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# Homeotropic Orientation of Polyimides Induced by Smectic Liquid Crystal of Precursor Solution

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## Introduction

Polyimides (PIs) have been widely used in industrial fields due to their high mechanical strength, thermal and chemical stabilities. In addition, control of orientation of molecular chains can introduce anisotropic physical properties such as refractive index, and electrical and thermal conductivity [1]. In particular, high thermal conductivity in the out-of-plane direction can be obtained by homeotropic alignment of polymer chains. In this study, we focused on liner PI precursors, poly (amic ester)s (PAEs), exhibiting smectic liquid crystallinity in NMP solution [2]. The smectic phase of the PAE solution epitaxially grows up from the air interface. To enhance the homeotropic alignment, we used segregation to air or substrate interface by introducing perfluoro alkyl chain at the end of PAE chain. Furthermore, we investigated the effect of side-chain lengths on the orientation, and discussed the relationship between the degree of orientation and chemical structure.

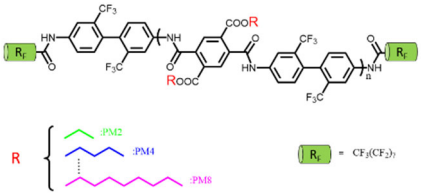


**Fig.1** Chemical structures of PAE

## Experimental

The PAE having amino end group at were prepared in NMP solution and perfluorooctyl acid chloride. PAE films were prepared by spin coating from NMP / 2-*n*-butoxyethanol mixed solution and subsequently dried at 50 °C for 1 h. The PAE films were imidized at 350 °C for 1 h. Uniaxial orientation order parameter $S$, defined by $S = (3 < \cos^2\theta > -1)/2$, where $\theta$ is the angle between the molecular long axis and averaged orientation direction was evaluated by pMAIRS method. Perfect homogeneous, random and homeotropic orientation provide $S = -0.5, 0$ and $1$ respectively.

## Results and Discussion

**Fig.2** shows the pMAIRS spectra and the $S$ value of spim-coated PM2 and PM8 films. $S$ values were calculated from dichroic ratio of absorbance peak of aromatic ring C=C stretching vibration (1490 $cm^{-1}$) whose transition moment is parallel to the main chain. PM2 film exhibited a higher homogeneous alignment than PM8, indicating that the interaction with substrate was reduced by highly hydrophobic longer alkyl side-chain. The effect of fluorinated terminal group will report on the presentation.

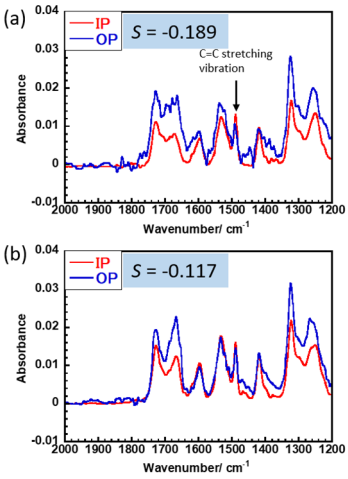


**Fig.2** In-plane (IP) and out-of-plane (OP) absorbance spectra, obtained by pMAIRS for (a) PM2, (b) PM8 with fluorinated end group

## References

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2) C. Neuber, R. Giesa, H. W. Schmit, *Macromol. Chem. Phys.*, **203**, 598-604 (2002)