

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

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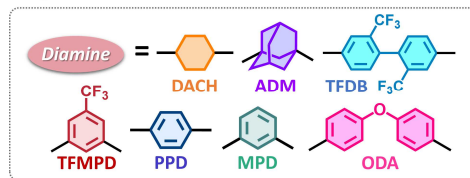
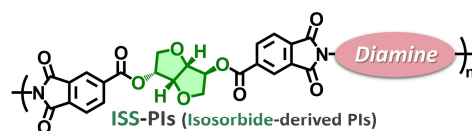
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### Introduction

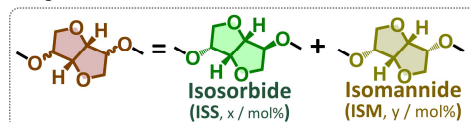
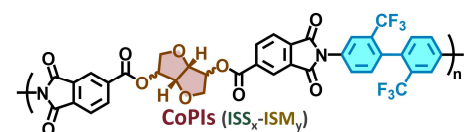
Polyimides (PIs) are high-performance polymers that exhibit excellent thermal and chemical stability, and mechanical toughness. However, their applications to opto-electronic and dielectric materials at high frequencies are still limited because of the strong coloration due to charge transfer (CT) interactions and high dielectric constants [1]. It is desirable to achieve better optical and dielectric properties, such as high optical transparency, low refractive index and birefringence, and low dielectric constant and dissipation factor, compared to the existing PIs such as Kapton. In addition, in recent years, emphasis has been placed on the effective utilization of bio-based resources for achieving of global sustainability. 1,4;3,6-Dianhydrohexitols (isohexides) derived from biomass cellulose have bulky and rigid structures consisting of two hetero-alicyclic rings connected in a V-shape and include stereoisomers, *i.e.* isosorbide (ISS) and isomannide (ISM) [2]. Although some PIs containing ISS or ISM skeletons in the main chain have been reported, the physical properties of ISM-containing polymers have not been investigated in detail because ISM is industrially unavailable due to its complicated synthesis procedure and low reactivity. In this study, a series of novel semi-alicyclic PIs incorporating ISS (ISS-PIs) and copolyimides containing both ISS and ISM (CoPIs) were synthesized using ISS- and ISM-derived dianhydrides (ISSDA and ISMDA) and various diamines (**Fig. 1, 2**). Their optical, dielectric, and thermal properties were analyzed for discussing their structure-property relationships and the effect of the introduction of the bent-shaped ISM moiety.

### Experimental

Poly(amic acid)s (PAAs), precursors of ISS-PIs, were synthesized by dissolving and stirring ISSDA and diamines in *N,N*-dimethylethanamide (DMAc). To obtain copolymerized PAA, ISMDA and ISSDA were added stepwise into a DMAc solution of a diamine (TFDB), as a mole fraction of ISSDA : ISMDA =  $x$  :  $y$ . PAAs spin-coated on Si or silica substrates were thermally imidized at 280 °C under N<sub>2</sub> flow, and then ISS-PI and CoPI thin films were prepared. The UV-visible (UV-vis) transparency, refractive index ( $n_{av}$ ), and birefringence ( $\Delta n$ ) of these films were measured. The dielectric constant ( $D_k$ ) and dissipation factor ( $D_f$ ) at 10 GHz in the transverse electric (TE) mode, glass transition, and 5 wt% weight-loss temperatures ( $T_g$ ,  $T_d^5$ ) were also investigated.



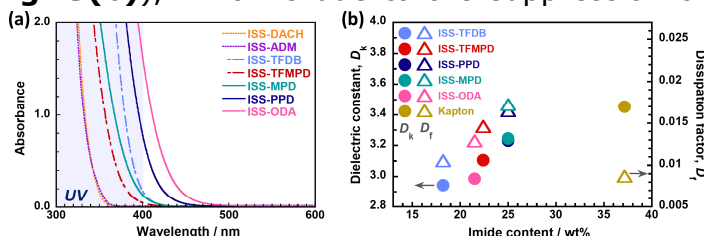
**Fig. 1** Chemical structures of ISS-PIs.



