Polyimides derived from biomass-based diamines

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1. Introduction

Aromatic polyimides are a class of polymers featuring high glass transition temperatures, high thermal stability, excellent mechanical and electrical properties, and good chemical resistance. Therefore, polyimides have been widely utilized for a variety of applications in the electronics, automotive, and aerospace industries. However, most of polyimides are prepared using petroleum-based monomers as the raw materials. Furthermore, some of these monomers, especially aromatic diamines, are highly toxic. Due to the foreseeable limit of fossil feedstocks and the increasing environmental concerns, it is of great scientific and practical significance to develop polyimides from bio-renewable raw materials. [1]

Recently, 1,4:3,6-dianhydrohexitols and their derivatives have been receiving more and more attentions as bio-based monomers for high performance polymers, because of their inherent rigidity, environmental friendliness, chirality, as well as biodegradability. 1,4:3,6-dianhydrohexitols are derived from cereal-based polysaccharides. There are three isomers of 1,4:3,6-dianhydrohexitols existing in the nature, namely namely isomannide(endo-endo conformation), isosorbide(endo-exo conformation), isoidide(exo-exo conformation). The reactivity of hydroxyl groups towards electrophilic substitution follows the trend of isoidide>isosorbide>isomannide due to their different spatial configurations and intermolecular hydrogen bond energies.[2] Due to the desired features mentioned above, a variety of polymers have been developed using 1,4:3,6-dianhydrohexitols and their derivatives as the monomers, including polyesters, polycarbonates, polyamides, etc.[3-6] However, to the best of our knowledge, no reports on 1,4:3,6-dianhydrohexitols-based polyimide can be found in the literature. In this work, we report the synthesis and characterization of bio-based polyimides from 1,4:3,6-dianhydrohexitol-derived diamines. The structure-property relationship of these polymers was also elucidated.

2. Results and Discussion

2.1 Monomer and Polymer Synthesis

The diamine monomers 2,5-diamino-2,5-deoxy-1,4:3,6-dianhrosorbito l(DADAS) and 2,5-diamino-2,5-deoxy-1,4:3,6-dianhroiditol(DADAI) were prepared according to the procedure in the literature[5], as depicted in Scheme 1. The structures of these two monomers were confirmed by ^{1}H NMR spectra. Then biobased polyimides were synthesized via a conventional one-step method in *m*-cresol, using aromatic dianhydrides and 1,4:3,6-dianhydrohexitol-derived diamines as the monomers (Scheme 2). The intrinsic viscosities of these polyimides were in the range of 0.7-1.5 dL/g, which indicated that all the polyimides possessed moderate to high molecular weights.

2.2 Properties of Polyimides

The solubility of bio-based polyimide was tested with various organic solvents, and the results were summarized in Table 1. All the polyimides showed good solubility in *m*-cresol and NMP. Polyimides based on 3, 4'-BPDA exhibited the lowest solubility in organic solvents, which can be rationalized in terms of their rigid architecture. For a given dianhydride, polyimides from isomannide diamines and isosorbide showed similar solubility in common organic solvents. The thermal properties and mechanical properties of biobased polyimides prepared were evaluated using thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), and tensile measurements. The 5% weight loss temperature ($T_{5\%}$) values ranged from 380 to 460 ^{o}C in nitrogen atmosphere. Polyimides derived from HPMDA showed the lowest thermal stability due to their fully aliphatic backbones. The glass transition temperature (T_g) values spanned a range of 215-322 ^{o}C, varying on the basis of dianhydride structures. For a given diamines, the T_g values of biobased polyimide followed the trend of HPMDA>3, 4'-BPDA>6FDA>BPADA, which suggested that T_g values for these polyimides were predominated by the imide contents in polymer backbones. Furthermore, all the polymers showed excellent mechanical properties, which was demonstrated by their high tensile strengths and modulus. Polyimides based on HPMDA exhibited the highest elongation at break, which can be attributed to their reduced inter- and intra-molecular interactions. For a given dianhydride, polyimides derived from isomannide diamine and isosorbide diamine showed similar thermal and mechanical properties.

