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Variable Temperature pMAIRS Analysis of Molecular Chain Orientation in Polyimide Thin Films during Thermal Curing

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[Introduction] Polyimides (PIs) are widely used as the alignment layers in a liquid-crystal display. In such applications, evaluating the degree of planar orientation of molecular chains is important issue. One of the most accessible techniques for this purpose is polarized Fourier-transformed infrared (FT-IR) absorption spectroscopy; however absorption spectra for both parallel and perpendicular electric fields to the surface are required and the latter 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 films during the thermal curing process.

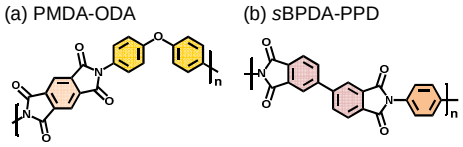

Fig. 1 Chemical structures of (a) PMDA-ODA and (b) *s*BPDA-PPD.

[Experimental] 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 heaters, to evaluate chain orientation in the precursor films of the target PIs (**Fig. 1**) deposited on Si wafers during the thermal curing process including solvent evaporation and imidization reaction.

[Results and Discussion] Typical IP (in-plane) and OP (out-of-plane) spectra of PMDA-ODA are presented in **Fig. 2**. The orientation order parameters of poly(amic acid) precursor , PAA, and PI segments were evaluated separately using absorption bands of aromatic C=C stretching and C–N stretching, respectively and the degree of imidization, χ, was estimated from an invariant, $2A_{IP} + A_{OP}$, of C–N stretching band. Here, A_{IP} and A_{OP} are absorbance of the IP and OP spectra, respectively.

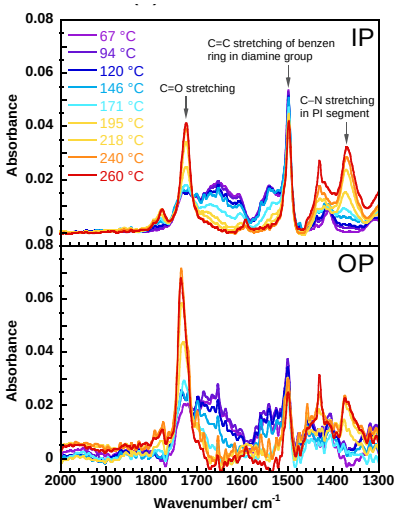

Fig. 2 IP and OP spectra of PMDA-ODA obtained at each curing temperature by VT-pMAIRS method.

The variations in uniaxial orientation order parameter, *S*, during heating strongly depends on the chemical structure. The temperature evolutions of *S* values for these PIs are shown in **Fig. 3**. It is remarkable that *S* of PAA segment, S_{PAA}, became positive and increased during heating, indicating perpendicular orientation, while *S* of PI segment, S_{PI}, decreased toward more planar orientation (negative *S* value). On the other hand, in *s*BPDA-PPD, the values of S_{PAA} and S_{PI} decreased simultaneously. These phenomena observed in VT-pMAIRS can be explained by the following models. For PMDA-based PIs, planar orientations of the PI segments spontaneously occurred with eliminating the perpendicularly oriented precursor PAA segments, while those of *s*BPDA-based PI segments occurred by large biaxial tensile stresses in the film induced by volumetric contraction following solvent evaporation and imidization reaction. 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 the lower fraction of residual solvent in the thin film induced much smaller volumetric contraction during the curing than the thicker films. We demonstrated that VT pMAIRS is a powerful tool for the analysis of complex behavior in multi-component thin films involving morphological changes, chemical reactions, and molecular orientations[2].

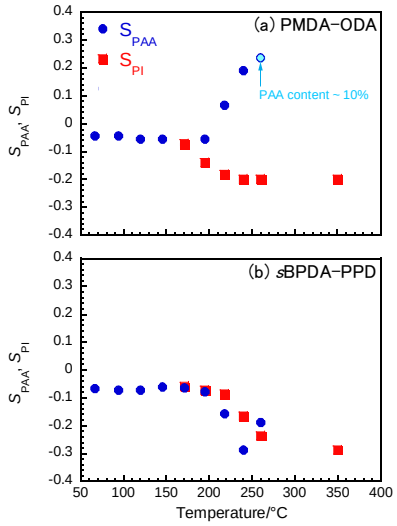

Fig. 3 Temperature dependence of S_{PAA} and S_{PI} values for (a) PMDA-ODA and (b) *s*BPDA-PPD.

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).