Transparent polyimide films containing 4,4'-isopropylidenedicyclohexanol (*cis*-HBPA) units: Preparation, characterization, thermal, mechanical and dielectric properties

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Abstract In order to develop colorless and soluble polyimide films, two novel monomers containing 4,4'-isopropylidenedicyclohexanol (*cis*-HBPA) unit, 4,4'-(4,4'-isopropenylbicyclohexyloxy) diphthalic anhydride (HBPADA) and 4,4'-(4,4'-isopropenylbicyclohexyloxy) dianiline (f) were designed and synthesized. PI－(1－5) were achieved from HBPADA and five kinds of aromatic diamines and PI−6 from HBPADA and semiaromatic diamine f via a two-step thermal imidization. All the polyimides could afford flexible, tough and transparent films with transparency as high as 86% at 450 nm. Surprisingly, the polyimides containing *cis*-HBPA unit exhibited excellent solubility not only in polar solvents such as N, N-dimethylacetamide, but also in other polyimide-insoluble solvents such as chloroform and dichloromethane. Additionally, analogues aromatic PI－7 derived from 4,4`-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) and 2,2-bis(4-aminophenyl)hexafluoropropane (e) were also obtained for comparation with PI−(1−6) on aspects of thermal, mechnical, optical, electrical and morphological properties. The structure-property relationships of PI−(1−7) were investigated in detail.
Keywords: Polyimide; *Cis*-HBPA; Structure-property relationships

1. INTRUDUCTION

Currently, diamines or dianhydrides containing alicyclic fragments have been favored due to their corresponding polyimides possess organic soluble, colorless as well as not worsening thermal and mechanical properties [1-4]. Hydrogenated bisphenol A (HBPA) is a diol which is derived from the hydrogenation addition of bisphenol A, due to different hydrogenation positions on carbon atoms linked with phenolic hydroxyl groups, HBPA owns two isomers including *cis*-HBPA and trans-HBPA. Both isomers possess nonplanar, flexible ether linkages and twisted molecular structure [5]. Incorporation of HBPA units into the backbone of polymers may lead to outstanding performance like good transparency, excellent durability, low viscosity and malleability, etc. [6]. Nevertheless, reports about polymers based on HBPA were rare which was largely because of the difficulty separation of the isomers.

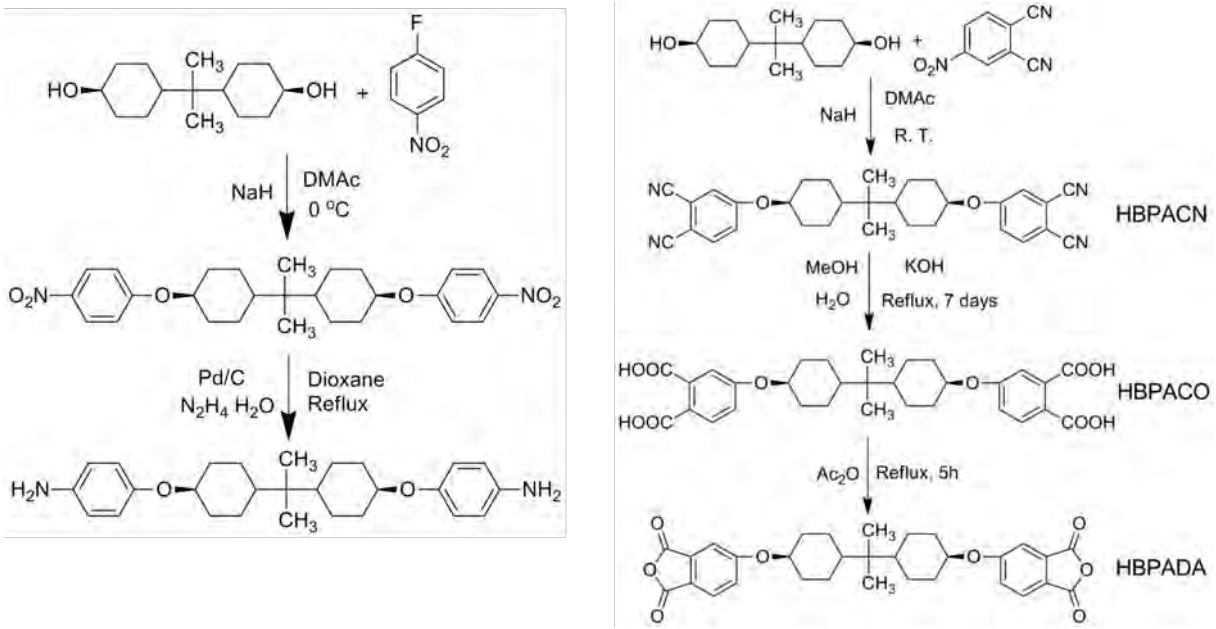
In this paper, *cis*-HBPA was successfully separated from its isomers, 4,4'-(4,4'-isopropenylbicyclohexyloxy) diphthalic anhydride (HBPADA) and 4,4'-(4,4'-isopropenylbicyclohexyloxy) dianiline (f) were prepared according to the synthetic routes presented in Scheme 1 and Scheme 2, respectively. Characterizations including FTIR, HRLC-MS, ^{1}H NMR, ^{13}C NMR, 2D NMR spectra and elemental analysis were utilized to confirm the chemical structure of monomers. PI−(1−5) displayed in Scheme 3 were achieved by the polycondensation of HBPADA and aromatic diamines, PI−6 (HBPADA/f) were derived from HBPADA and diamine f, while aromatic PI－7 (BPADA/e) was taken for comparison with that of PI－(1－6) on their morphology, solubility, thermal, mechanical, electrical and optical performance. The chemical structure of polyimdes was characterized by FTIR and ^{1}H NMR spectra. The introduction of *cis*-HBPA unit in the backbone of polyimide films was expected to simultaneously weaken the intermoleculer cohensive force and impede the formation of inter- and intramolecular charge transfer complexes, which could improve the transmittance and solubility of the polyimide films without compromising thermal and mechanical performance.

