

Composite of liquid-crystalline precursor with nanoclay toward vertically aligned rigid polyimide

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[Introduction] Polyimides (PIs) are used as insulating layers in electronic circuits and high thermal conductivity in the film thickness direction is required. Vertical orientation of the molecular chains is the most effective strategy for it. However, when rigid PIs are coated on a substrate, the molecular chains are easy to align in-plane direction due to interactions with substrate and shear flow. In this study, we attempted to prepare vertically oriented PIs by using lyotropic smectic liquid-crystalline (Sm LC) precursor poly(amic ester)s (PAEs, BP n , n : side chain length) (**Fig. 1(a)**). The CnRf groups bound at the PAE terminus (**Fig. 1(b)**) are strong surfactant and form a self-assembled monolayer on the surface, which serves as a scaffold for the stacking growth of the Sm layer structure and induces vertical orientation. When surface-modified hydrophobic montmorillonite (nanoclay, NC) is added to the PAE lyotropic solution, NCs are planarly aligned in the film. The stacking growth of the layer from the hydrophobic surface of NCs is expected to promote the vertical orientation of molecular chains not only on the surface but also inside the film (**Fig. 1(c)**).

[Experiments] BP n CnRf ($n = 2, 6$) were synthesized by reacting CnRf termini subsequent to a conventional polycondensation. Two NCs (TMSA (NC1), DMDAA (NC2)) with different graft chain density were added to BP n CnRf solution and spin-coated to prepare the PAE/NC composite films. The formation mechanism of the vertically oriented domains was investigated by infrared spectroscopy (ATR-FTIR, pMAIRS) and grazing incidence X-ray scattering (GI-WAXS) methods.

[Results and Discussion] In-situ GI-WAXS measurements during a drying process of BP2CnRf solution (initial thickness: 30 μm) were conducted. The GI-WAXS patterns exhibit sharp diffraction appeared on the meridian in the early stage, and their intensity gradually increased (**Fig. 2**). This suggests the stacking growth of the Sm layer structure from the surface. Furthermore, sharp diffraction on the equator corresponding to the planar domains was observed in the late stage. The results indicate that the vertical orientation is generated on the surface, while the planar orientation is promoted inside the film due to shear flow and effects of the substrate. Orientation order parameter, S , of thin films (300-500 nm thickness) was evaluated at 0.01 by the pMAIRS, and the fraction of vertically oriented regions, ϕ_v was estimated less than 35%. In contrast, S increased in PAE/NC composite. Particularly, S reached 0.23 in the case of NC2 with higher graft density of the alkylene surfactants ($\phi_v \sim 50\%$) (**Fig. 3**). In the GI-WAXS image of the film, scattering derived from NCs was observed only in the meridional direction, indicating the planar orientation of NCs. This supports the model that the NC surface induces Sm phase layer growth of PAE and vertical orientation of molecular chains.

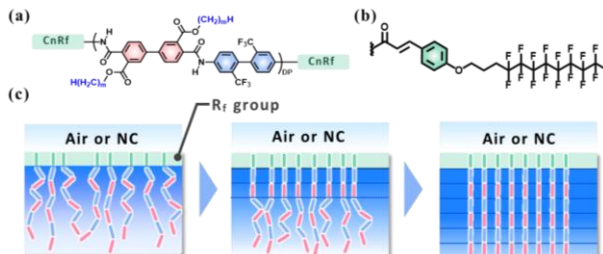


Fig. 1 Chemical structure of (a) PAE and (b) CnRf and (c) schematic mechanism of vertical orientation of PAE at the surface and inside of the film.

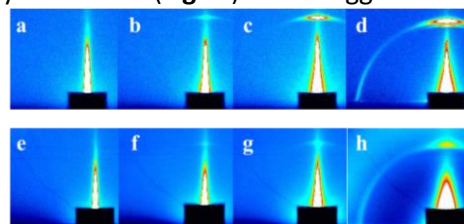


Fig.2 GI-WAXD images of BP2CnRf solution in the drying process at (a) 0, (b) 17, (c) 72, (d) 160 mins and BP6CnRf after (e) 0, (f) 17, (g) 72, (h) 160 mins from the initial diluted state.

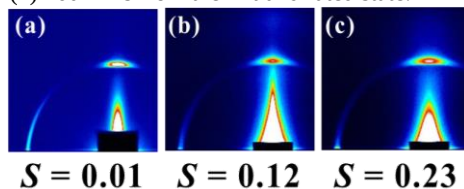


Fig.3 GI-WAXD images and orientation order parameter S of (a) BP2CnRf, (b) BP2CnRf/NC1, (c) BP2CnRf/NC2.

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