



Optically Transparent and Thermal-Stable Polyimide Films Derived from a Semi-Aliphatic Diamine: Synthesis and Properties

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A novel semi-aliphatic diamine with bulky cyclohexyl and *ortho*-substituted *tertiary* butyl groups (4,4'-(cyclohexylmethylene)bis(2-(*tert*-butyl)aniline), CHMBTBA) is synthesized via Mannich and rearrangement reactions of cyclohexanecarboxaldehyde and 2-*tert*-butylaniline. Afterward, several semi-aliphatic polyimides are prepared by the high-temperature one-pot polymerization of CHMBTBA with various aromatic dianhydrides respectively. The resulting PIs exhibit outstanding solubility in common organic solvents (i.e., trichloromethane, etc.) and are easily processed into light color or colorless transparent films (thickness: $25 \pm 1 \mu\text{m}$) by the blade coating of polymer solution. The transmittance of all resulting films is above 86% in the visible light region (400–760 nm). Their glass transition temperatures exceed 310°C and reach even to 374°C (by differential scanning calorimetry). They also display low water absorption (0.29–0.87%) and good mechanical properties (tensile strength: 50.9–87.7 MPa, Young's modulus: 2.0–2.5 GPa, elongation at break: 3.8–7.6%). Thus, they are promising potential candidates for flexible display substrates.

dielectric constants, remarkable mechanical property, and so on).^[1–3] However, the drawbacks of deep color and poor processability of conventional aromatic PIs seriously limited their applications in modern optoelectronic field, especially in flexible electronic and display technology. Generally, the present of intramolecular and intermolecular charge transfer complexes (CTC) are considered to cause the deep color of PIs, and the rigid backbones lead to the insolubility and infusibility of PIs.^[4] In addition, the processing temperature on flexible polymer substrates was usually over 300°C in the fabrication of thin-film-transistors used in flexible active matrix organic light emitting display devices.^[5] A lot of efforts have been launched to develop high-performance colorless polyimides with superior heat-resistance (glass transition

temperature (T_g) $> 300^\circ\text{C}$), suitable coefficient of thermal expansion (CTE $< 50 \text{ ppm } ^\circ\text{C}^{-1}$) and good processability.^[6] But so far, it is still a great challenge to balance the mutual restriction of colorless transparency/processability and heat-resistance/low CTE of PIs. In order to lessen or remove the deep color of PIs, the formation of CTC must be depressed by incorporating aliphatic/alicyclic moieties or asymmetric noncoplanar structures, and fluorine elements in polyimide main chains. Simultaneously these approaches could also improve the processability of PIs, but inevitably accompanying with the thermostability of PIs decreasing and the CTE or synthetic cost increasing.^[7–15]

Fortunately, the introduction of bulky pendant substituents can improve the processability and optical transparency without seriously sacrificing the thermal stability of PIs.^[16–21] In other words, PIs containing alicyclic moieties as bulky pendant substituents were more stable than those as structural units in main chains.^[22–24] In addition, our earlier works indicated *tert*-butyl as *ortho*-substituent of amino-groups in diamine was greatly enhanced the solubility of corresponding PIs while restrained the formation of CTC to improve the transparency of PI films.^[25–28] Therefore, we speculate that introducing bulky cyclohexyl and *ortho*-substituted *tertiary* butyl groups into the backbone of PIs can improve the colorless transparency as well as retain the high thermally stability. Herein, a novel diamine

1. Introduction

Over the past few decades, polyimides (PIs) were widely used in various high-tech fields on account of their excellent comprehensive performance (i.e., thermal stability, low

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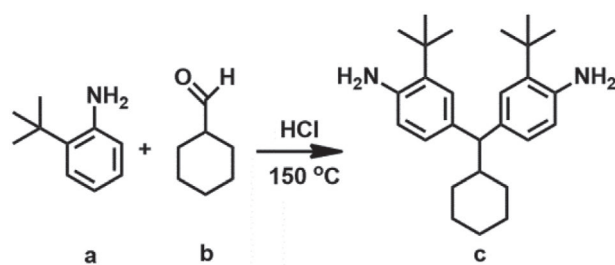
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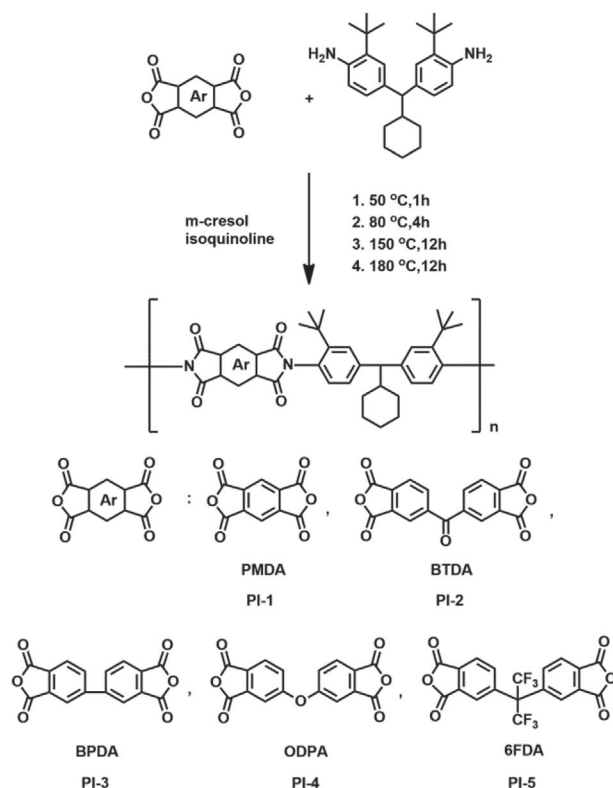
Scheme 1. Synthesis of semi-aliphatic diamine CHMBTBA.

