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Soluble aromatic polyimides with high glass transition temperature from benzidine containing *tert*-butyl groups

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Abstract A series of soluble polyimides with high glass transition temperature (T_g) were prepared from four commercial aromatic dianhydrides (i.e., BPDA, OPDA, 6FDA and BPADA) with a rigid aromatic diamine containing *tert*-butyl groups (3,3′-di-*tert*-butylbenzidine) (**1**). The number-average molecular weights of them were in the range from 4.21×10^4 to 1.25×10^5 with the polydispersity indexes between 2.34 and 3.04 by means of gel permeation chromatography relative to a polystyrene standard. They were able to form transparent, flexible and tough films by polymer solution casting. The transmittance of them was higher than 90 % in a wavelength range of 400–700 nm by UV–vis measurement. The XRD results demonstrated that they were amorphous glassy polymers. Except for polyimide **1**-BPADA, the T_gs of the rest were higher than 330 °C, and especially the T_g of polyimide **1**-BPDA reached up to 375 °C. They did not show appreciable decomposition up to 500 °C under a nitrogen atmosphere, in other words, the 5 % weight losses of them were in the range from 508 to 523 °C. Most of them exhibited high tensile strength and modulus with a low elongation at break at room temperature. They are potential candidates for high performance materials.

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Abbreviations

BPDA	3,3′,4,4′-biphenyltetracarboxylic dianhydride
OPDA	3,3′,4,4′-diphenylether tetracarboxylic dianhydride
6FDA	2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride
BPADA	2,2-bis [4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride

Introduction

Aromatic polyimides are a very interesting polymer family with incredibly strong mechanical properties and astoundingly heat and chemical resistant. They often replace glass and metals, such as steel, in many demanding industrial applications, including advanced composites, engineering plastics and so on [1]. Polyimides are even used in many everyday applications, such as used for the struts and chassis in some cars as well as some parts under-the-hood because they can withstand the intense heat and corrosive lubricants, fuels, and coolants cars require. They can also be used in circuit boards [2], insulation [3], fibers for protective clothing [4], composites and adhesives [5, 6]. However, the commercial applications of traditional aromatic polyimides are limited because of their poor solubility and high softening or melting temperatures [7]. Therefore, the processing is usually carried out with a poly(amic acid) intermediate, which then can be converted into the polyimide via rigorous thermal treatment or chemical treatment. Unfortunately, this process has some inherent drawbacks, such as the release of volatile byproducts (e. g., H_2O) and the storage instability of poly(amic acid) [8]. In order to overcome such problems, many considerable efforts have been made to improve the solubility and melting processability of polyimides in completely imidized form, including the

incorporation of flexible linkages [9–16], aliphatic moiety [17, 18], fluorine atoms and bulky pendent groups into the polymer backbone during the past decades [19–23]. Generally the incorporation of flexible linkages and aliphatic moiety into the backbones may deteriorate the inherent thermal performance of polyimides, especially result in the decreasing of T_gs [9–18]. Meanwhile the introduction of fluorine atoms into the backbone may drastically increase the cost of polyimides. On the contrary, the introduction of bulky pendent groups into the backbone can not only improve the processability of polyimides through destroying the close-packing of their backbones, but also maintain the high T_g of polyimides by reducing the torsional mobility of their main chains [24].

According to some previous reports, *tert*-butyl groups have been introduced into aromatic polyimides as a large pendent group in order to improve their solubility without sacrificing thermal stability [25–29]. However, most of them have relatively lower T_gs comparing with traditional aromatic polyimides due to one or more flexible linkage existing in their repeating units. Early this century, we also synthesized some highly soluble aromatic polyimides with better thermal stability by attaching *tert*-butyl groups to the polyimide backbones [30, 31]. Nevertheless, there is a flexible linkage (−CH$_2$-) still between the two benzene rings of the diamine 4,4′-methylenebis(2-tertbutylaniline) (MBTBA) resulting in a relatively lower T_gs. In this paper, we first synthesized a more rigid aromatic diamine 3,3′-di-*tert*-butylbenzidine (**1**) containing *tert*-butyl groups but without a flexible linkage between the two benzene rings. Then a series of aromatic polyimides were prepared from diamine **1** and various commercial dianhydrides. We expect these polyimides can possess the high T_gs while still keep the good solubility and thermal stability.

