Analysis of Molecular Orientation of Polyimide Thin Films Using Infrared p-Polarized Multiple-angle Incidence Resolution Spectrometry (p-MAIRS)

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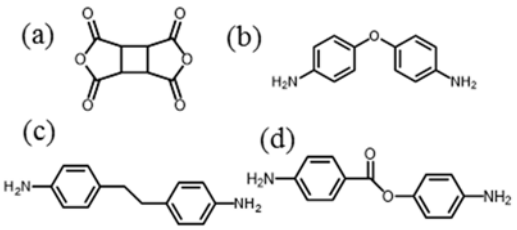
Introduction: Polyimides (PIs) have been used as alignment layer of liquid crystal displays. In order to investigate the function of alignment layer, it is essential to estimate the molecular orientation of PI chains. In general, the molecular orientation in thin films is analyzed using polarized infrared (IR) transmission, attenuated total reflection (ATR)-IR [1], or reflection absorption spectrometry (RAS) [2]. However, ATR-IR cannot be applied to film thinner than 1 μm. Moreover, RAS measurement needs samples formed on Au substrate, but the molecular orientation could be influenced by the surface of substrates. In this study, we attempted to analyze the orientation of PI main chains and imide rings of thin PI films formed on Si substrate using IR p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) [3] which enable us to observe not only in-plane (IP) but also out-of- plane (OP) molecular orientation.



Scheme 1 Structures of (a) **CBDA**, (b) **ODA**, (c) **ETDA**, and (d) **BAAB**

Experimental: Poly(amic acid) (PAA) solution were prepared from CBDA and three kinds of diamines (Scheme 1), and PI films were formed by spin coating of the PAAs onto Si substrate and subsequent curing at 230°C for thin (d =150 nm) and thick films (250 nm). p-MAIRS spectra were measured by JASCO FT/IR-4200 attached with MAIRS unit (AM-4000).

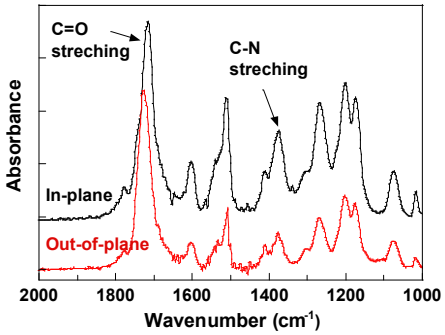


Fig. 1 In-plane and out-of-plane p-MAIRS spectra of CBDA-BAAB.

Table 1 Estimated order parameters of PIs.

Polyimide	P_C	P_I
CBDA-ODA	-0.1843	0.0894
CBDA-ETDA	-0.1678	-0.0040
CBDA-BAAB	-0.2650	-0.0201

Result and Discussion: The IP and OP spectra of CBDA-BAAB PI are shown in **Fig.1**. The peaks at 1715 cm^{-1} and 1380 cm^{-1} are assigned to C=O asymmetric stretching and C–N stretching vibration. The transition moments of these modes are parallel to the imide ring and the PI main chain, respectively. The orientational parameter (P) was evaluated using intensities of these peaks as $P = (I_{OP}-I_{IP}) / (2I_{IP}+I_{OP})$. P = 1.0 and P = −0.5 correspond to the perfect OP and IP alignments, respectively, and P = 0 is indicative of random orientation. The P values estimated for PI chain (P_C) and imide ring (P_I) for 250 nm-thick films are summarized in Table 1. The P_I are close to null for all PIs. On the other hand, P_C ranges from −0.16 to −0.26 depending on the structure, which indicates that imide rings are randomly oriented, while PI chains are significantly aligned in the IP direction. CBDA-BAAB having a rigid and linear structure demonstrates a higher degree of IP orientation than the others. In contrast, CBDA-ODA having a bent and flexible structure shows more isotropic orientations of PI chains and imide rings. In case of thinner PI films at 150 nm, orientations of imide rings and PI chains are more significant than the thick films, suggesting that three-dimensional orientation of PI chains in thin films is dependent on the film thickness.

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[2] T. Hasegawa, D.A. Myrzakozha, T. Imae, J. Nishijo, Y. Ozaki, *J. Phys. Chem. B* **103**, 11124 (1999).
[3] T. Hasegawa, *J. Phys. Chem. B* **106,** 4112 (2002).

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