Evolution of Chain Orientation in Aromatic Polyimides Thin Films during Thermal Curing Analyzed by Variable Temperature Polarized Multiple-angle Incidence Resolution Spectroscopy (VT-pMAIRS)

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Polyimides (PIs) are widely used for the alignment layer in a liquid-crystal display (LCD). The PI alignment layers of LCD are usually fabricated by rubbing process, where the PI thin films are rubbed by velvet cloth and the chains at the outermost surface are aligned along the rubbing direction by strong shear force. In such applications, degree of planar orientation of PI chains in the as-coated film dominates the alignment property after the rubbing process and the evaluation of the planar orientation is important issue. One of the most accessible techniques to evaluate the chain orientation is polarized Fourier-transform infrared (FT-IR) absorption spectroscopy; however, absorption spectra with both incidence electric fields parallel and perpendicular to the surface must be required, and that in perpendicular (out-of-plane) direction is difficult to obtain by usual transmission geometry. In this study, we combined a new FT-IR method (polarized multiple-angle incidence resolution spectroscopy, pMAIRS)[1] with a home-made heating system and investigated the evolution in the planar orientation of PI thin film during the thermal curing process.

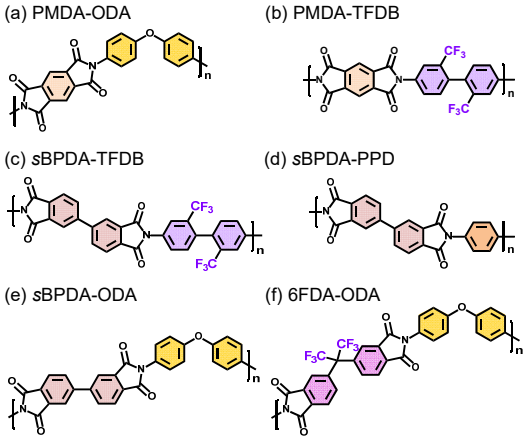

Fig. 1 Chemical structures of six kinds of fully aromatic PIs investigated by VT-pMAIRS FT-IR method.

Variable-temperature pMAIRS (VT-pMAIRS) were conducted by JASCO FT/IR-6100 FT-IR with vacuum chamber, a rotating sample stage, and home-made heating system based on micro-ceramic heater. Chain orientation of six kinds of fully aromatic PIs deposited on Si wafers were analyzed by VT-pMAIRS during the thermal curing process including solvent evaporation and imidization reaction from poly(amic acid), PAA, to PI. The thickness of the films were about 100 nm, which satisfied the condition for "thin-film approximation" required for pMAIRS method [1].

Typical VT-pMARIS spectrum of PMDA-ODA (**Fig. 1**) is shown in **Fig. 2**. The orientation of PAA and PI segments can be separately evaluated using absorption of aromatic C=C stretching and C–N stretching bands, respectively and the degree of

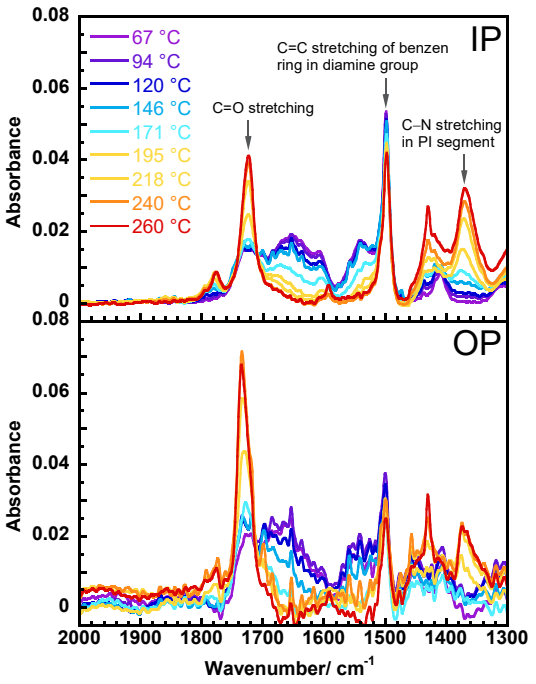

Fig. 2 In-plane (IP) and out-of-plane (OP) IR absorption spectra of PMDA-ODA measured by VT-pMAIRS.