2. MATERIALS AND METHOD

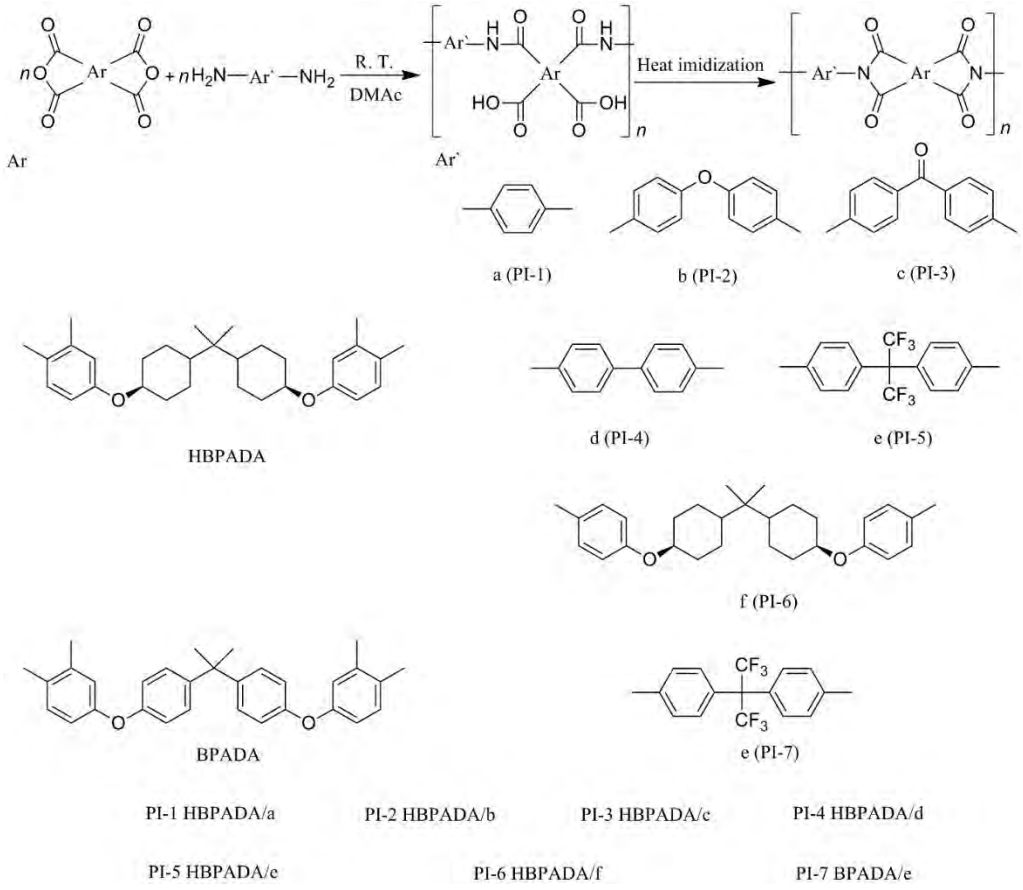
Hydrogenated bisphenol A (isomers mixture of *cis*-HBPA and trans-HBPA) was bought from Aladdin Industrial Corporation, Shanghai, China, pure *cis*-HBPA was seperated from isomers by recrystallization, and the detailed process was described in Supporting Information. P-phenylenediamine (a), 4,4'-oxydianiline (b), 4,4'-diaminobenzophenone (c), 4,4'-diaminobiphenyl (d) and 2,2-bis(4-aminophenyl)hexafluoropropane (e) were supplied by Tokyo Chemical Industry

