Relationships between Molecular Structure and Optical, Dielectric, and Thermal Properties of Novel Semi-alicyclic Polyimides Containing Bio-derived Isohexides

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Introduction

Polyimides (PIs) are high-performance polymers exhibiting excellent thermal stability, chemical stability, electrical insulation, and mechanical strength. However, their application to optoelectronics is still limited because of the low transparency and coloration due to the charge-transfer (CT) interaction and the high water absorption caused by polar imide groups [1]. It is desirable to achieve high optical transparency, low refractive index, and low dielectric constant, as well as sufficient thermal and mechanical properties. In addition, in recent years, the use of plant-derived resources has been emphasized for the reduction of environmental load and sustainability of resources. Isosorbide (ISS) and isomannide (ISM), types of 1,4;3,6-dianhydrohexitols (isohexides), are diols derived from renewable biomass resources such as cellulose. They have bulky and rigid structures consisting of two alicyclic rings with oxygens connected by V-shaped linkage at 120° [2]. This unique alicyclic structure differs from other aliphatic structures and is presumed to have superior tolerance and functionality. In other words, the introduction of ISS and ISM into PIs can contribute to develop highly functional plant-derived PIs. Although some PIs containing ISS or ISM skeletons in the main chain were reported [3,4], no research has been conducted with the main objective of analyzing their structure-property relations and improving their physical properties. In particular, the method for effective utilization of ISM has not been clarified because of the specific structure of ISM.

In this study, we synthesized novel semi-alicyclic homo-PIs containing ISS (ISS-PIs) and copolyimides (CoPIs) containing both ISS and ISM using ISS- and ISM-derived dianhydrides (ISSDA and ISMDA) and various diamines (**Fig. 1, 2**), and we also analyzed their optical, dielectric, and thermal properties. Furthermore, the effects of introduction of the specific ISS and ISM structures on the various physical properties are discussed in terms of intermolecular interactions, free volume, and molecular mobility of PI chains.

Experimental

Poly(amic acid)s (PAAs), precursors of PIs, were synthesized by dissolving and stirring ISSDA and diamines in DMAc. To obtain Copolymerized PAA, ISMDA and ISSDA were added in that order into a DMAc solution of a diamine (TFDB), as mole fraction of ISSDA : ISMDA = x : y. PAAs casted on Si or silica substrates were thermally imidized at 280 °C under N_2 flow, and thus ISS-PIs and CoPIs thin films were prepared. The optical transparency, refractive index (n_{av}) and birefringence (Δn) of the ISS-PI and CoPI films were measured. The dielectric constant (D_k) and dissipation factor (D_f) at 10 GHz, glass transition and 5 wt % weight-loss temperatures (T_g, T_d^5) were also investigated.

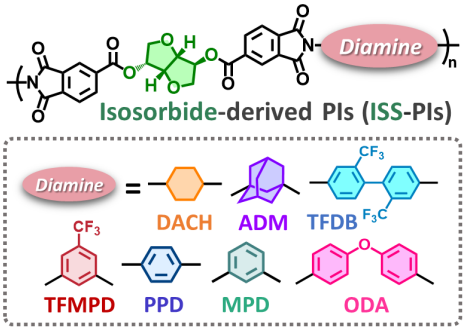

Fig. 1 Chemical structures of ISS-PIs.

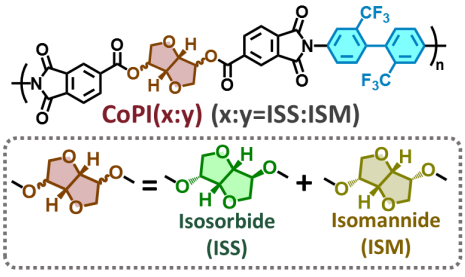

Fig. 2 Chemical structures of CoPIs.