imidization, χ, was estimated from an invariant, $2A_{IP} + A_{OP}$, of C–N stretching band normalized by that obtained for the final film cured at 350 °C. Here, A_{IP} and A_{OP} are absorbance intensities of the in-plane and out-of-plane spectra, respectively.

The changes in uniaxial orientation order parameter, S, during the heating strongly depends on chemical structure. Those of PMDA-ODA asd sBPDA-PPD for typical cases are shown in **Fig. 3**. For PMDA-ODA, it is interesting that S of PAA, S_{PAA}, became positive and increased during heating, indicating perpendicular orientation, while S of PI, S_{PI}, decreased; that is, planar orientation. On the other hand, for *s*BPDA-PPD, S_{PAA} and S_{PI} decreased simultaneously. These phenomena can be explained by the following model. For PMDA-based PIs, planar orientations of the PI segments spontaneously occurred with eliminating perpendicularly oriented precursor segments, while those of *s*BPDA-based PI segments occurred in the film as a result of large biaxial tensile stresses induced by solvent evaporation and imidization reactions. Furthermore, the orientation mechanisms in these thin films (thickness ≤ 500 nm) were found to be significantly different from those of the corresponding thick films (thickness > 500 nm) because lower levels of residual solvent induced much smaller shrinking stress during the curing than the thick films. We demonstrated that VT pMAIRS is a powerful tool for the analysis of complex behavior in multicomponent thin films involving morphological changes, chemical reactions, as well as molecular orientations [2].

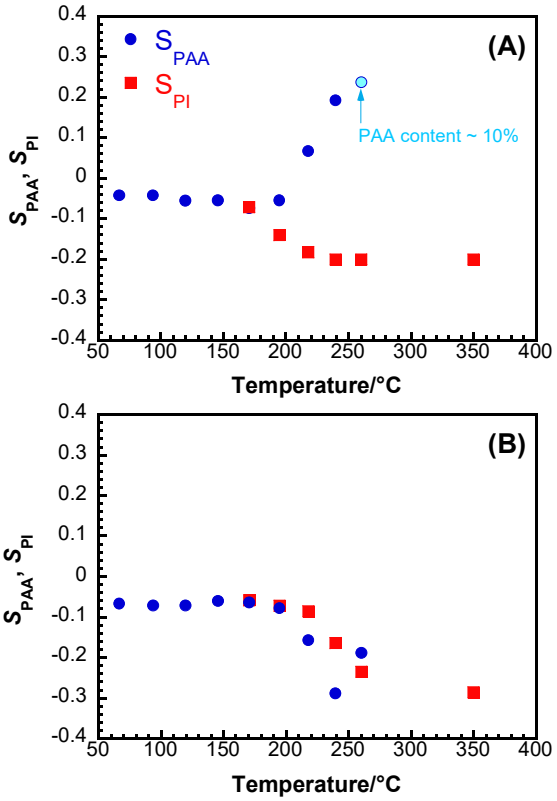

Fig. 3 Temperature dependence of the uniaxial orientation order parameter of the PAA segments, S_{PAA}, and that of the PI segments, S_{PI}, for A) PMDA-ODA and B) *s*BPDA-PPD PI films estimated by VT-pMAIRS. The symbol for PAA in A) at 260 °C is lightly colored when the PAA content is small (~10%).

Reference :

[1] T. Hasegawa, *J. Phys. Chem. B* **2002**, *106*, 4112-4115.

[2] R. Ishige, K, Tanaka, S. Ando, *Macromol. Chem. Phys.* **2017**, 1700370 (DOI: 10.1002/macp.201700370).

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