(TCI) and used as received. 4-Nitrophthalonitrile, 60 wt% sodium hydride (NaH), potassium hydroxide (KOH) and methanol were purchased from Aldrich and used as received. The other commercially available reagents and solvents were directly used without further purification.

Diamine and dianhydride were prepared according to **Scheme 1**. PIs were synthesized in traditional two steps: synthesis of polyamic acid solution(PAA) and thermal imidization were shown in **Scheme 2**.



Scheme 1 Preparative route of diamine and dianhydride



Scheme 2 Synthesis of PIs

3. RESULT AND DISCUSSION

HBPADA was gently synthesized with satisfactory yield by the reported method in our previous work [1]. The chemical structure of the monomers was characterized by FTIR spectra, ^{1}H NMR, ^{13}C NMR and 2D NMR spectra, HRLC-MS and elemental analysis.

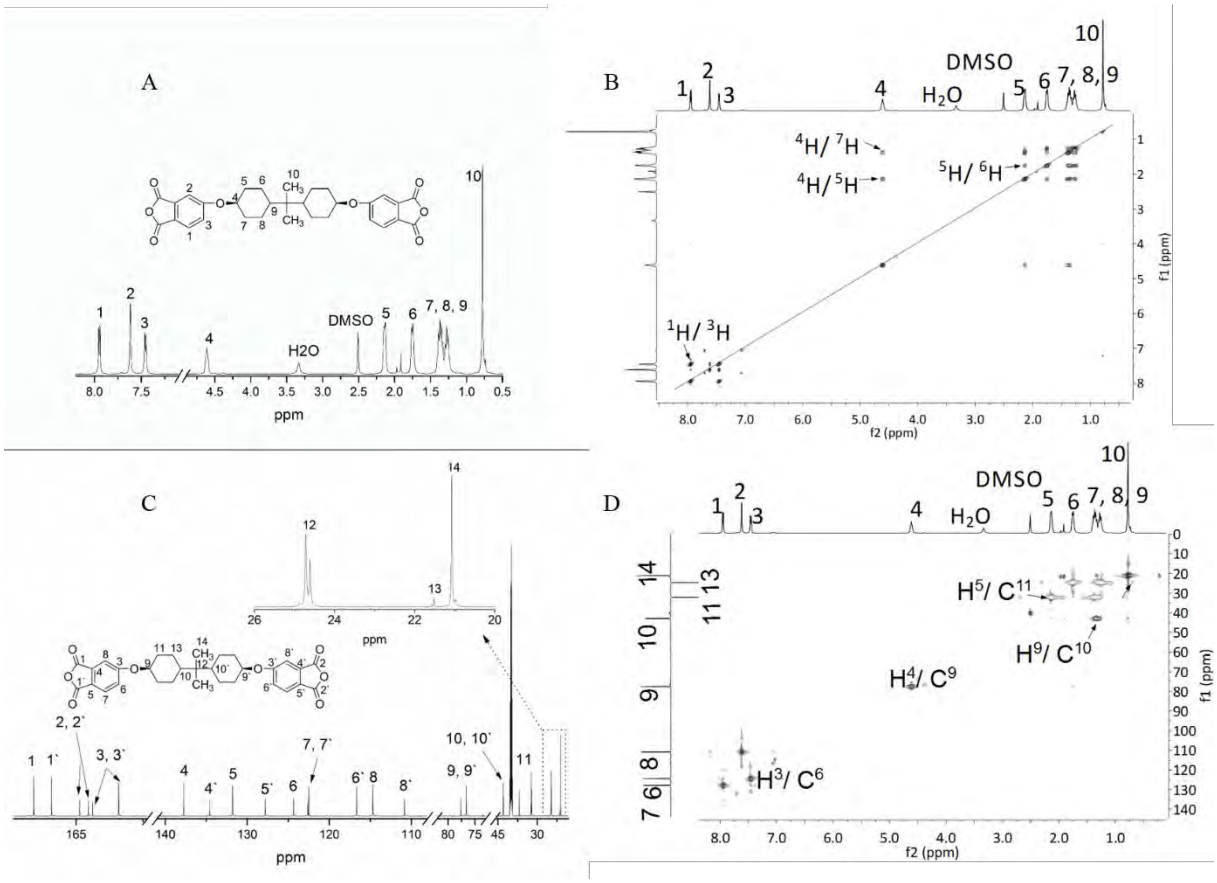


Figure 1 (A) ^{1}H NMR spectrum of HBPADA in DMSO-d_6; (B) 500 MHz correlation spectrum (COSY) of HBPADA in DMSO-d_6; (C) ^{13}C NMR spectrum of HBPADA in DMSO-d_6; (D) 500 MHz heteronuclear single quantum correlation (HSQC) spectrum of HBPADA in DMSO-d_6.

To estimate the thermal properties of PI−(1−7) from different perspectives, characterizations including DSC, DMA, TMA, and TGA were employed and the results were listed in Table 1. As shown in Figure 5 and Figure 6A, the glass transition temperature (T_g) of polyimides determinated by DSC and DMA exhibited a range of 214 − 266 °C and 210−280 °C, respectively. Accroding to the Flory theories [7] in regard