# Composite of Liquid-Crystalline Precursor with Nanosheets toward Vertically Aligned Rigid Polyimide

Kazuki Oyama*, Shohei Hara, Shinji Ando, Ryohei Ishige
Dept. Chem. Sci. Eng. Tokyo Institute of Technology, 2-12-1-E4-6, Ookayama, Meguro-ku, Tokyo, 152-8552 Japan
* E-mail address: oyama.k.ad@m.titech.ac.jp

**Introduction:** Polyimides (PIs) are used as insulating layers in electronic circuits and high thermal conductivity in the film thickness direction is required. Vertical alignment (VA) of the molecular chains is the most effective for it. However, when rigid PIs are coated, the molecular chains easily align in planar direction due to interactions with a substrate and shear flow. In this study, we used lyotropic smectic (Sm) liquid-crystalline precursor, poly(amic ester)s (PAEs, BP2) for preparing VA films[1]. The $CnR_f$ termini of the PAE (**Fig. 1(a)**) are strong surfactant and spontaneously form a monolayer on the surface, which serves as a scaffold for the growth of the layer of Sm phase and induces VA[2]. Furthermore, surface-modified hydrophobic montmorillonite (nanoclay, NC) was added to the PAE solution, because planar-oriented NCs in the film are expected to facilitate the Sm-layer growth even inside the film (**Fig. 1(b)**).

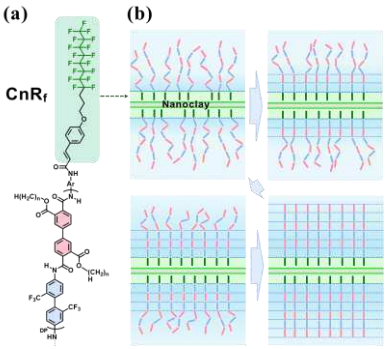


**Fig. 1** (a) Chemical structure of $BP2CnR_f$ and (b) schematic mechanism of VA PAE at the surface and inside the film by NC.

**Experiments:** $BP2CnR_f$ were prepared in the solution polycondensation and subsequently the $CnR_f$ terminus were bound to the ends of BP2. Two NCs (NC1, NC2) with different surface graft-density were added to $BP2CnR_f$ solution at various fractions (1–3wt%) and composite films were prepared in the cast method. Orientation order *S* and VA fraction was investigated by infrared spectroscopy (pMAIRS). The temperature evolution of *S* values for PAE and PI during the imidization was traced by variable-temperature pMAIRS (VT-pMAIRS).

**Results and Discussion:** Optimal fraction of NCs for VA was clarified by *S* measured by pMAIRS. **Fig. 2** shows obvious increase in *S* and facilitating VA by NCs. Furthermore, maximum *S* was obtained in the 3wt% and 2wt% for NC1 and NC2, respectively. The graft density of alkylene chains per unit surface area of NC2 is larger than that of NC1, and the surface hydrophobicity is also larger in NC2. Thus, NC2 has better ability to facilitate the Sm-layer growth and VA. **Fig. 3** shows temperature evolution in *S* of PAE and PI during the thermal imidization for $BP2CnR_f$ and the composite films. Interestingly, $S_{PI}$ at 180°C in the early stage of imidization was significantly larger than $S_{PAE}$, and then $S_{PI}$ gradually decreased toward the $S_{PAE}$ before imidization. The results suggested that imidization preferentially started in the VA region and subsequently progressed in the planar-oriented region.

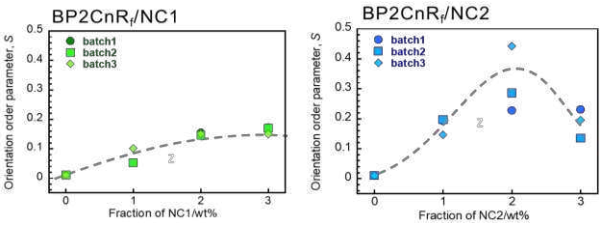


**Fig. 3** Variable *S* depending on the fractions of the NCs.

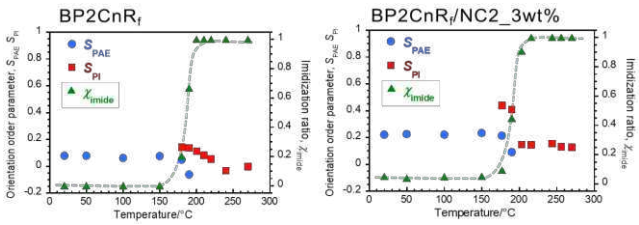


**Fig. 3** Temperature evolution of *S* for the residual PAE segments, $S_{PAE}$, and the generated PI segments, $S_{PI}$, and $\chi_{imide}$.

**Keywords:** Polyimides, Vertical alignment, Smectic liquid-crystalline precursor, Nanoclay

[1] Tanaka, K.; Ando, S.; Ishige, R. *Macromolecules* **2019**, 52 ,13, 5054.
[2] Hara, S.; Ando, S.; Ishige, R. *Polymer* **2023**, 281, 126100.