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Lyotropic Liquid Crystalline Behavior of Fully-Aromatic Poly(Amic Ester)s and In-Situ Orientation Analysis during Solvent-Evaporation and Thermal Imidization Processes by Synchrotron X-Ray Diffraction Method

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ABSTRACT:

【 Introduction 】 Fully aromatic polyimides (PI) are representative super engineering plastics [1-2]. In particular, PI thin films with uniaxially oriented main chains can be used as liquid crystal alignment layers. According to the previous study [3], we designed rod-shaped poly(amic ester)s (PAE) with long alkyl chains as a precursor of PI and found the PAE in NMP solution exhibits lyotropic liquid crystal (LC) behavior at lower temperatures. A uniaxially oriented PAE film can be successfully prepared by applying shear to the lyotropic LC solution. In this study, on the basis of temperature variable polarization microscopy and synchrotron radiation X-ray diffraction (SR-WAXD), we investigated the phase behavior of PAE solutions and the orientation evolution of uniaxially oriented PAE solution during solvent evaporation and thermal imidization processes. Relationships between the LC behavior and the evolution of polymer chain orientation with chemical structural change are discussed.

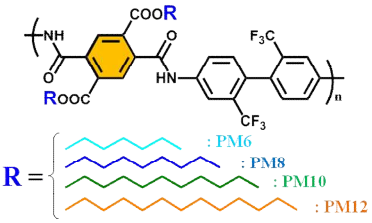

Fig.1 Chemical structures of PAEs.

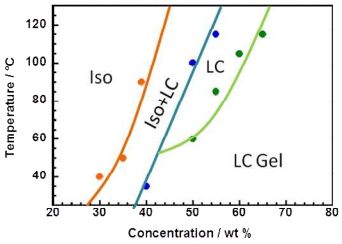

Fig.2 Phase diagram of PM6 in NMP solution.

【 Results and Discussion 】 The chemical structure of PAEs and the phase diagram of PM6 in NMP solution are shown in **Figs. 1** and **2**, respectively. This solution exhibits isotropic phase (Iso), liquid crystalline phase (LC), liquid crystalline gel phase (LC Gel), and coexistence phase of LC and Iso (Iso + LC), depending on the concentration and temperature. Shear deformation was applied to the PAE solution in the LC phase to obtain uniaxially oriented liquid crystalline films. **Fig. 3 (a), (b)** shows the SR-WAXD images with X-rays irradiated perpendicular to the surface of uniaxially oriented films. Sharp diffraction along the shear flow direction and diffuse scattering along the direction perpendicular to the shear flow direction were observed. Since the d-spacing of the sharp diffraction corresponds to the repeating unit length, the long axis of the PAE chains were oriented along the shear direction and the repeating unit forms smectic phase like layer structure. The diffuse scattering indicates liquid-like packing of the molecular chains in the layer (lateral direction). From the azimuthal angle intensity distribution $I(\beta)$ of diffuse scattering, we evaluated the orientation order of the molecular chains according to the formula (1), (2).

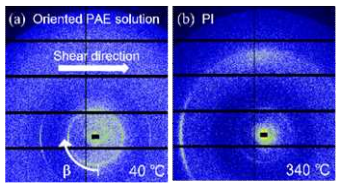

Fig.3 SR-WAXD patterns of oriented films of PM10 in (a) PAE solution, (b) PI state.

$$S = (3\langle\cos^2\varphi\rangle - 1)/2 \qquad (1)$$

$$\langle\cos^2\varphi\rangle = \int_0^{\pi} I(\beta)\cos^2\varphi\sin\varphi\,d\varphi \Big/ \int_0^{\pi} I(\beta)\sin\varphi\,d\varphi, \quad \cos\varphi = \cos\beta\cos\theta \qquad (2)$$

where φ is the angle between the shear flow direction and the molecular long axis, <...> is statistical mean value, β is azimuth angle on the diffraction pattern, and 2θ is scattering angle. **Fig. 4** shows the temperature dependence of S value and the degree of imidization. The degree of imidization was evaluated by thermogravimetric analysis assuming that the imidization reaction perfectly completed at the 400 °C. Oriented solution of PM8 and PM10 were successfully prepared on thin Kapton film. When the solution films were dried prior to heating, higher orientation was achieved for both PM8 and PM10. It is considered that molecular mobility was decreased with decreasing the residual solvent and the orientation relaxations were suppressed. The S value in PI films of PM 10 is larger than that of PM8, indicating the orientation relaxation due to the thermal motion during imidization is more suppressed in PM10 rather than in PM8 because the imidization starting temperature of PM 8 was 250 °C while that of PM 10 was 200° C.

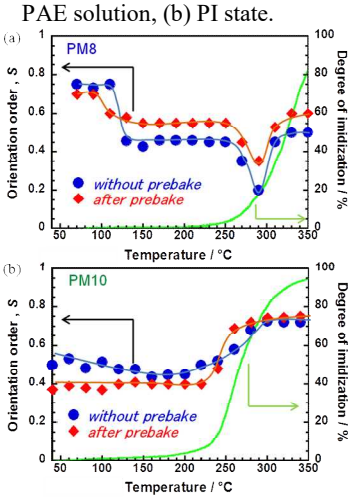

Fig.4 Temperature dependence of (a) orientation order, S and (b) degree of imidization evaluated by SR-WAXD and TGA.

【References】[1] T. Okada and S. Ando, *Polymer*, **86**, 83-90 (2016) [2] R. Ishige et al, *Macromolecules*, **46**, 747-755 (2013) [3] C. Neuber, R. Giesa, and H. W. Schmit, *Macromol. Chem. Phys*., **203**, 598-604 (2002)

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Keywords: Polyimide, Poly(amic ester), Liquid crystal, Orientation, synchrotron radiation X-ray diffraction