CHMBTBA containing bulky cyclohexyl and *ortho*-substituted *tertiary* butyl groups was synthesized via Mannich and rearrangement reactions from cyclohexanecarboxaldehyde and 2-*tert*-butylaniline in the presence of hydrochloric acid (HCl). The corresponding PIs were prepared by the one-pot polycondensation of CHMBTBA with various aromatic dianhydrides and their properties were investigated in detail.

2. Results and Discussion

The synthesis processes of novel semi-aliphatic diamine CHMBTBA (c) and corresponding PIs are shown in **Scheme 1**. In the presence of HCl as the catalyst, cyclohexanecarboxaldehyde (b) was used as a linker to bridge 2-*tert*-butylaniline (TBA; a) to produce CHMBTBA. No other organic solvent was required in the reaction process because excessive TBA itself could be used as the reaction solvent.

The chemical structure of CHMBTBA was confirmed by means of ^1H NMR and ^{13}C NMR measurements in dimethyl sulfoxide (DMSO)- d_6 and the resulting spectra are shown in **Figure 1**. According to the ^1H NMR spectrum, the peaks ranging from 0.67 to 1.18 ppm and from 1.44 to 1.65 ppm were ascribed to the CH_2 protons of cyclohexane moiety, while the peak at around 1.31 ppm was assigned to the *tert*-butyl groups. The signal of amino groups appeared at about 4.48 ppm and three signals of benzene rings were found in the range from 6.48 to 7.00 ppm. Furthermore, the signals of ^{13}C NMR spectrum were also ascribed to the corresponding



Scheme 2. Synthesis of PIs from diamine CHMBTBA with various dianhydrides.

carbon atoms of CHMBTBA. The melt point of CHMBTBA was observed at 210 °C by the differential scanning calorimetry (DSC) analysis.

Furthermore, the preparation process of corresponding PIs is shown in **Scheme 2**. According to the previous studies, the reactivity of diamines was reduced by introducing *tert*-butyl groups into the *ortho*-position of amino group.^[25–28] Thus the high-temperature one-step method should be used to prepare PIs. In this study, all the PIs were synthesized in *m*-cresol with isoquinoline as the catalyst at the solid content of 10 wt% by the high-temperature one-step method.

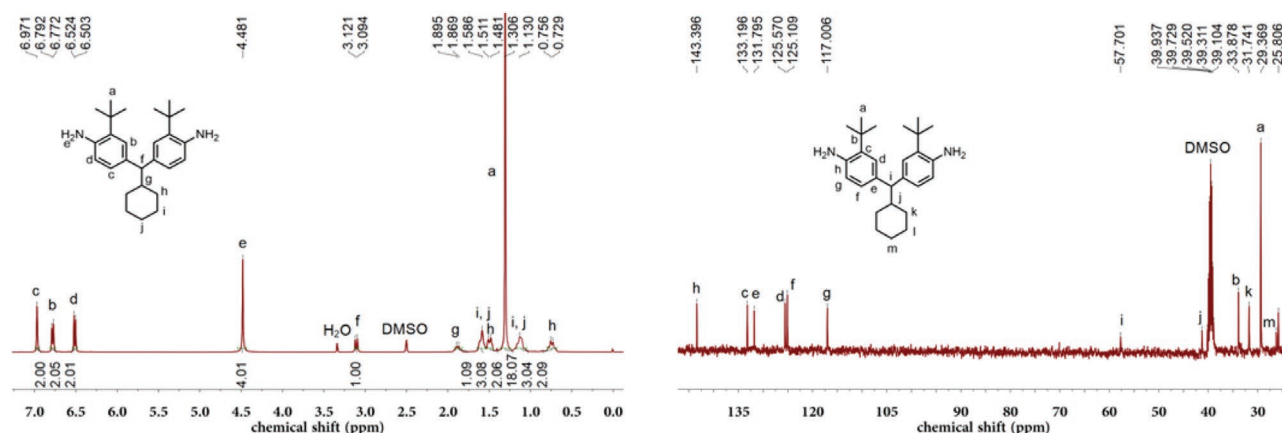


Figure 1. ^1H and ^{13}C NMR spectra of diamine CHMBTBA.

