Synthesis and characterization of partly biobased degradable polyimides derived from isosorbide

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Abstract

A series of partly biobased degradable polyimides derived from isosorbide had been synthesized and characterized. Transmittance, thermal stability, mechanical properties as well as processing performance had been assessed. Compared with traditional polyimides prepared from full aromatic compouds, while maintaining good thermal stability and mechanical properties, thoese partly biobased degradable PIs also exhibite higer transmittance, ecellent processing performance.

Key words: Isosorbide Biodegradable PIs Transmittance

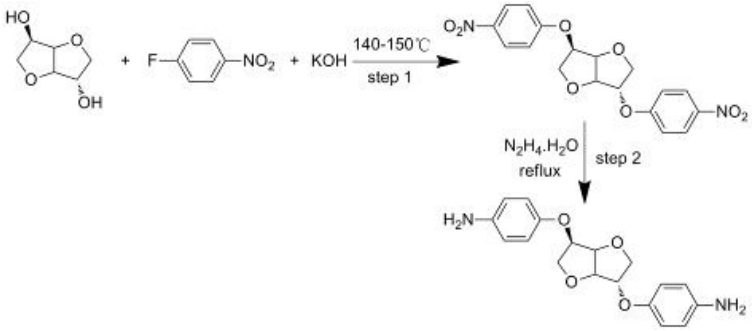
Intruduction

Much attention has been paid to the development of biodegradable materials[1]. Despite studies and reports on degradable materials -plastics, for instance, many of the specific problems can not be solved, the biodegradable bags low load-bearing capacity and limited repeated use can not meet customer requirements, some of them faded yellow, low transparency, giving a not clean and ugly feeling. Biodegradable materials that can replace petroleum originated have draw much attention[1b]. Isosorbide, a corn-derived biodegradable diol, has been applied to the synthesis of polyimides aimed at observing high transparency, good thermal stability, ecellent mechanical properties and simple processing performance. Owing to its special wedge-shaped structure and nonaromatic characteristics, isosorbide can not only show unique properties in optical but can also partly replace petroleum derived proucts, which have a significant impact on environmental protection and rational utilization of non-renewable resources[2].