**Fig. 2** Chemical structures of CoPIs.

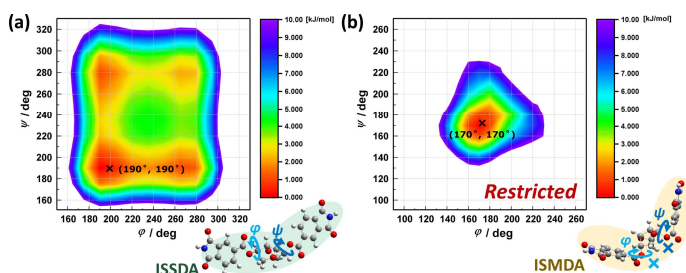
## Results and Discussion

As seen in the UV-vis absorption spectra (**Fig. 3(a)**), ISS-PI films are optically transparent and completely colorless with shorter absorption edges ( $\lambda_E < 450$  nm) than conventional PIs such as Kapton (PMDA-ODA,  $\lambda_E = 550$  nm). This indicates that the bulky and flexible ISSDA skeleton increases the free volume of the main chain and suppresses the intermolecular CT interactions. ISS-PIs also exhibited lower  $n_{av}$  ( $\leq 1.60$ ) and  $D_k$  ( $\leq 3.33$ ) than Kapton (**Fig. 3(b)**), which is due to the suppression of dense aggregation and the lower polarizability of the repeating units. Furthermore, the macroscopic anisotropy of ISS-PIs with flexible and disordered main chains lowers the  $\Delta n$  ( $\leq 0.021$ ). However, the  $D_f$  values of ISS-PIs are slightly higher than Kapton due to the rotatable ester linkages in the main chain [3].

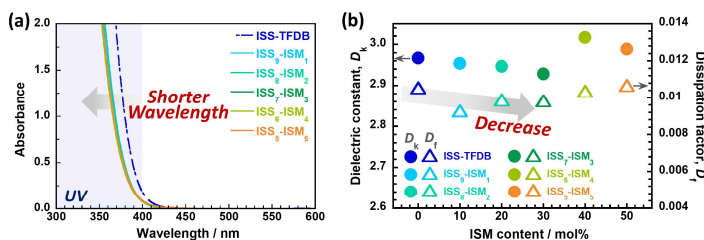


**Fig. 3** (a) UV-vis absorption spectra, and (b) dielectric constants ( $D_k$ ) and dissipation factors ( $D_f$ ) at 10 GHz of ISS-PIs.

According to the conformational energy surfaces of ISSDA and ISMDA in **Fig. 4**, the range of stable conformations allowed for ISMDA is extremely smaller, whereas ISSDA has a wide range of stable conformation due to its flexible structure. This indicates that there is a significant steric hindrance and rotational barrier around ISM moiety, which leads to a rigid boat-like structure [4]. In fact, CoPIs containing both ISS and ISM in the main chain exhibited better optical transparency with shorter  $\lambda_E$  and smaller  $D_k$  ( $= 2.92$  for ISS<sub>7</sub>-ISM<sub>3</sub>) than homo ISS-TFDB and conventional PIs, as shown in **Fig. 5**. This strongly suggests that the boat-like morphology of ISMDA increases the free volume of the main chain and then reduce the intermolecular interaction compared to linear ISSDA. Moreover, the structural rigidity of ISMDA effectively suppresses the local molecular motion of the main chain by including only 10 mol% of ISM. This implies that the incorporation of an inherently rigid and sterically constrained ISMDA is effectively lower the  $D_f$  at 10 GHz.



**Fig. 4** Conformational energy surfaces of (a) ISSDA and (b) ISMDA.



**Fig. 5** (a) UV-vis absorption spectra, and (b) dielectric constants ( $D_k$ ) and dissipation factors ( $D_f$ ) at 10 GHz of CoPIs.

## References

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