Orientation Control of Polyimide Film toward Homeotropic Alignment Using Smectic Liquid Crystalline Precursors on Hydrophobic Substrate

Shohei Hara, Keita Yanase, Kazuyuki Tanaka, Shinji Ando, Ryohei Ishige

(Dept. Chem. Sci. Eng., Tokyo Institute of Technology)

[Introduction] Highly oriented polyimides (PIs) can afford a variety of applications. Although, rigid polymers strongly tend to align parallel to a substrate due to multiple attractive interactions, vertically aligned PI films have much interests as high thermal conductive layers in the thickness direction. In this study, we focused on one of the precursors of PIs, poly(amic ester)s (PAEs), which are semi-rigid and exhibit smectic liquid crystal in the concentrated NMP solution [1,2]. The smectic layer structure can form homeotropic alignment (HA) structure by growing in layer by layer mechanism (epitaxial growth) from the air interface. Therefore, the PAE solutions are potential precursors for HA-PI films. To enhance the epitaxial growth, we introduced hydrophobic perfluoro-alkyl (R_f) end groups, and also used hydrophobic Si substrates modified with R_f group to reduce the attractive interactions at the interface.

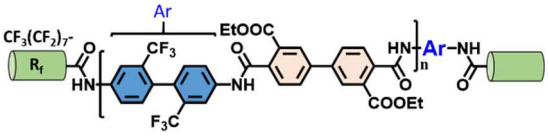

Fig. 1 Chemical structures of PAE

[Experimental] A PAE having R_f (= $CF_3(CF_2)_7$-) end group (**Fig. 1**) was prepared from a PAE and perfluorooctyl acid chloride in NMP solution. PAE films were prepared by the push coating method [3] at 50 °C for 1 h, followed by heating at 350 °C for 1 h to convert PI films. Uniaxial orientation order parameter S, defined by $S = (3\langle\cos^2\vartheta\rangle - 1)/2$, where ϑ is the angle between the molecular long axis and averaged orientation direction, was evaluated by infrared pMAIRS method. The S values of −0.5, 0, and 1 represent perfectly homogeneous, random, and homeotropic orientation, respectively. Molecular orientation distribution was estimated by GI-WAXD at Photon Factory (Tsukuba, Ibaraki, BL6A, λ = 1.5 Å, Proposal number 17G693).

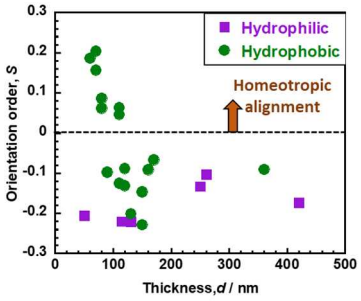

Fig. 2 Thickness dependence of S values of PAE films

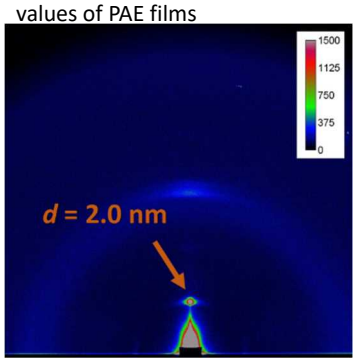

Fig. 3 2D GI-WAXD pattern of push-coated PAE film measured

[Results and discussion] **Fig. 2** shows the thickness dependence of S values of PAE films. The S values were calculated from dichroic ratio of absorbance peak at 1490 cm^{-1} which was assigned to aromatic C=C stretching vibration with a transition moment parallel to the main chain. The S values of PAE film on hydrophobic substrate are higher than that on hydrophilic substrate, and exhibit HA like behavior in the thinner region. These results indicate that the epitaxial growing was enhanced by increasing the specific surface area. **Fig. 3** shows the 2D GI-WAXD pattern of a PAE film coated on hydrophobic substrate. Shape layer reflection (d = 2.0 nm) was observed on the meridian and broad one was on the equator, indicating a double orientation. The former one shows the epitaxial growth of the smectic layer and the fraction of homeotropically aligned region was evaluated at 0.35, which is consistent with the results of pMAIRS. We demonstrated that push-coated PAE films formed on hydrophobic substrate are promising candidates for functional HA films.

[References] [1] C. Neuber et al, *Macromol. Chem. Phys*, **203**, 598-604 (2002). [2] K. Tanaka, S. Ando, R. Ishige, *Macromolecules*, **52**, 5054-5056 (2019). [3] M. Ikawa, T. Hasegawa et al, *Nat. Comm*, **10**, 1038 (2012).

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