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Lyotropic Liquid-Crystalline Behavior of Poly(amic ester)s as Precursors for Fully Aromatic Polyimides and Control of Orientation by Shear Flow

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Fully aromatic poly(imide)s (PIs) are typical super-engineering plastics owing to their high thermal-stability (degradation temperature is larger than 400 °C), high insulation-property, high-mechanical strength, and high chemical- and environmental-stability. Nowadays, it is increasingly important to design not only chemical structure but also higher-ordered structure of polymeric materials for controlling the physical properties. For instance, thermal conductivity and dimensional stability of polymers are more remarkable in the main chain direction. Moreover, PIs are used for the alignment layer of liquid-crystals (LCs), where the chain-orientation induced by rubbing process is believed to be the factor most essential to the LC orientation. Therefore, the control of the chain-orientation is one of the most effective methods to obtain better physical properties, although PIs are usually difficult to control the chain-orientation in whole region of a large film.

We focused on the control of chain-orientation of poly(amic ester)s (PAEs) which are precursors of PIs and known to have a potential to form a lyotropic LC in a concentrated solution at high temperature [Neuber *et al*. *Macromol. Chem. Phys.* **2002**, *203*, 598.]. In this study, novel PAEs were designed and synthesized to obtain lyotropic LC state at lower temperatures, and orientation property of the lyotropic solution by shear deformation was quantitatively discussed on the basis of wide-angle X-ray diffraction (WAXD) analysis and polarized Fourier-transform infrared spectroscopy (*p*-FT-IR) analysis. A PAE consisting of *biphenyltetracarboxylic acid diethyl ester* showed the best orientation, *i.e.* uniaxial orientational order parameter (*S*) reached larger than 0.6. The orientation of the PAE perfectly remained during thermal imidization process to provide a highly oriented PI film. The structural changes of the PAEs during imidization process were also investigated by in-situ synchrotron WAXD measurement. The details will be discussed in the presentation.