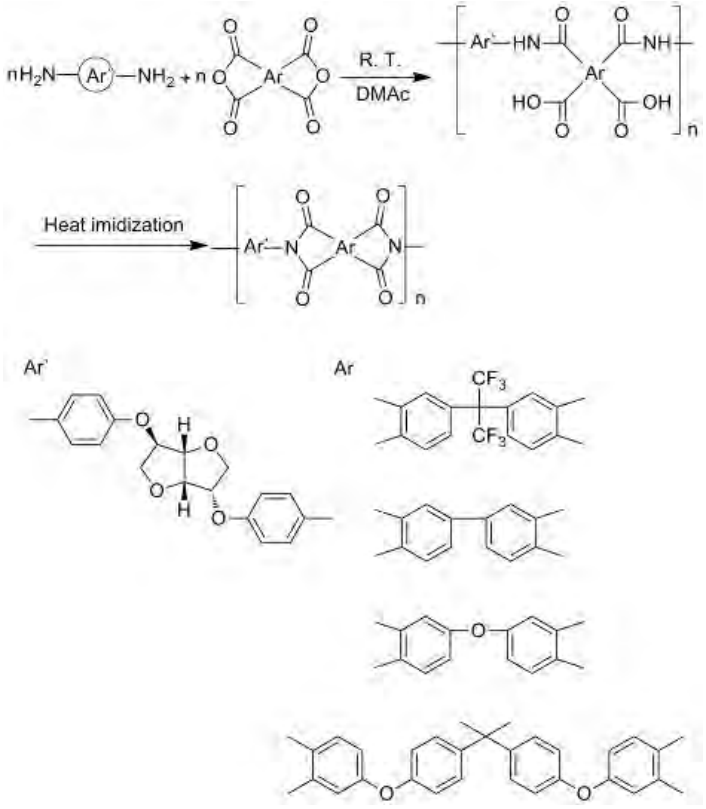
Materials and Method

Isosorbide was provided by Energy Chemical, 3,3`,4,4` -oxydiphthalic anhydride (ODPA), 3,3',4,4'-biphenyltetracarboxylic acid dianhydride(BPDA), 4,4`- (Hexafluoroisopropylidene)-diphthalic anhydride (6FDA), 4,4'-[Isopropylidenebis(p-phenyleneoxy)]diphthalic anhydride(BPADA) were supplied by Sinopharm Chemical Reagent Beijing Co. Ltd, and these aromatic dianhydrides were all recrystallized from acetic anhydride and then dried in vacuum at 150 °C for 10 h prior to use. 10% palladium on charcoal (Pd/C) (Acros), and 80% hydrazine monohydrate (Acros) were used as received. N,N-dimethylformamide (DMF), toluene and N,N-dimethylacetamide (DMAc) were purified by vacuum distillation over CaH_2 and stored over 4 Å molecular sieves prior to use. The other commercially available reagents and solvents were also used without further purification.

Dinitro compound and diamino compound derived from isosorbide and 1-fluoro-4-nitrobenzene were prepared according to step 1 and step 2 in **Scheme 1** respectively. Partly biodegradable PIs derived from diamino compound and other dianhydrides were synthesized in traditional two steps: synthesis of polyamic acid solution(PAA) and thermal imidization were shown in **Scheme 2**.



Scheme 1 Synthesis of diamine monomer



Scheme 2 Synthesis of PIs

Result and discussion

For dinitro compound and diamino compound, both structure were characterized by ^{1}HNMR, HRMS, IR, elemental analysis, melt point(measured by DSC). As shown in **Figure 1**, ^{1}HNMR spectrum of the diamine monomer illustrates that the nitro groups in were reduced, in which the signal of amino groups appeared at around d 4.5-4.75. HRLC-MS (ESI):329.1 $(M + H)^{+}$ of diamine monomer can also confirm this piont.

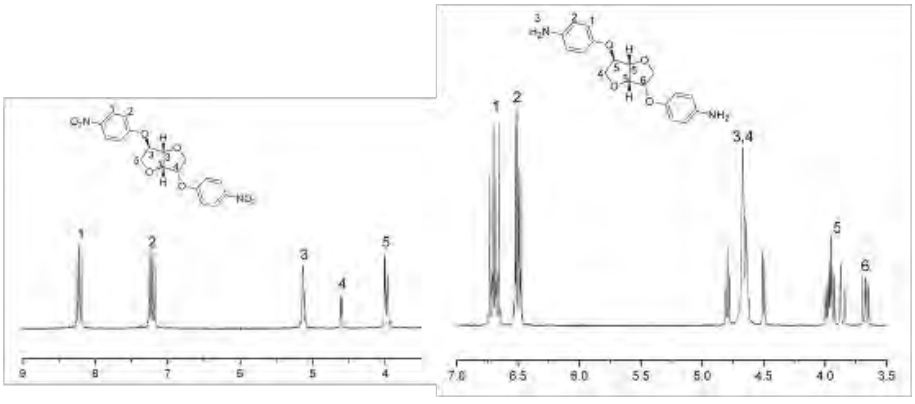


Figure 1 [1]HNMR of dinitro compound and diamino compound

For PIs, thermal, mechanical and optical properties were obtained by DSC,TGA and DMA,the result were shown in **Figure 2**, four kinds of films derived from diamine monomer and 6FDA, BPDA, ODPA, BPADA were named as PI-1-PI-4,respectively. Thermal properties of the polyimides were determined by DSC, TGA, and the results were listed in **Table 1**. Glass transition temperatures (T_g) of the polyimides were in the range of 216.6 ℃ to 284.4 ℃ , as obtained by DSC in **Figure 2**, The decomposition temperatures (Td) at 5% and 10% weight loss in nitrogen were determined from the original TGA thermograms and were also given in **Table 1**. The 5% weight loss temperatures ($T_{5\%}$) and 10% weight loss temperatures ($T_{10\%}$) of the polymers in nitrogen were recorded in the range of 450.6 ℃ to 461.8 ℃ and 460.6 ℃ to 476.7 ℃, respectively.