with conformational rigidity of polymers: the conformational rigidity of a single molecular chain could be reasonably assumed to be dictated by the rigidity of the repeating units. For PI−(1−5), the rigid p-phenylenediamine unit endowed PI−1 (HBPADA/a) the highest T_g at 266 °C, whereas the lowest T_g of PI − 2 (HBPADA/b, 214 °C) may be a result of the flexible structure of ether linkage in 4,4'-oxydianiline residue. aromatic PI−7 (BPA/e) exhibited T_g of 219 °C, the comparison between PI−(1−6) and PI−7 demonstrated that the semiaromatic polyimides possessed similar T_g values with the analogous aromatic ones despite the introduction of aliphatic *cis*-HBPA units in the backbone of polymers.

In Table 2, In comparasion with PI−(5−7), the transparence of alicyclic segments containing PI−6 was 87%, 1% and 2% higher than that of fluorinated PI − 5 (85%) and PI − 7 (86%), respectively, explaination can be that when the aliphatic residue was in the diamine, it was less effective in reducing CT interactions than the trifluoromethyl groups in similar diamine, however, when the aliphatic structure was in the dianhydride, the situation was opposite. In other words, the alicyclic fragment in dianhydride was more determinant in transmittance of polyimides than that in diamine [2]. Additionally, a comparision of tensile strength between PI − (1 − 6) and aromatic PI − 7 (98 MPa) indicated that the

introduction of aliphatic *cis*-HBPA units into the backbone of polyimides did not compromising their mechanical properties significantly.