All the polyimides are colorless or pale yellow, and showed good optical transparency. The cutoff wavelength of absorption for these biobased polyimides ranged from 260 to 370 nm. Polyimides based on HPMDA and 6FDA showed better optical properties than those based on 3,3-BPDA and BPADA. The poor electron-donating property of the isomannide and isosorbide diamines prevented the formation of inter- and intro-molecular charge transfer complex, which accounted for the good optical properties of bio-based polyimides. The specific rotations of these chiral polyimides ranged from 3.75° to +15.69° depending on the structures of the dianhydrides and diamines.

3 Conclusions

In this work, a series of bio-based polyimides were synthesized from 1,4:3,6-dianhydrohexitol-derived diamines and dianhydrides, and were characterized in terms of thermal, mechanical, and optical properties. All the polyimides showed comparable thermal and mechanical properties to those derived from petroleum-based diamines. Furthermore, these polyimides also possessed good solubility in organic solvents and excellent optical transparency, which can be contributed to the reduced inter- and intro-molecular interactions stemmed from the poor electron donating nature of bio-based, aliphatic diamines. Due to a combination of impressive properties and moderate biobased content, these polyimides showed great potential in the applications of solar cell and liquid crystal alignment, replacing polyimides from petroleum-based diamines. This study provides new insights on how to design and prepare high performance polymers from bio-renewable feestocks.

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References

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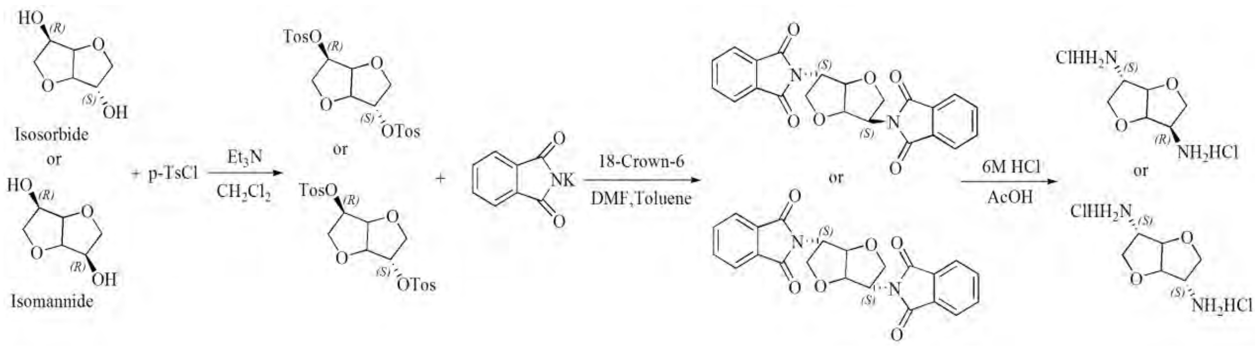
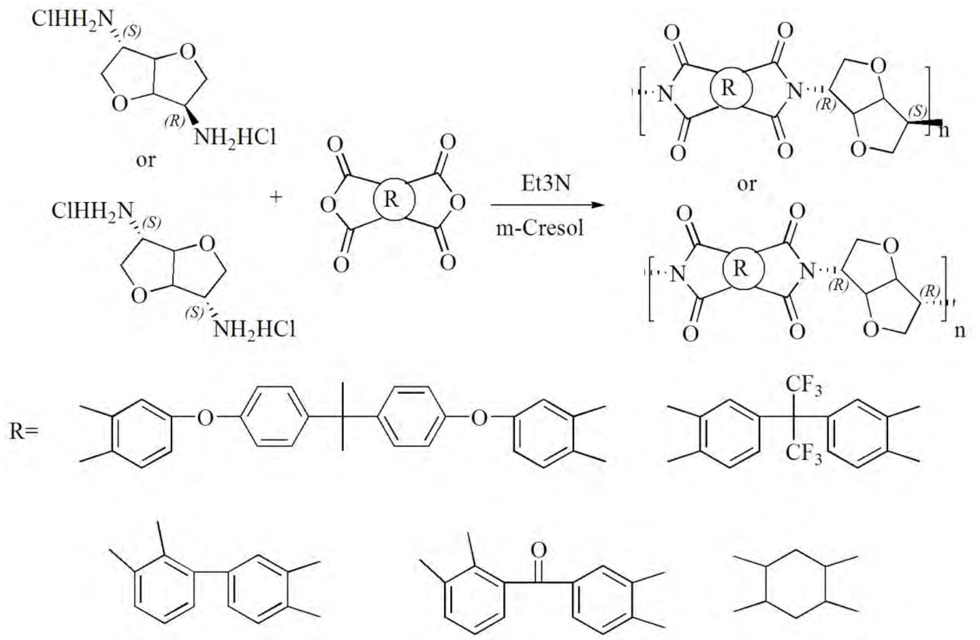


