Effects of Chemical Structure, Molecular Chain Orientation, Anisotropy of thermal expansion on the Thermo-optic Coefficients of Polyimide Films

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Temperature dependence of refractive index, which is called 'thermo-optic coefficient' (TOC) is an important property for optical materials. For instance, small TOC is preferable for an optical lens which requires environmental stability. Therefore, effective suppression of TOC based on a new molecular design concept is one of the most important issues in polymer optical materials. In this study, for providing a new concept to suppress TOC, we investigated the effects of anisotropy in thermal expansion, molecular chain orientation (P_{200}), and chemical structures on the TOC of polyimide (PI) films.

Ten kinds of PIs having linear or flexible structures were synthesized from *s*BPDA dianhydride combined with various diamines by thermal imidization process (Fig. 1). The TOC and out-of-plane coefficient of thermal expansion ($CTE_{\perp}$) of the PI films were evaluated in the range of 80~280°C by optical interferometry method in the near-infrared region. Firstly, a clear linear correlation was observed between TOC and $CTE_{\perp}$ indicating that $CTE_{\perp}$ is the predominant factor of TOC (Fig. 2). Secondly, PI films exhibiting significant in-plane orientation tend to exhibit large TOC values (P_{200}= −0.5 for the perfect in-plane orientation, and 0 for random orientation) (Fig. 3). From the viewpoint of the chemical structure, PIs having linear structures exhibit significant in-plane orientation, whereas those with bent structures exhibit much less $|P_{200}|$ value. In addition, PI having bulky methyl side chains exhibited a relatively high TOC. This is because the linear PIs having rotational freedom around the chain axis and bulky side groups easily increase the intermolecular distance, which weakens the intermolecular interactions and enhances the $CTE_{\perp}$ and TOC values.

Keywords: Polyimide, thermo-optic coefficient, thermal expansion, In-plane orientation

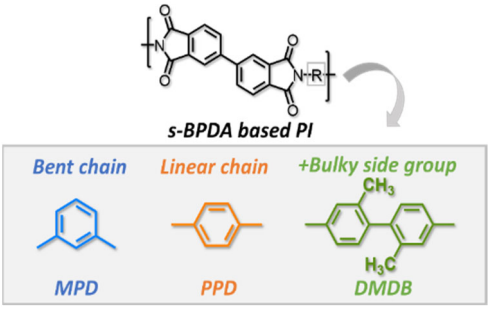

Fig 3. Chemical structures of the target PIs.

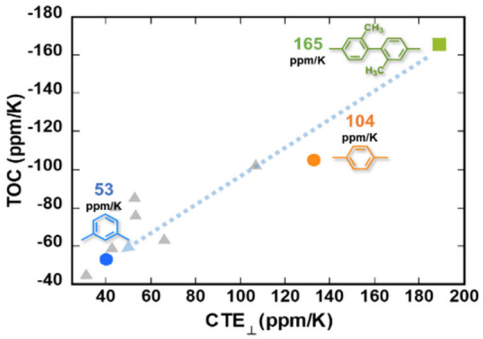

Fig 3. Plot of TOC vs. $CTE_{\perp}$ for the PIs.

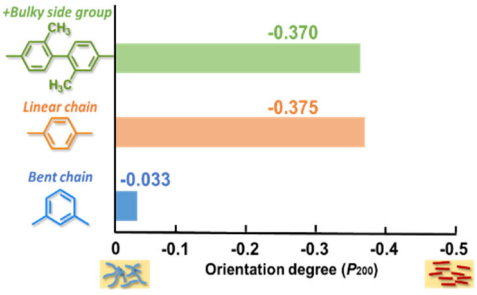

Fig 3. Degree of molecular chain orientation.