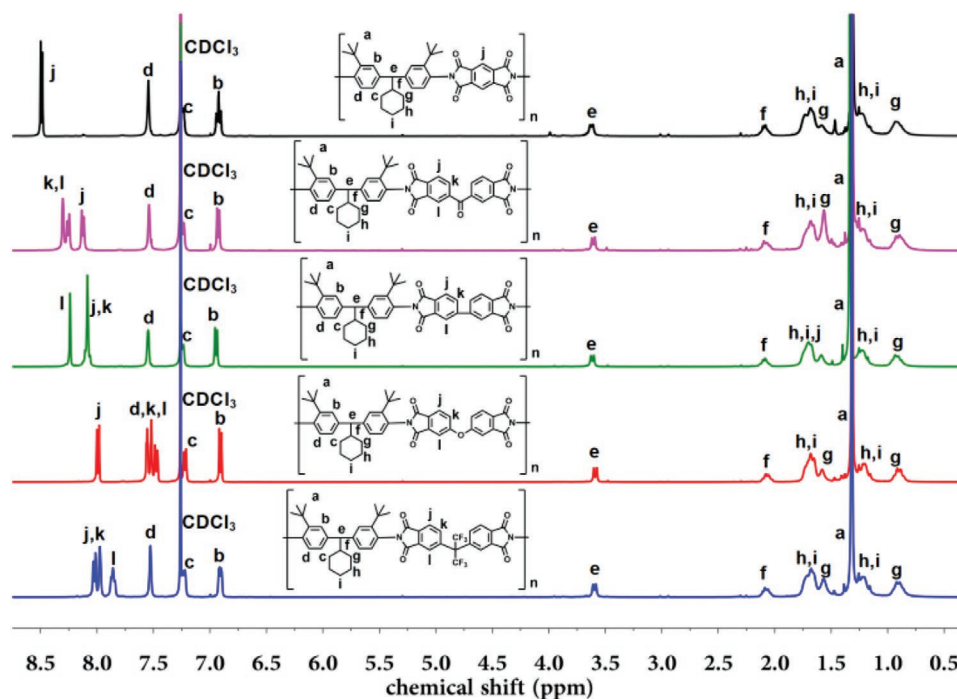


Figure 2. ^1H NMR spectra of PIs.

The resulting PIs were characterized by ^1H NMR, fourier transform infrared spectroscopy (FTIR), elemental analysis, and gel permeation chromatography (GPC) measurements. The ^1H NMR spectra are shown in **Figure 2**, and all the signals have been labeled and assigned to the corresponding protons. The FTIR spectra of the PIs are shown in **Figure 3**. As shown in the FTIR spectra, the characteristic bonds of imide units of all PIs appear at $1367\text{--}1374\text{ cm}^{-1}$ (C–N asymmetric stretching), $1725\text{--}1730\text{ cm}^{-1}$ (C=O symmetrical stretching), and $1778\text{--}1787\text{ cm}^{-1}$ (C=O asymmetrical stretching). In addition, the carbon–hydrogen bond in *tert*-butyl could be observed at $2927\text{--}2932\text{ cm}^{-1}$. No obvious signals of amide units were observed in the

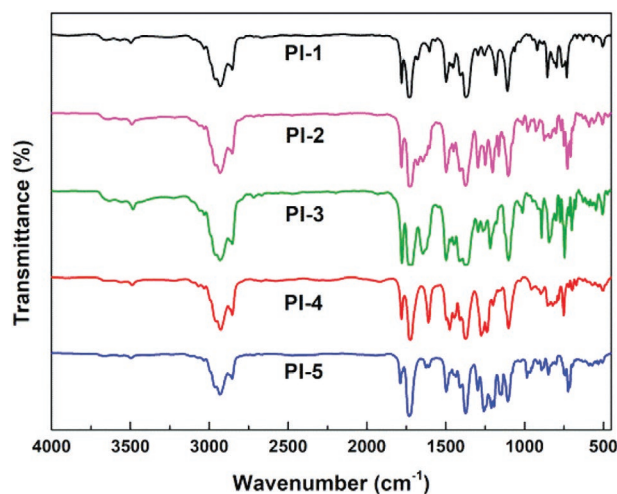


Figure 3. FTIR spectra of PIs.

region between 3220 and 3440 cm^{-1} (N–H stretching), which indicated the PIs were imidized completely.

