Relations between In-plane thermo-optic coefficients and anisotropy in thermal expansion of polyimide films.

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I. INTRODUCTION

Temperature dependence of refractive index (thermo-optic coefficient, TOC, dn/dT) is an important property for optical materials. For instance, small TOC is preferable for optical lens which requires environmental stability, whereas a large TOC is demanded for optical waveguide materials for thermal switch with low energy consumption.

There are several researchs on averaged TOC (dn_{av}/dT) for isotropic polymers, as represented by eq. (1), in which coefficient of volumetric thermal expansion (CVE) is the dominant factor. However, polymer films generally exhibit anisotropy in thermal expansion between in-plane and out-of-plane derections, $CTE_{//}$ and $CTE_{\perp}$, and CVE is expressed as $2 \cdot CTE_{//} + CTE_{\perp}$. There are few reports on the anisotropy in TOC [1] (in-plane and out-of-plane TOC are defined as $dn_{//}/dT$, $dn_{\perp}/dT$, and $dn_{av}/dT = 2dn_{//}/dT + dn_{\perp}/dT$).

This study aimed to clarify the relationships among $dn_{//}/dT$, $CTE_{//}$, $CTE_{\perp}$, degree of in-plane/out-of-plane orientation (P_{200}), and chemical structures of polyimide (PI) films.

$$dn_{av}/dT = -(n_{av}^2 - 1)(n_{av}^2 + 2)/6n_{av} \times \mathrm{CVE} \quad (1)$$

A. Sample preparation and Measurements

DMAc solutions of poly(amic acid)s synthesized from sBPDA dianhydride and ten types of aromatic diamines having linear or flexible structures were spin-coated on Si substrates, subsequent thermally imidized at 350 °C, and finally annealed at 350 °C to release internal stress (Fig. 1). The film thickness was set ca.10 μm.

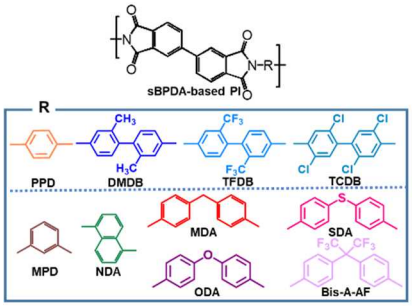

Figure 1. Chemical structure of PIs.

B. Measurement

$dn_{//}/dT$ and $CTE_{\perp}$ of PI films were evaluated in the temperature range of 80~280 °C by optical interferometry method in the near-infrared region[2]. $CTE_{//}$ of PI films was measured by thermomechanical analysis (TMA).

II. RESULT AND DISCUSSION

A. Relation between $dn_{//}/dT$ and $CTE_{//}$, $CTE_{\perp}$

A linear correlation was clearly observed between $dn_{//}/dT$ and $CTE_{\perp}$, indicating that $CTE_{\perp}$ is the predominant factor of $dn_{//}/dT$.

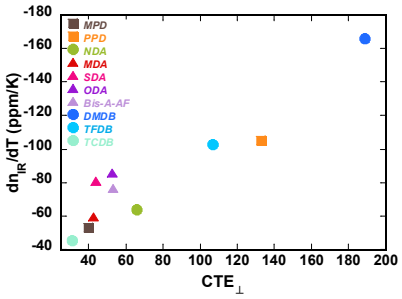

Figure 2. Relation between $dn_{//}/dT$ and $CTE_{\perp}$

B. The effect of P_{200} and chemical structure for $dn_{//}/dT$

Firstly, for the values of $dn_{//}/dT$ exhibiting a linear correlation with P_{200}. (P_{200}= −0.5 for the perfect in-plane orientation, and 0 for completely random orientation) (Fig. 3), That is because strong in-plane orientation PI has the less covalent bond and the more intermolecular interaction bond then non-oriented one, so weak force works out-of-plane direction, so dn///dT show greatly increases as CTE ⊥ increases [3].

Secondly, the PIs having linear structures tend to exhibit significant in-plane orientation, whereas those with bent structures exhibit much less orientation. As expected, PIs having bulky side chains exhibited relatively lower in-plane orientation and smaller $dn_{//}/dT$ values. This originates from restricted molecular motion owing to the higher energy barrier of internal rotation, leading to a small temperature change in P_{200}.

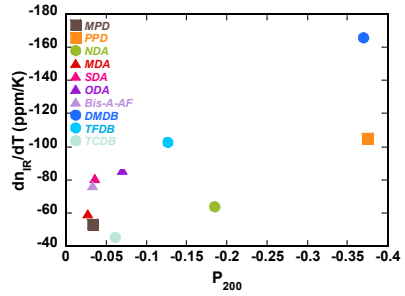

Figure 3. Relation between $dn_{//}/dT$ and P_{200}

C. Conclusion

$dn_{//}/dT$ is the predominant factor for $CTE_{\perp}$ of PI films, and additionally degree of in-plane orientation (P_{200}) and rigidity/flexibility of chemical structures significantly affect their $dn_{//}/dT$ values.

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