Highly oriented aromatic polyimide prepared through liquid crystal state

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Introduction

Highly oriented films of polyimide (PI) were used for variable functional materials such as alignment layers of liquid crystalline displays (LCDs), optical retardation plate, etc., owing to the high thermal and chemical resistances, size stability, and mechanical strength. In this study, we developed novel liquid-crystalline (LC) precursors of a PI to aim highly oriented large-area films by simple shearing method at room temperature and investigated the mechanism of the orientation enhancement during imidization by in-situ variable temperature (VT) polarized Fourier transform infrared spectroscopy (pFTIR) and wide-angle X-ray diffraction measurements using synchrotron beam (SR-WAXD).

Experiment

The LC precursors, PM*m*, (**Fig. 1**) were synthesized by conventional solution polycondensation.[1] In-situ VT SR-WAXD were conducted in BL-6A beamline of Photon Factory (KEK, Tsukuba, Japan) and a FT/IR-4000 spectrometer (JASCO, Japan) was used for pFTIR spectroscopy measurements to evaluate the uniaxial orientation order parameter; $S = (3\langle\cos^2\theta\rangle - 1)/2$, θ is an angle between symmetric axis and molecular axis, and $\langle\ldots\rangle$ represents statistical average. The value S reaches unity for perfect orientation and zero for a random sample.

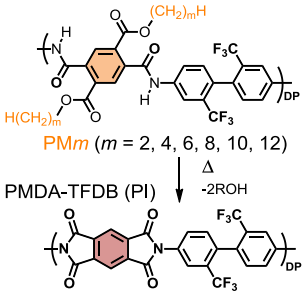

Fig. 1 Chemical structure of PM*m* and resultant PI.

Results and Discussion

The concentrated solutions (40–50 wt%) of PM*m* in NMP exhibited lyotropic LC phase and the phase transition behaviors defined by polarized optical microscope observation were similar to theoretical prediction for semi-flexible molecules in the solution.[1] Particularly, PM10 solution exhibited the LC phase from r.t. to over 100°C at 60 wt% and hereafter we focused on PM10. The oriented film of viscous solution of PM10 was prepared on a substrate at r.t. and then used for in-situ SR-WAXD and pFTIR. SR-WAXD method selectively provides the *S* value in oriented region in the sample, whereas pFTIR provides that in whole region. The *S* values in these two methods exhibited same value before imidization (<270 °C in **Fig. 2**), indicating that the film was homogeneous and did not contain amorphous region dissimilar to conventional semi-crystalline polymers. Furthermore, during imidization, the *S* value of precursor segments once decreased and then increased again, whereas that of PI segments spontaneously and monotonically increased from 0.5 to 0.9 (>270 °C in **Fig. 2**) even for a free-standing state. This unique phenomenon distinctly differs from the behavior of conventional amorphous PI precursors. In the present case, the rigid PI segments with longer persistence length spontaneously grow along the *n*-director of the LC matrix of the precursor and a kink structure occurs between the precursor and PI segments, which induce a temporal decrease in *S* of precursor segment during imidization (schematic mechanism in **Fig. 2**). In the late stage of imidization, these *S* values reached equal value (~ 0.9). This methodology is useful to prepare highly oriented homogeneous film in large scale and can be applied to various aromatic polymers involving intramolecular cyclic reactions or polymerization followed by an increase in the persistence length.

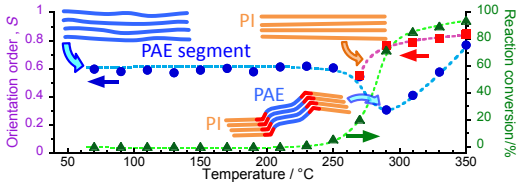

Fig. 2 Temperature evolution of *S* value of precursor and PI segments. Schematic drawings of orientation mechanism are inset.

Reference: [1] Tanaka, K.; Ando, S.; Ishige, R.* *Macromolecules* **2019**, *52*, 5054−5066.