The elemental analysis results in **Table 1** were in accordance with the theoretically calculated values of them and further confirmed their chemical structures. The number-average molecular weights (M_n) and the polydispersity indices (PDIs) of these PIs were in the range from 2.28 to 15.43×10^4 and 2.38 to 5.78 , respectively, in **Table 2**. The water absorption rates of the resulting PIs were measured at the room temperature and the data are listed in **Table 2**. Obviously, the water absorption rates were in the range from 0.28% to 0.87% , which were far lower than that of the commercial Kapton film (3.1%).^[29]

The solubility of the resulting PIs was determined by dissolving 10 mg polymer in 1 mL solvent at $25\text{ }^\circ\text{C}$ and the results are displayed in **Table 3**. All the PIs exhibited excellent solubility in various organic solvents not only polar solvents DMSO, NMP but also low boiling solvents THF, CHCl_3 , etc. Obviously the introduction of *tert*-butyl and cyclohexyl groups into PIs significantly inhibited the formation of CTC while the steric hindrance of bulky pendant groups increased interchain spacing. The synergistic effect of both enhanced the solubility of the resulting PIs.

These highly soluble PIs were easily processed into light color or colorless transparent films by the blade coating of polymer solution. The morphology of the resulting PI films was studied by X-ray diffraction (XRD) and the corresponding diffractograms were shown in **Figure 4**. Evidently, all the PI films were in amorphous patterns, which suggested the *tert*-butyl and cyclohexyl groups disturbed the packing of PI chains and decreased their packing density.

The thermal properties of the PIs were evaluated by DSC, dynamic mechanical analyzer (DMA), and thermogravimetric analysis (TGA) measurements under N_2 atmosphere. The DSC

Table 1. Elemental analysis data of PIs.

PIs	Formula		C	H	N
PI-1	$C_{37}H_{38}N_2O_4$	Calculated	77.33	6.66	4.87
		Found	76.36	6.61	4.72
PI-2	$C_{44}H_{42}N_2O_5$	Calculated	77.85	6.24	4.13
		Found	76.90	6.32	4.10
PI-3	$C_{43}H_{42}N_2O_4$	Calculated	79.36	6.50	4.30
		Found	78.57	6.61	4.25
PI-4	$C_{43}H_{42}N_2O_5$	Calculated	77.45	6.35	4.20
		Found	76.85	6.48	4.12
PI-5	$C_{46}H_{42}F_6N_2O_4$	Calculated	68.99	5.29	3.50
		Found	68.43	5.64	3.50

and DMA curves of PIs were shown in Figure 5a,b. Both of the corresponding T_g s were collected in Table 2. Accordingly, the T_g s of the resulting PIs were from 310 to 374 °C by DSC measurement as well as from 314 to 394 °C by DMA measurement. The variation trends of both agreed well with each other. Among them, PI-4 possessed the lowest T_g due to the flexible ether linkage of ODPDA dianhydride whereas PI-1 displayed the highest T_g because of the rigid structure of PMDA. Therefore, the introduction of bulky pendant groups (*tert*-butyl and cyclohexyl groups) did not decrease the T_g s of the resulting PIs because they increased the steric hindrance and hindered the motion of PI chains.

The TGA curves of the resulting PIs are displayed in Figure 5c and the values of $T_{5\%}$ were also summarized in Table 2. Evidently, all the PIs exhibited high thermal stability and maintained their weight within 5% up to 480 °C. In the same way, the introduction of *tert*-butyl and cyclohexyl groups did not sacrifice the inherent thermal stability of PIs.

The UV-vis spectra of the resulting PI films (Thickness: $25 \pm 1 \mu\text{m}$) are displayed in Figure 5d and the corresponding optical properties are listed in Table 4. The transparency of all PI films was above 86% in the visible light range (400–760 nm) and the cut-off wavelengths were in the range of 306–350 nm. In particular, the PI-5 film prepared from CHMBTBA and 6FDA had the highest average transparency (90%) and the lowest cut-off wavelength (306 nm).

The optical photographs of the PI films are shown in Figure 6 and the thickness of all the PI films was $25 \pm 1 \mu\text{m}$. Obviously PI-4 to PI-5 presented better transmittance and

Table 2. Characterization data of PIs.

PIs	$M_n \times 10^{-4}$ ^{a)} [g mol ⁻¹]	PDI ^{b)}	T_g ^{c)} [°C]	T_g ^{d)} [°C]	$T_{5\%}$ ^{e)} [°C]	Water absorption [%]
PI-1	15.43	2.38	374	394	517	0.84
PI-2	2.28	5.78	325	340	487	0.28
PI-3	7.87	3.20	352	378	500	0.87
PI-4	2.28	3.31	310	314	525	0.29
PI-5	4.97	3.72	317	322	526	0.34

^{a)} M_n , number-averaged molecular weight; ^{b)}PDI, polydispersity index; ^{c)} T_g , glass transition temperature, evaluated by DSC; ^{d)} T_g , glass transition temperature, evaluated by DMA; ^{e)} $T_{5\%}$, temperature at 5% weight loss.

Table 3. Solubility of PIs.

