Strategy toward Perpendicularly Aligned Rigid Polyimide: a New Coating Method Based on Liquid Crystal Precursor and Hydrophobic Substrate

S. Hara, K. Yanase, K. Tanaka, R. Ishige, and S. Ando
Department of Chemical science and Engineering
e-mail: shara@polymer.titech.ac.jp

I. INTRODUCTION

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 vertically aligned PI film can be used for the high thermal conductive layer in the thickness direction (**Fig. 1**). In this study, we focused on one of the precursors of PIs, poly (amic ester)s (PAEs), which have remarkable rigidity to exhibit smectic liquid crystal in the concentrated NMP solution [1,2]. Smectic layer structure can form vertical orientation (VO) structure by growing in layer by layer mechanism (epitaxial growth) from the air interface. Therefore, the PAE solutions are potential precursors for VO PI films. In addition, to enhance the epitaxial growth, we introduced hydrophobic perfluoro-alkyl (R_f) end groups, which facilitates segregation at the interface. However, PI chains strongly tend to align parallel to the substrate. To reduce the parallel orientation, we used hydrophobic Si substrates modified with R_f group having low surface free energy.

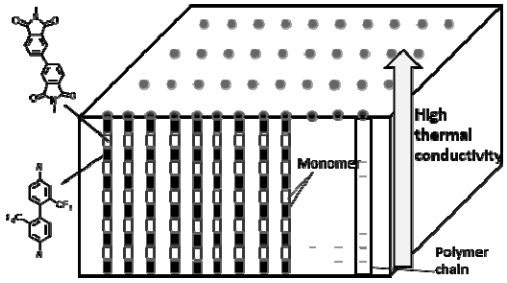

Fig. 1 Prospective application of vertically oriented PI

II. EXPERIMENTAL SECTION

A PAE having R_f (= $CF_3(CF_2)_7$-) end group (**Fig. 2**) was prepared from PAE and perfluorooctyl acid chloride in NMP solution. PAE films were prepared by the push coating method at 50 °C for 1 h [3], followed by heating at 350 °C for 1 h to convert PI films. Uniaxial orientation order parameter S, defined by $S = (3\langle\cos^2\theta\rangle - 1)/2$, where θ is the angle between the molecular long axis and averaged orientation direction, was evaluated by pMAIRS FT-IR method. The S values of −0.5, 0, and 1 represent perfectlly parallel, random, and vertical orientation, respectively.

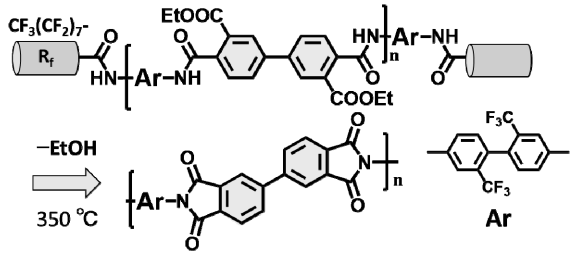

Fig. 2 Chemical structures of newly designed PAE and PI

III. RESULTS AND DISCUSSION

Fig. 3 shows the pMAIRS spectra for PAE and the thickness dependence of S values. The S values were calculated from dichroic ratio of absorbance peak at 1490 cm^{-1} which was assigned to aromatic C=C stretching vibration transition moment parallel to the main chain. The PAE films exihibit VO behavior in the thinner film region, which indicates that PAE chains grew epitaxicially from the interface because R_f end groups strongly segregate at the interface, and the thinner films have larger specific surface area to enhance the epitaxial growing.

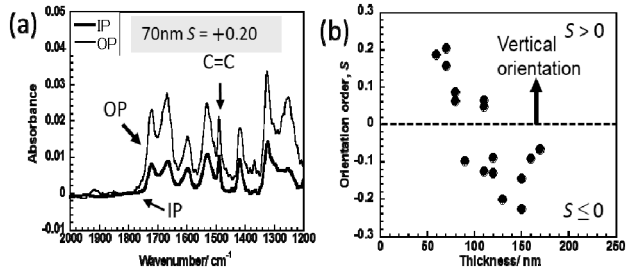

Fig. 3 (a) In-plane (IP) and out-of-plane (OP) absorbance spectra, obtained by pMAIRS, (b) film thickness dependence of S values for the PAE precursor

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