14th Multidisciplinary International Student Workshop (MISW2023)
August 3-4, 2023, Tokyo Institute of Technology, Tokyo, Japan

Extended Abstract

Synthesis and characterization of bio-based semi-alicyclic polyimides derived from an isosorbide-containing diamine

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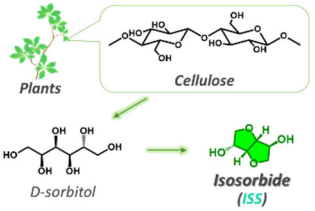
I. Introduction

Polyimides (PIs) are well-known super engineering plastics exhibiting excellent heat resistance, mechanical properties, and electrical insulation properties. They are commonly used as interlayer insulating films in electrical devices. However, conventional PIs present certain issues, such as yellowish coloration, high refractive indices and dielectric constants owing to their strong intermolecular interactions, which affects their optical and dielectric properties [1]. In recent years, from the viewpoint of carbon neutrality, there has been a demand for the development of PIs using plant-derived source materials. Therefore, we focused on isosorbide (ISS), a cellulose derivative (**Scheme 1**). Since ISS has a rigid and V-shaped bent alicyclic structure [2], the incorporation of ISS skeleton into the PI main chain cause bending PI backbone, which could suppress aggregation of PI chains and potentially improve the optical and dielectricproperties. Furthermore, ISS-ISSD, which contains ISS cores in both the dianhydride and diamine moieties, shows a quite high bio-based content (weight fraction of plant-derived compound to the total mass in the repeating units) as high as 34.2%, and it expects excellent properties. In this study, we synthesized a series of semi-alicyclic PIs (ISSD-PIs) (**Fig. 1**) including ISS-ISSD from a diamine having an ISS core (ISSD) and existing dianhydrides and investigated their optical and dielectric properties.



Scheme 1. Conversion scheme of isosorbide (ISS).

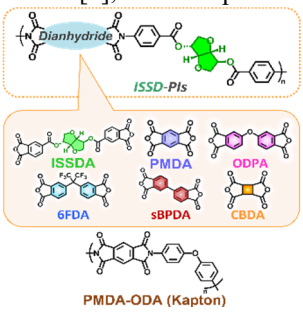


Fig. 1. Chemical structures of ISSD-PIs and PMDA-ODA.

II. Experimental

For preparing poly (amic acid) (PAA) solutions as a precursor of PIs, dianhydrides listed in **Fig. 1** were added to ISSD dissolved in *N,N*-dimethylacetamide under a nitrogen flow. The PAA solution was spin-coated onto silica or silicon substrates, dried at 70 °C for 50 min, and thermally imidized at 220 or 280 °C for 1.5 h to obtain PI thin films (ISSD-PIs).

III. Result & Discussion

The UV-visible (UV-vis) absorption spectra (**Fig. 2**) show that ISSD-PIs were completely colorless and transparent in the visible region. This is due to the introduction of a bulky and bent ISS skeleton in the diamine moiety, which suppresses aggregations of PI chains and intramolecular charge transfer (CT) interactions. The refractive indices of ISSD-PIs measured at 1310 nm (1.554–1.633) are smaller than that of conventional PI such as PMDA-ODA (Kapton) (1.652) (**Fig. 3**) [3]. This may be due to the fact that ISSD-PIs has an alicyclic ISS skeleton with small polarizability and the enlarged free volume due to the bent PI chains [4], resulting in the reduction of the polarizability per unit volume. The birefringence of ISSD-PIs (0.009–0.0317 at 1310 nm) is also smaller than that of PMDA-ODA (0.0759). This could be attributed to the bent structure of ISSD-PIs which suppresses the in-plane orientation of the PI chains and reduces the macroscopic anisotropy of polarizability.

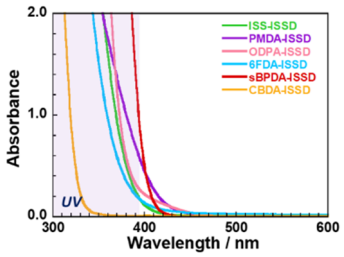


Fig. 2. UV-vis absorption spectra of ISSD-PIs.

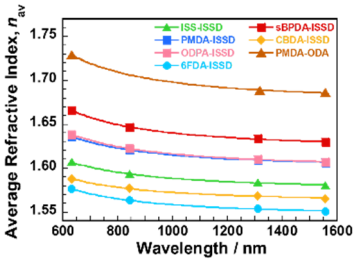


Fig. 3. Wavelength dissipation of refractive indices of ISSD-PIs.

The average value of the dielectric constant (D_k) of ISSD-PIs is 3.17 at 10 GHz, which is lower than that of PMDA-ODA (3.40). This is due to that the ISS skeleton in the diamine moiety decreases the weight fraction of polar groups such as imides and esters. Meanwhile, the average value of the dielectric dissipation factor (D_f) of ISSD-PIs (0.0137 at 10 GHz) is higher than that of PMDA-ODA (0.00834). As described above, the bent and bulky ISS skeleton reduces aggregation and increases the inter-chain free volume, which promotes the mobility of polar imide and ester groups, facilitating the response to the electromagnetic fields at 10 GHz. In addition, the slightly higher water absorption of ISSD-PIs further increases the D_f because the water has the peak maximum of D_f at around 20 GHz.

Consequently, ISSD-PIs exhibit excellent optical and dielectric properties. In particular, the optical properties of ISS-ISSD are comparable to those of fluorine-containing PIs. These results demonstrate that the ISSD-PIs are promising bio-based super engineering plastics with high-functionality.

References

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