PIs	DMSO ^{a)}	NMP ^{b)}	CHCl ₃ ^{c)}	THF ^{d)}	acetone	Methylbenzene	<i>n</i> -Hexane
PI-1	++ ^{e)}	++	++	++	++	+ ^{f)}	– ^{g)}
PI-2	++	++	++	++	+-	+-	–
PI-3	++	++	++	++	–	+-	–
PI-4	++	++	++	++	+-	+-	–
PI-5	++	++	++	++	++	+-	–

^{a)}DMSO, dimethyl sulfoxide; ^{b)}NMP, *N*-methyl-2-pyrrolidone; ^{c)}CHCl₃, trichloromethane; ^{d)}THF, tetrahydrofuran; ^{e)}++, soluble at 25 °C; ^{f)}+-, swelled slightly or partial soluble; ^{g)}–, insoluble.

colorlessness than PI-1 to PI-3 in visible light range, which was agreed with the results of UV-vis spectra. In a word, two bulky pendant groups (*tert*-butyl and cyclohexyl groups) significantly restrained the formation of CTC and resulted in the excellent optical properties of PI films.

The dimensional stability of the PI films was evaluated by thermomechanical analysis (TMA) measurements and the values of CTE were outlined in Table 5. Generally, PIs with linear/stiff backbones usually had low CTE values due to their large packing density.^[30,31] What's more, the level of in-plane orientation of PI films played a more important part in dominating the low CTE than that of the backbone.^[32–34] However, the high molecular mobility usually caused orientational relaxation in annealing. Here, the introduction of *tert*-butyl and cyclohexyl groups was able to increase the free volume and improve the molecular mobility in the blade-coating process. Thus these PI films exhibited relatively high CTEs from 47 to 71 ppm °C⁻¹. On the other hand, the structure of dianhydrides also had effects on the CTEs of PI films. For example, PI-1 (CHMBTBA-PMDA) displayed the lowest CTE (47 ppm °C⁻¹) on the base of the rigid structure of PMDA. On the contrary, PI-4 (CHMBTBA-ODPA) showed the largest CTE (71 ppm °C⁻¹) due to the flexible ether-linkage of ODPDA with the high segmental motion. The mechanical properties of the PI films were measured by tensile tests at 25 °C and

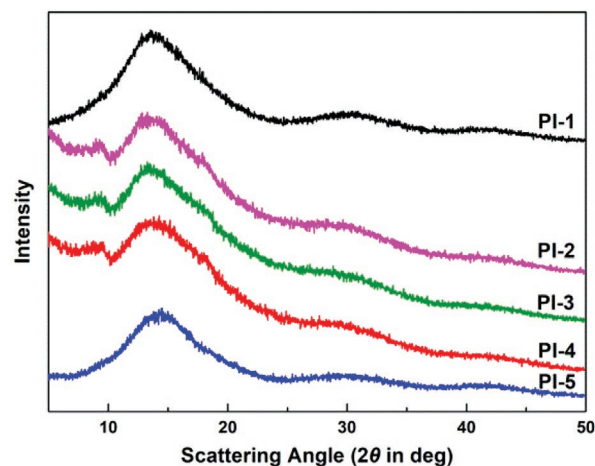


Figure 4. X-ray diffraction curves of PI films.

