Orientation Control of Polyimides Films toward Homeotropic alignment Using Smectic Liquid Crystalline Precursor

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Polyimides (PIs) have been widely used in industrial fields due to their high mechanical strength, thermal and chemical stabilities. Highly oriented PIs can provide further useful applications, for example high thermal conductive film in the out-of-plane direction, which can be made from homeotropically oriented PIs.

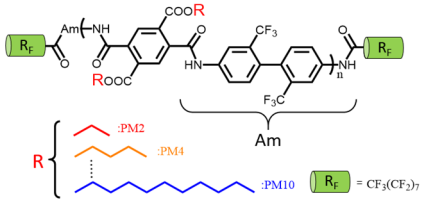

Fig.1 Chemical structures of PAE, PM*m*

In this study, we focused on one of the precursors of PIs, poly (amic ester)s (PAEs), which have sufficient rigidity to exhibit smectic liquid crystal in concentrated NMP solution (**Fig. 1**). Smectic layers are known to grow epitaxially from the air interface to form homeotropic alignment (HA) structure. Therefore, PAE solution is a potential precursor for HA PI films. To enhance epitaxial growth from the interfaces, we designed hydrophobic perfluoro-alkyl (R_f) end groups, which segregate at the surface, and used hydrophobic Si substrates modified with R_f group. To prevent dewetting of the solution on the hydrophobic Si wafer, we used *push coating* method, in which PAE solution is sandwiched between the substrate and a polydimethylsiloxane sheet, through which solvent vapor penetrates slowly.

Uniaxial orientation order parameter *S*, which can be evaluated by new infrared spectroscopic method, *p*MAIRS, was used to quantify molecular orientation of the push-coated films. Perfect homogeneous, random, and homeotropic orientated films provide $S = -0.5$, 0, and 1, respectively. **Fig. 2** shows the *p*MAIRS spectra and the *S* value of the films of PM8 and PM8 with R_f end groups (PM8Rf). The *S* values were calculated from dichroic ratios of absorbance peak of aromatic C=C stretching vibration mode (1490 cm^{-1}), which is parallel to the main chain. The PM8Rf film exhibited a lower homogeneous alignment than PM8, indicating that attractive interaction between the substrate and the molecules can be reduced by R_f groups. The effect of side-chain length, *m*, on the orientation will be discussed in the presentation.

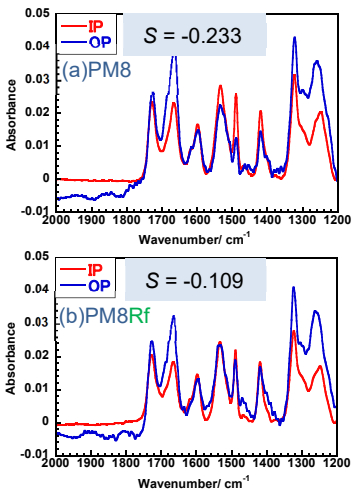

Fig.2 In-plane (IP) and out-of-plane (OP) absorbance spectra, obtained by pMAIRS for (a) PM8, (b) PM8 with fluorinated end group

Keywords Polyimide, Poly (amic ester), liquid crystal, homeotropic orientation, pMAIRS, push coating method