Scheme 1. The synthetic route to d1,4:3,6-dianhydrohexitol-derived diamines



Scheme 2. Synthesis of biobased polyimides

Table 1. Solubility of biobased polyimides

Polyimide	*m*-Cresol	DMAc	Chloroform	NMP	DMSO	1, 4-dioxane
Isomannide-HPMDA	++	+-	++	+	-	+
Isomannide-3,4-BPDA	++	-	-	+	+	-
Isomannide-6FDA	++	+	++	++	-	++
Isomannide-BPADA	++	++	+-	++	-	-
Isosorbide-HPMDA	++	+	-	+	++	-
Isosorbide-3,4-BPDA	++	-	+-	+	-	-
Isosorbide-6FDA	++	+	++	+	-	+-
Isosorbide-BPADA	++	-	++	+	-	+

Key: ++: soluble at room temperature; +: soluble upon heating;

+-: partially soluble upon heating; -: insoluble.

Table 2. Thermal and mechanical properties of biobased polyimides

Polyimide	Glass transition temperature (°C)	5% Weight loss temperature (°C)	Tensile Strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	η_{inh} (dL g^{-1}) [a]
Isomannide-HPMDA	322.00	397.38	103.23	3.43	44.39	0.70
Isomannide-3,4-BPDA	318.00	448.00	112.15	3.15	5.42	0.68
Isomannide-6FDA	291.00	457.05	113.67	3.16	6.23	0.90
Isomannide-BPADA	219.00	459.00	101.77	2.53	9.21	0.92

Isosorbide-HPMDA	320.00	378.49	89.70	3.54	50.94	1.05
Isosorbide-3,4-BPDA	313.00	451.91	129.64	3.24	9.18	0.79
Isosorbide-6FDA	292.00	457.27	110.87	3.25	5.11	1.07
Isosorbide-BPADA	214.00	461.52	102.84	2.81	10.35	1.49

[a] measured in m-Cresol at a concentration of 0.5g/dL at 30℃

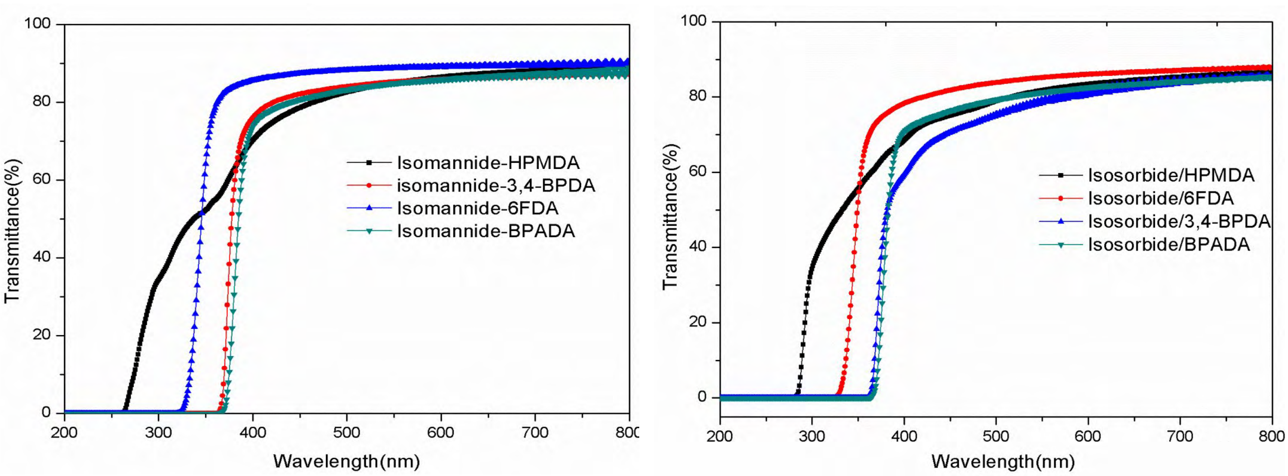


Figure 1. UV-Vis spectra of biobased polyimides