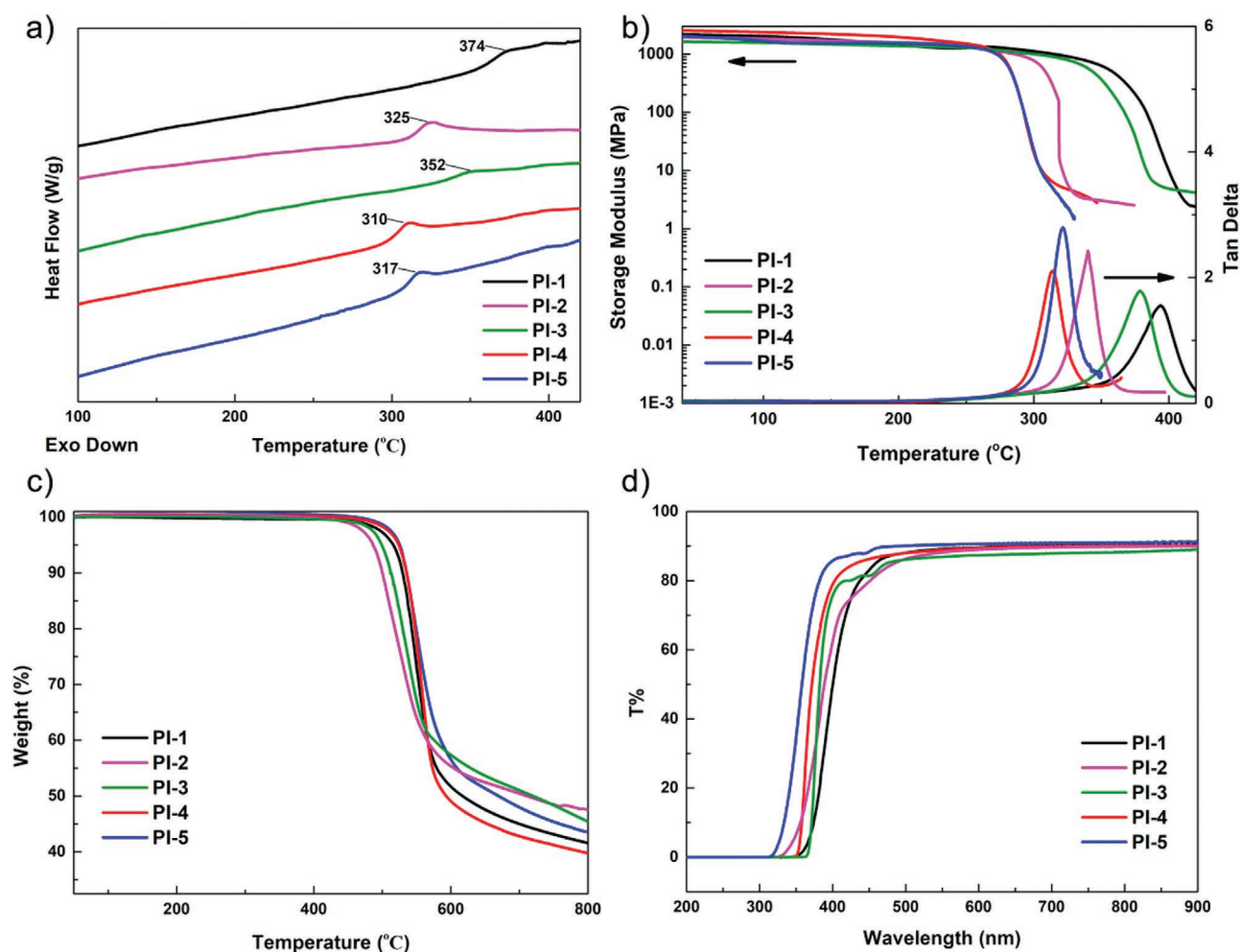


Figure 5. a) DSC curves of PIs; b) DMA curves of PIs; c) TGA curves of PIs; d) UV-vis spectra of PI films (Thickness: $25 \pm 1 \mu\text{m}$).

the results were listed in Table 3. The tensile strength values, tensile modulus, and elongation at break were in the range of 50.9–87.7 MPa, 2.0–2.5 GPa, and 3.8–7.6%, respectively.

3. Conclusions

A series of semi-aliphatic polyimides with bulky pendent *tert*-butyl and cyclohexyl groups were synthesized and

Table 4. Optical properties of PI films.

PIs	Film thickness [μm]	$T_{\text{vis}}^{\text{a})}$ [%]	$T_{400}^{\text{b})}$ [%]	$\lambda_0^{\text{c})}$ [nm]
PI-1	24	87	50	338
PI-2	26	86	62	326
PI-3	24	86	76	350
PI-4	25	88	79	343
PI-5	24	90	86	306

^{a)}The average transmittance in the visible light range (400–760 nm);

^{b)}Transmittance at 400 nm; ^{c)}UV cut-off wavelength.

characterized in detail. All of them exhibited excellent solubility and good film-forming property. The transparent and colorless tough PI films with the thickness of $25 \pm 1 \mu\text{m}$ were obtained by the blade coating. These films exhibited good mechanical properties, outstanding thermal stability, and excellent optical properties. The average transmittance of them was from 86% to 90% in the visible light range (400–760 nm) and the cut-off wavelength ranged from 306 to 350 nm. It is feasible approach to improve the transparency and reduce the color of PI films without sacrificing their thermal property by introducing *tert*-butyl and cyclohexyl groups into PI. These transparent and colorless PI films were potential candidates used as transparent flexible substrates in optical fields.



Figure 6. Optical photographs of the PI films (thickness: $25 \pm 1 \mu\text{m}$).

Table 5. Mechanical behaviors and CTEs of PIs.