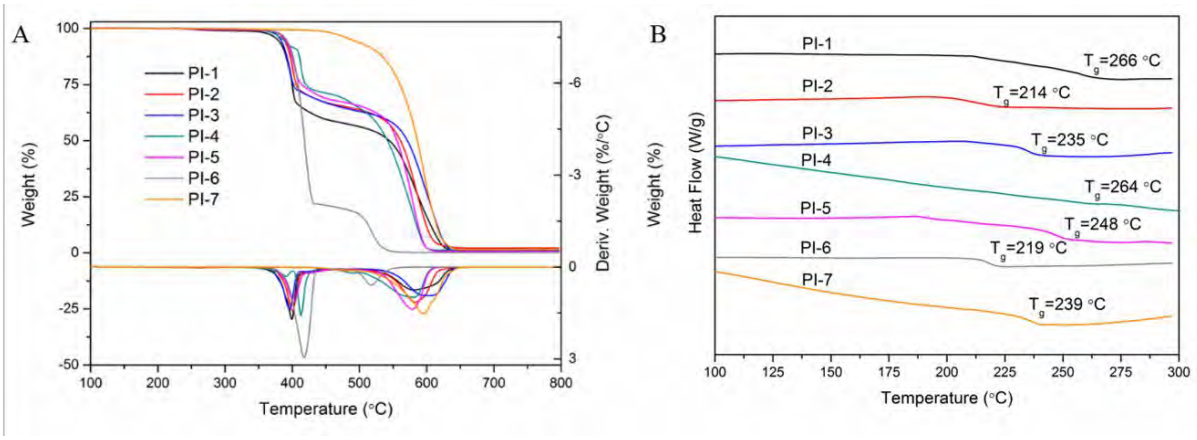


Figure 2 TGA and DSC of PIs

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

Polyimides	Aliphatic fragment (wt%)	T_g (°C)		$T_{5\%}$ (°C)		$T_{10\%}$ (°C)		R_W (°C)
		DSC	DMA	In N_2	In air	In N_2	In air	
PI–1	39	266	273	388	379	395	388	28
PI–2	34	214	210	387	382	396	395	37
PI–3	34	235	238	386	383	393	390	37
PI–4	35	264	280	407	387	411	409	36
PI–5	29	248	233	394	390	400	397	27
PI–6	52	219	221	399	391	405	399	1.8
PI–7	0	239	241	523	488	540	524	59

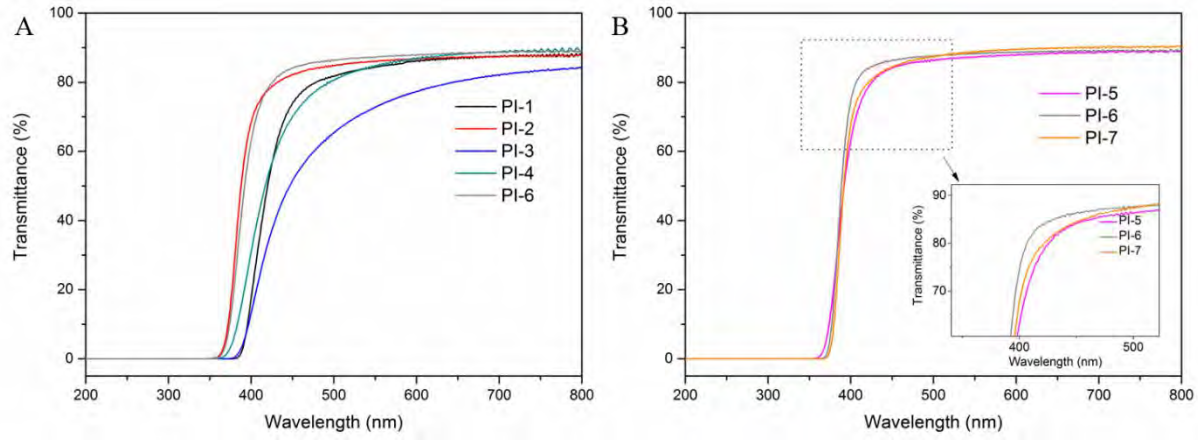


Figure 3 UV-visible spectra of the PIs.

Table 2 Optical and mechanical properties of polyimides

Polyimides	Transmittance (%, 450 nm)	Fluorine content (%)	T_S (MPa)	T_M (GPa)	E_B (%)
PI–1	74	0	122	1.4	11
PI–2	82	0	83	1.2	9
PI–3	52	0	91	1.0	10
PI–4	70	0	105	1.2	11
PI–5	84	13.7	86	0.8	8
PI–6	86	0	85	0.9	14
PI–7	85	30.7	98	1.1	9

4. CONCLUSIONS

In summary, *cis*-HBPA was separated from the isomers HBPA, and two novel monomers, HBPADA and diamine f were gently synthesized. A series of polyimides containing *cis*-HBPA units were obtained by a two-step thermal imidization. PI−(1−6) exhibited T_g and $T_{5\%}$ (in N_2) in range of 214−266 °C (DSC) and 386−407 °C respectively, and T_S in the range of 85−122 MPa, indicating that the introduction of alicyclic *cis*-HBPA fragments did not deteriorate their thermal and mechanical properties compared with the aromatic PI−7. Importantly, all the polyimide films were colorless with the transmittance as high as 86% at 450 nm, Their favorable comprehensive properties, especially outstanding transmisttance and processability combined with low dielectric constants and fine mechanical performance made these polymers ideal candidates for optoelectronic device substrates.

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