimated by GI-WAXD were larger than those by pMAIRS, as shown in **Fig. 2**. This result 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 the diluted solution, and then quenched by so fast solvent-evaporation during spin-coating and a prebaking process that LC phase could not grow sufficiently.

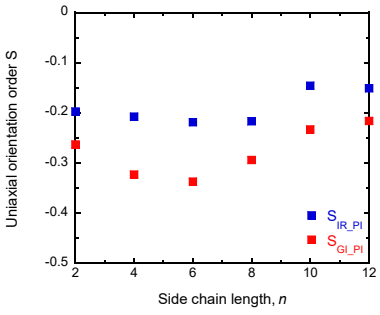

Fig. 2 Orientation order parameter S of a series of PAEs with different side chain length (blue) and resultant PI (red).

References: 1) R. Ishige, K. Tanaka, S. Ando, *Macromol. Chem. Phys.*, **219**, 1700370 (2018).
2) C. Neuber, R. Giesa, H-W. Schmidt, *Macromol. Chem. Phys.*, **203**, 598 (2018).