Pis	Film thickness [μm]	Tensile strength [MPa]	Tensile modulus [GPa]	Elongation at break [%]	CTE [ppm °C ⁻¹]
PI-1	77	87.7	2.1	7.6	47
PI-2	42	50.9	2.0	5.3	60
PI-3	44	68.6	2.5	3.8	57
PI-4	56	71.9	2.3	6.5	71
PI-5	41	63.5	2.0	5.5	61

4. Experimental Section

Materials: 2-*tert*-Butylaniline (Changzhou Yonghe Fine Chemical Co. Ltd.) and *m*-cresol (Shanghai Macklin Biochemical Co. Ltd.) were purified by the vacuum distillation before use. Pyromellitic dianhydride (PMDA, Sinopharm Chemical Reagent Co. Ltd.), 3,3',4,4'-diphenylether tetracarboxylic dianhydride (ODPA, Adamas Reagent Co. Ltd.), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, J&K Chemical Co. Ltd.), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA, Adamas Reagent Co. Ltd.), and 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA, Shanghai Titan Scientific Co. Ltd.) were purified by recrystallization from acetic anhydride before use. Cyclohexanecarboxaldehyde (Adamas Reagent Co. Ltd.), isoquinoline (Shanghai Titan Scientific Co. Ltd.), hydrochloric acid (Sinopharm Chemical Reagent Co. Ltd.), and other materials were used as received.

Measurements: The ¹H and ¹³C NMR measurements were carried out on a 400 MHz Varian NMR spectrometer with CDCl₃ or DMSO-*d*₆ as solvents. The spectra of liquid chromatography-mass spectrometer and high resolution mass spectrometer (HRMS) were measured by ACQUITYTM UPLC & Q-TOF MS Premier. The FTIR spectra were obtained on a Perkin-Elmer Fourier transform infrared spectrometer. The molecular weights were measured with a Perkin-Elmer series 200 GPC analyzer (polystyrene calibration), using *N,N*-dimethylformamide as eluent containing 0.02 M LiBr (0.6 mL min⁻¹). Elemental analysis was performed on a vario EL cube elemental analyzer. The mechanical property of the polyimide films was performed using an INSTRON 4465 tensile tester at a drawing speed of 1 mm min⁻¹. The transparency of films (25 μm thick) was obtained on a Perkin-Elmer Lambda 20 UV-vis spectrometer. The XRD measurement was carried out on a Bruker D8 advance X-ray diffractometer using Cu/K-α radiation with 2θ in the range from 5 to 50°. The rates of water absorption were determined by immersing the vacuum-dried films in 25 °C water for 24 h and calculated from the differences of the weights. DSC curves were obtained on a TA Discovery DSC Q2000 thermal analyzer under N₂ atmosphere at a heating rate of 20 °C min⁻¹ from 40 to 420 °C. TGA was performed on a TA Discovery TGA Q5000 thermal analyzer under nitrogen at a heating rate of 20 °C min⁻¹ from 50 to 800 °C. DMA was carried out by a DMA Q800 (TA Instruments) thermal analysis system with a heating rate of 5 °C min⁻¹ and a load frequency of 1 Hz under nitrogen atmosphere. The CTE values of PI specimens (15 mm long, 6 mm wide, and above 40 μm thick) were detected through TMA on a Mettler Toledo TMA/SDTS841e thermal analyzer system under nitrogen at a heating rate of 10 °C min⁻¹ from 50 to 200 °C with a 0.02 N expansion force.

Synthesis of CHMBTBA: A total of 50 g (0.3350 mol) 2-*tert*-butylaniline and 5.7 mL (0.067 mol) hydrochloric acid (36–38 wt%) were added into a 250 mL three-necked flask under the stirring and nitrogen atmosphere. After heating the above mixture to 120 °C, 15.03 g (0.1340 mol) cyclohexanecarboxaldehyde was added dropwise over 1 h. Then it was heated to 150 °C and kept at this temperature for 10 h. When the mixture was cooled to 25 °C, 13.4 mL (0.201 mol) aqueous ammonia (28–30 wt%) and 50 mL CH₂Cl₂ were added into it. After washing with water (3 × 50 mL) and concentration under reduce pressure, some brown oil was obtained. The resulting oil was distilled

and collected through fraction boiling at 240–250 °C (25 Pa) to give some yellow solid. The solid was further purified by recrystallization in anhydrous alcohol to afford colorless CHMBTBA needles. Yield: 39%; melting point: 210 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.97 (s, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 2H), 4.48 (s, 4H), 3.11 (d, *J* = 10.8 Hz, 1H), 1.88 (d, *J* = 10.5 Hz, 1H), 1.59 (s, 3H), 1.50 (d, *J* = 12.1 Hz, 2H), 1.31 (s, 18H), 1.13 (s, 3H), 0.74 (d, *J* = 11.1 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 143.40, 133.20, 131.80, 125.34, 117.01, 33.88, 31.74, 29.37, 26.02. HRMS (ESI, *m/z*): [M+H]⁺ calculated for C₂₇H₄₁N₂⁺, 393.3270; found, 393.3264.

