2K18

Synthesis of Novel Fluorescent Polyimides Having High Orientation Ability Using Liquid Crystalline Precursor and Molecular Orientation Analysis Based on Polarized Fluorescence

Keita Yanase[1], Kazuyuki Tanaka[1], Kenta Kanosue[1], Ryohei Ishige[1], and Shinji Ando[1]
([1]Department of Chemical Science and Engineering, Tokyo Institute of Technology,
Ookayama 2-12-1-E4-5, Meguro-ku Tokyo 152-8552, Japan)
[1]Tel: +81-3-5734-2889, Fax: +81-3-5734-2889, E-mail: kyanase@polymer.titech.ac.jp

[Introduction] Aromatic polyimides (PIs) have been attracting much interests due to the potential applications as novel fluorescent (FL) materials bearing high durability. We have previously reported that an aromatic PI with bulky side groups in the diamine moiety showed FL emission, in which the C(aromatic)-N(imide) band was twisted by the steric hindrance, and the locally excited (LE) state with FL emission became dominant. In typical aromatic PIs, charge transfer (CT) excited state without FL ability is dominant [1]. In this study we focused on lyotropic liquid-crystalline (LC) PI precursor, poly (amic ethylester)s (PAEs), to fabricate PIs exhibiting polarized FL emission by using facile orientation of LC [2]. We designed a novel PAE having bulky $-CF_3$ groups (**Fig. 1**) in the side chains and discussed the relationship between the chain orientation order and the degree of polarization of FL emission in the PAE precursor and PI state.

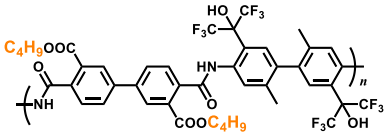

Fig. 1 Chemical structure of PAE exhibiting fluorescent emission.

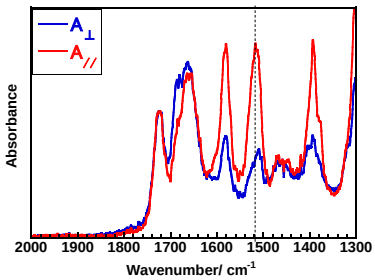

Fig. 2 Polarized FT-IR spectra observed by rotating a polarizer.

[Experiments] Uniaxially oriented PAE films were prepared by coating of 60 wt% NMP solution of PAE on Si wafer by applying shear deformation and heated from 30 to 350 °C by 10 °C/min. Uniaxial order parameter *S*, which represents the degree of chain orientation, was evaluated by polarized FT-IR and polarized fluorescence measurements. Here, *S* is defined as eq. (1), where φ is the angle between the individual molecular-long-axis and the direction of shear flow, and <…> represents a statistically average value.

$$S = (3\langle\cos^2\varphi\rangle - 1)/2 \qquad (1)$$

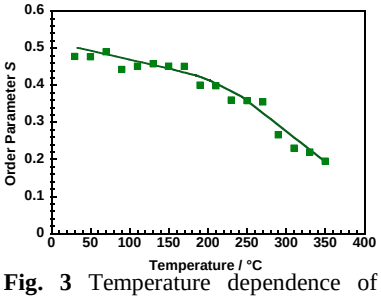

Fig. 3 Temperature dependence of orientation order *S* determined by IR.

[Results and Discussion] In the FT-IR measurements, clear dichroism was observed when the electric field of the incident IR light was rotated from parallel ($A_{//}$) to perpendicular ($A_{\perp}$) to the shearing direction of the sample (**Fig. 2**). This is because the aromatic ring C=C stretching vibration (1510 cm^{-1}) have a transition dipole moment parallel to the long axis of the molecular chain. **Fig. 3** shows the temperature variation of *S* value evaluated from the dichroic ratio *D* of the IR band based on eq. (2). The degree of orientations of PAE was as high as 0.5, and the orientation order was gradually decreased during thermal curing because the molecular orientation was relaxed with the solvent evaporation and imidization. In the polarized FL measurement, non-polarized excitation light was irradiated on the oriented sample, and a polarization analyzer was rotated to estimate the degree of polarization of the FL emission. As shown in **Fig. 4**, the oriented PAE films exhibited the strongest fluorescence when the transmission of analyzer was parallel to the orientation direction. The *S* value evaluated from the FL intensity ratios based on eqs. (1), (3) were 0.51 (PAE) and 0.20 (PI) respectively, which agreed well with those from the FT-IR measurements, 0.48 (PAE) and 0.20 (PI). Consequently, we have successfully prepared uniaxially oriented PI films which emit linearly polarized fluorescence through lyotropic liquid crystalline state of PAE precursor.

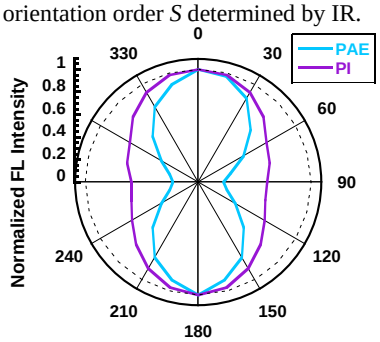

Fig. 4 Polar diagrams of polarized fluorescence of PAE and PI.

$$S = (D-1)/(D+2), D = A_{\parallel}/A_{\perp} \quad (2), \quad \langle\cos^2\varphi\rangle = D/(D+2), D = F_{\parallel}/F_{\perp} \quad (3)$$

[Acknowledgement] We are grateful to Mr. T. Ogawa, Mr. Y. Tanaka, Dr. A. Takahashi, and Mr. K. Matsunaga in Central Glass Co. for kindly providing the fluorinated diamine monomer.

[Reference] [1] M. C. Choi, J. Wakita, C.-S. Ha, S. Ando, *Macromolecules*, **42**, 5112-5120 (2009). [2] C. Neuber, R. Giesa, H. W. Schmit, *Adv. Funct. Mater.*, **13**, 387-391 (2003).