Results and Discussion

From the UV-visible absorption spectra of ISS-PIs (**Fig. 3**), the ISS-PI and CoPI films are transparent and either totally colorless or pale yellow, which is much better than conventional wholly aromatic PIs such as Kapton (PMDA-ODA) which has dark brown color. Here, the coloration of PIs is due to the intra- and intermolecular CT interaction between the diamine and dianhydride moieties, indicating that wholly aromatic PIs with highly planarity show the absorption edges at longer wavelengths (λ_E > 550 nm [5]). In contrast, ISS-PIs can effectively suppress the intermolecular CT interactions by their large free volume of the main chain due to the bulky, flexible and nonplanar structure as shown in **Fig. 3**, resulting in the blue shifts of absorption edges (λ_E < 450 nm). Additionally, ISS-PIs exhibit not only lower n_{av} (< 1.60) but also lower D_k (< 3.33) than the conventional PIs, which is attributable to the inhibition of main chain aggregation and reduction in polarizability, which is due to the specific bulky structure of the ISS-PI main chain. Furthermore, the Δn of ISS-PIs are also much smaller (< 0.021) than that of Kapton (= 0.076), suggesting small polarizability anisotropy of the repeating units in addition to the suppression of main chain orientation [6].

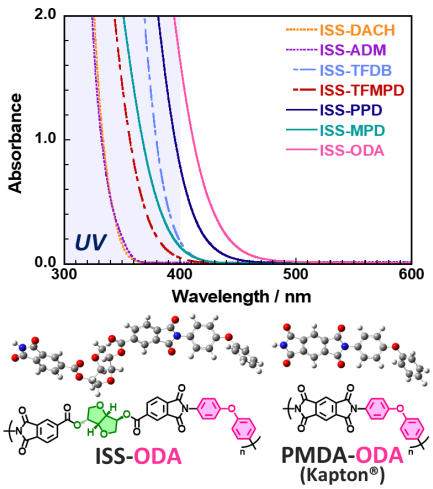

Fig. 3 UV-vis absorption spectra of ISS-PIs (top), and structural difference between the ISS-ODA and Kapton® (bottom).

It is noteworthy that CoPIs containing both ISS and ISM in the main chain exhibited better optical and dielectric properties than ISS-TFDB (HomoPI) and also conventional PIs. It can be confirmed that CoPIs show the shorter λ_E, *i.e.*, higher optical transparency (**Fig. 4**), close or lower n_{av}, and smaller Δn than HomoPI. In particular, CoPI with 30 mol% of ISM (ISS_7-ISM_3) exhibited sufficiently low D_k and D_f at 10 GHz (2.89 and 9.69×10^{-3}, respectively) in addition to the excellent optical properties as shown in **Fig. 5**. These are readily attributable to the bulky and hairpin-like structure of ISM moiety [2], which has a quite low polarizability anisotropy of the repeating unit. It is suggested that the introduction of ISM in the main reduces the structural anisotropy and increases the free volume, resulting in the inhibition of intermolecular CT interaction which is enhanced by chain orientation and dense packing. Moreover, the smaller D_f values of CoPIs indicates that ISM moiety can suppress local molecular motion of the main chain at 10 GHz because of the rigidity and steric hindrance around ISM moiety.

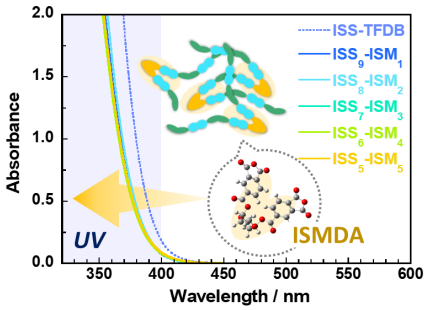

Fig. 4 UV-vis absorption spectra and molecular structure of CoPIs.

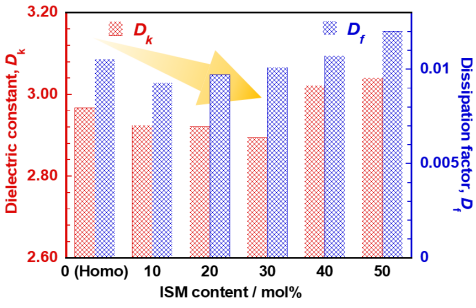

Fig. 5 Dielectric constants (D_k) and losses (D_f) of CoPIs measured at 10 GHz.

References

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