Synthesis of PIs: All the PIs were synthesized by a high-temperature one-pot method. As a typical example, the polyimide of CHMBTBA-6FDA was synthesized according to the following procedure. 5 g (0.0127 mol) CHMBTBA, 5.642 g (0.0127 mol) 6FDA, 60 mL *m*-cresol, and ten drops isoquinoline were added into a 250 mL three-necked flask and the mixture was stirred at 50 °C for 1 h under N₂ atmosphere. Then the mixture was raised successively to 80 °C for 4 h, 150 °C for 12 h, and 180 °C for 12 h. After cooled to 25 °C, 30 mL chloroform was added into the viscous mixture. Then the mixture was poured slowly into 500 mL methanol under the vigorous stirring to afford some white fiber-like precipitate. The polyimide was collected by filtration and dried in vacuum at 100 °C for 24 h. The polyimide was purified by precipitating twice.

PI-5 (CHMBTBA-6FDA): Yield: 92%. FTIR (blade-coating film, cm⁻¹): ν = 2932 (CH₂-H), 1787 (C=O), 1730 (C=O), 1607, 1497, 1374 (C-N), 1257, 1146, 1106, 984, 848, 724, 570. ¹H NMR (400 MHz, CDCl₃) δ 8.08–7.95 (m, 4H), 7.85 (d, 2H), 7.53 (s, 2H), 7.23 (m, 2H), 7.00–6.83 (m, 2H), 3.61 (m, 1H), 2.06 (s, 1H), 1.67 (m, 3H), 1.50 (m, 2H), 1.32 (s, 18H), 1.28–1.16 (m, 3H), 0.92 (m, 2H).

Other polyimides were synthesized by the same procedure as that of CHMBTBA-6FDA.

PI-1 (CHMBTBA-PMDA): Yield: 96%. FTIR (blade-coating film, cm⁻¹): ν = 2931 (CH₂-H), 1780 (C=O), 1729 (C=O), 1603, 1497, 1372 (C-N), 1182, 1108, 856, 733, 505. ¹H NMR (400 MHz, CDCl₃) δ 8.49 (m, 2H), 7.54 (s, 2H), 7.23 (m, 2H), 6.92 (m, 2H), 3.63 (m, 1H), 2.08 (s, 1H), 1.66 (s, 3H), 1.53 (s, 2H), 1.31 (m, 18H), 1.24 (m, 3H), 0.93 (s, 2H).

PI-2 (CHMBTBA-BTDA): Yield: 96%. FTIR (blade-coating film, cm⁻¹): ν = 2932 (CH₂-H), 1778 (C=O), 1727 (C=O), 1644, 1497, 1367 (C-N), 1217, 1101, 892, 844, 746, 701, 505. ¹H NMR (400 MHz, CDCl₃) δ 8.39–8.21 (m, 4H), 8.13 (m, 2H), 7.54 (s, 2H), 7.23 (s, 2H), 6.95 (m, 2H), 3.62 (m, 1H), 2.06 (m, 1H), 1.68 (m, 5H), 1.29 (m, 18H), 1.18 (m, 3H), 0.91 (m, 2H).

PI-3 (CHMBTBA-BPDA): Yield: 97%. FTIR (blade-coating film, cm⁻¹): ν = 2931 (CH₂-H), 1780 (C=O), 1729 (C=O), 1603, 1497, 1372 (C-N), 1182, 1108, 856, 733, 505. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 2H), 8.09 (m, 4H), 7.53 (d, 2H), 7.25 (m, 2H), 6.96 (m, 2H), 3.63 (m, 1H), 2.08 (m, 1H), 1.79 (m, 5H), 1.34 (s, 18H), 1.22 (m, 3H), 0.92 (m, 2H).

PI-4 (CHMBTBA-ODPA): Yield: 94%. FTIR (blade-coating film, cm⁻¹): ν = 2927 (CH₂-H), 1780 (C=O), 1725 (C=O), 1609, 1475, 1373 (C-N), 1275, 1102, 843, 751, 501. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (m, 2H), 7.53 (m, 6H), 7.23 (m, 2H), 6.91 (m, 2H), 3.60 (m, 1H), 2.08 (s, 1H), 1.68 (s, 3H), 1.54 (s, 2H), 1.32 (m, 18H), 1.25 (m, 3H), 0.90 (m, 2H).

Film Preparation: The polyimide films were prepared by the blade-coating method. A typical procedure to prepare CHMBTBA-6FDA film (Thickness: 25 ± 1 μm) was as follows: 2.9577 g CHMBTBA-6FDA was dissolved in 60 mL *N,N*-dimethylacetamide and the solution was kept at 60 °C for 12 h. The solution was filtered by a 0.7 μm fiberglass syringe filter and then blade-coated on a clean glass substrate at 60 °C by using Elcometer 4340 Automatic Film Applicator. The blade height and coating speed were set to 500 μm and 0.2 inches s⁻¹, respectively. The solution on the glass substrate was kept 60 °C to evaporate the solvent for 4 h to form film, and then dried under vacuum at 100 °C for 6 h and 200 °C for 12 h to remove the residual solvent. After cooling down to 25 °C, the polyimide film was obtained by immersing the glass substrate in deionized water.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

colorlessness, films, polyimides, semi-aliphatic diamine, transparency

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