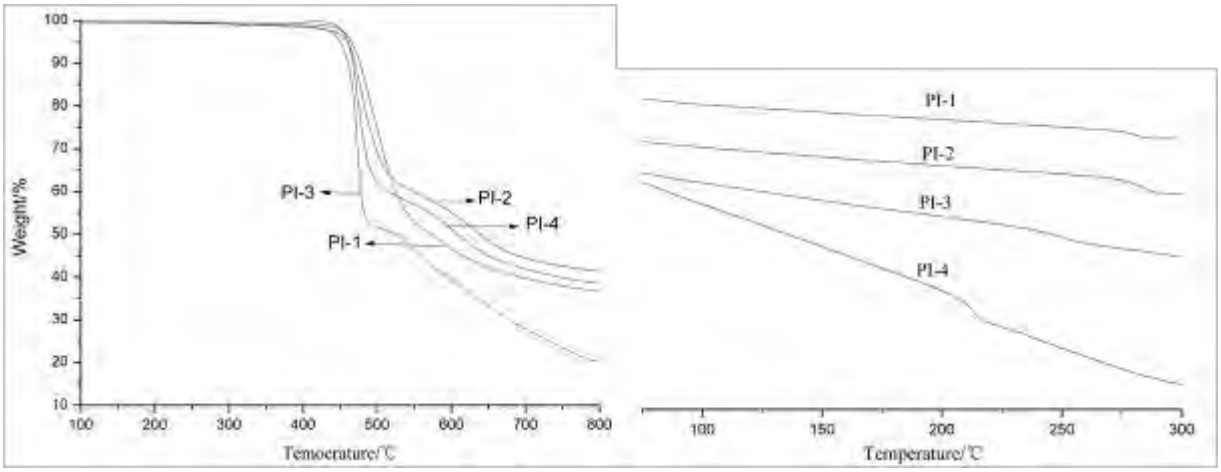


Figure 2 TGA and DSC of PIs

Table 1 $T_{5\%}$, $T_{10\%}$ and T_g of PIs

diamine monomer	dianhydride	$T_{5\%}$/℃	$T_{10\%}$/℃	T_g/℃
2,5-bis (4-aminophenoxy) isosorbide	6FDA	450.6	460.6	281.5
	BPADA	461.8	476.7	284.4
	ODPA	460.5	467.3	250.2
	BPDA	458.0	469.0	216.6

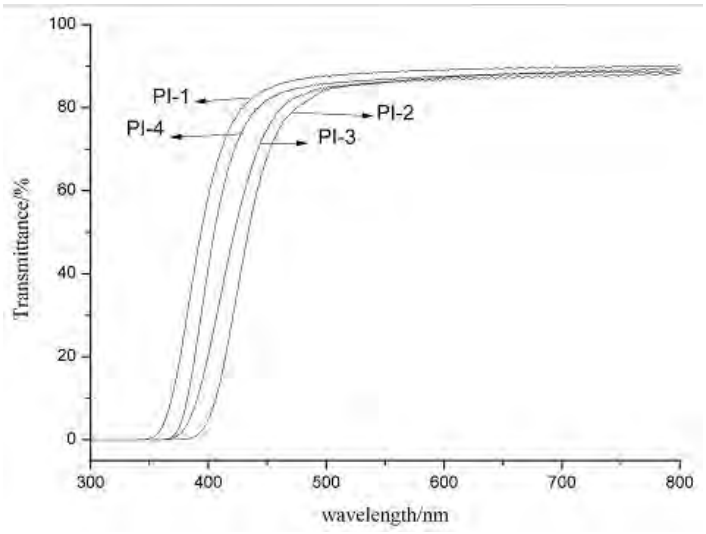


Figure 3 UV-visible spectra of the PIs.

Table 2 Optical properties of the PIs,transmittance at 450nm

PIs	Film thickness (μm)	Transmittance[a]/%
PI-1	16	84.58
PI-2	20	68.59
PI-3	19	75.12
PI-4	21	81.85

The transmittance (%) of the polyimide films at 450 nm decreased in the order of 84.58% (PI-1) > 81.85% (PI-4) > 75.12% (PI-3) >68.529% (PI-2), displaying high transparency.

Conclusions

Four kinds of polyimides based on biodegradable isosorbide were prepared and characterized Compared with analogues polyimides derived from wholly aromatic[3], those partly biodegradable polyimides showed similar thermal propertiesand thermal stability but higher transparency. These features are desirablefor polyimides as potential candidates for optical material applications and reaplcement of full petroleum derived monomers.

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