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

Megumi FUJITA[1], Mari HARADA[1], Ryohei ISHIGE[1], Shinji ANDO[1]

[1] Dept. of Chemical Science and Engineering, Tokyo Institute of Technology

Introduction

Temperature dependence of refractive index (thermo-optic coefficient, TOC) is an important property for optical materials. For instance, small TOC is preferable for 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.

Experiment

Target PIs were synthesized from *s*BPDA and aromatic diamines having linear or flexible structures (Fig. 1). The film thickness of spin-coated film was adjusted to ca. 10 μm. TOC and out-of-plane coefficient of thermal expansion ($CTE_{\perp}$) of PI films were evaluated in the range of 80~280°C by optical interferometry method in the near-infrared region [2]. In-plane CTE ($CTE_{//}$) was measured by thermo-mechanical analysis (TMA).

Results and Discussion

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 show large values of TOC (P_{200}= −0.5 for the perfect in-plane orientation, and 0 for random orientation) (Fig. 3). PIs having linear structures exhibit significant in-plane orientation, whereas those with bent structures exhibit much less orientation. A PI having bulky methyl side chains exhibited a relatively high TOC. This is attributable to the larger intermolecular distance, which weakens the intermolecular interactions and enhances the $CTE_{\perp}$ and TOC. For the PI films with higher in-plane-orientation, inter molecular interactions, which is much weaker than covalent bonds along the main-chain, play an important role for the out-of-plane thermal expansion ($CTE_{\perp}$) [3], and this is the crucial factor for the enlarged TOC.

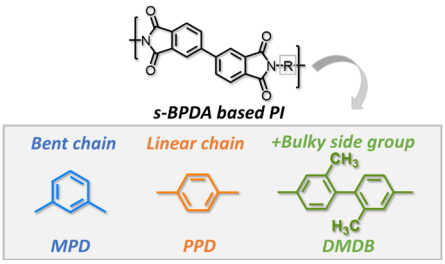

Fig 3. Chemical structures of the target PIs.

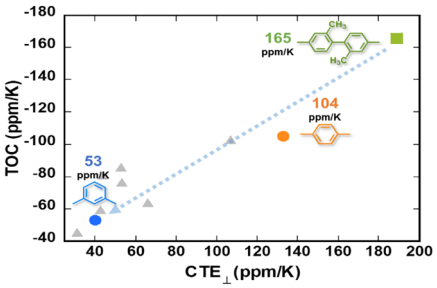

Fig 3. Relation between TOC vs. $CTE_{\perp}$.

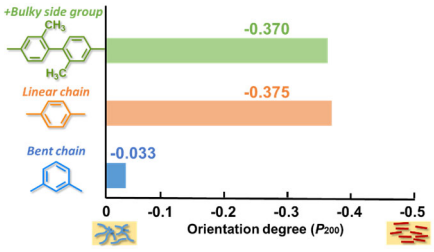

Fig 3. Degree of molecular chain orientation.

References

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