Experimental

Materials

2-*tert*-butylaniline (Wuxi TPW Pharmaceutical Technology Co. Ltd.) was purified by distillation under reduced pressure before use. *m*-Cresol (Sinopharm Chemical Reagent Co. Ltd.) was purified by the vacuum distillation over P$_2$O$_5$ before used. Pyromellitic dianhydride (PMDA, Sinopharm Chemical Reagent Co. Ltd.), 3,3′,4,4′-diphenylether tetracarboxylic dianhydride (OPDA, TCI Chemicals), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA, J&K Chemical Co. Ltd.), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, J&K Chemical Co. Ltd.), 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA, J&K Chemical Co. Ltd.) and 2,2-bis [4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA, Shanghai Research Institute of Synthesis Resins) were

recrystallized from acetic anhydride and dried under vacuum at 150 °C for 12 h before used. Isoquinoline (J&K Chemical Co. Ltd.) and other materials purchased from domestic chemical markets were used without further purification.

Measurement

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Varian NMR spectrometer with DMSO-d_6 and CDCl$_3$ as solvents. The FTIR spectra were measured with a Perkin-Elmer Fourier transform infrared spectrometer. The mechanical behaviour of the polyimide films was performed by a CMT-4104 (SANS, Shenzhen, China) tensile tester with a crosshead speed of 1 mm/min at 25±2 °C. The X-ray diffraction (XRD) data were recorded on a Rigaku D/max-2200/PC X-ray diffractometer using Cu/K-α radiation with 2θ in the range from 5 to 40°. The molecular weights of the polymers were evaluated by a Perkin-Elmer Series 200 gel permeation chromatography (GPC) analyzer relative to polystyrene standards. The UV–vis spectra were obtained on Perkin-Elmer Lambda 20 spectrometer. Differential scanning calorimetry (DSC) was carried out on a PE Pyris-1 thermal analyzer under nitrogen atmosphere at a heating rate of 20 °C/min from 40 to 430 °C. Thermogravimetric analysis (TGA) was performed on a PE Pyris-7 thermal analyzer under nitrogen at a heating rate of 20 °C/min from 50 to 800 °C. The molecular weight of diamine **1** was measured with a waters Q-Tof Premier mass spectrometry.

Intermediate and monomer synthesis

2-*tert*-Butyl-4-iodo-phenylamine (**2**)

1.49 g (10 mmol) 2-*tert*-butylaniline, 1.50 g (18 mmol) NaHCO$_3$ were added into 10 mL vigorously stirred deionized water in a 50 mL single-neck flask. The mixture was cooled to 0 °C and then 2.54 g (10 mmol) I$_2$ was added into it in batches. The reaction mixture was warmed up to room temperature and kept stirring constantly at room temperature for 12 h. The reaction mixture was further diluted with additional 10 mL deionized water and extracted with CH$_2$Cl$_2$ (3×10 mL). The combined organic layer was washed with 10 mL saturated NaHSO$_3$ solution, 10 mL saturated NaHCO$_3$ solution, 10 mL deionized water and at last dried with anhydrous Na$_2$SO$_4$ overnight. After filtration and concentration under reduce pressure, some black oil was obtained. It was purified by column chromatography to give 2.39 g yellow oil (**2**). Yield: 87 %; ^{1}H NMR (400 MHz, CDCl$_3$, δ) 7.47 (d, *J*=2 Hz, 1H; Ar-H), 7.29 (dd, *J*=8, 2 Hz, 1H; Ar H), 6.42 (d, *J*=8 Hz, 1H; Ar H), 1.39 (s, 9H; CH$_3$); ^{13}C NMR (101 MHz, CDCl$_3$, δ) 170.53 (Ar C), 144.37 (Ar C), 135.21 (Ar C), 134.87 (Ar C), 119.42 (Ar C), 59.93 (Ar C), 28.87 (C), 20.49 (CH$_3$).

3,3′-Di-tert-butylbenzidine (1)

483 mg (1.755 mmol) **2**, 19.7 mg (0.088 mmol) Pd(OAc)$_2$, 282 mg (0.876 mmol) tetrabutylammonium bromide, 186 mg (1.346 mmol) K$_2$CO$_3$ were added to a stirring mixture of 0.875 mL i-PrOH, 3.948 mL DMF and 1.535 mL deionized water under N$_2$ atmosphere. The reaction mixture was heated to and kept at 110 °C for 12 h under the stirring. 30 mL EtOAc was added into after the reaction mixture was cooled to room temperature. The organic layer was separated by the separatory funnel, washed with deionized water (3×20 mL) and dried with anhydrous Na$_2$SO$_4$. Some red oil was produced after the filtration and concentration under the reduce pressure. After purified by column chromatography, the crude production of **1** was obtained. Furthermore, it was purified by recrystallization in ethanol for three times and afford 132 mg light red solid **1**. Yield: 51 %; M. p.: 137.02 °C (determined by means of DSC measurement); ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.23 (d, J=2 Hz, 2H; Ar H), 7.08 (dd, J=8, 2 Hz, 2H; Ar H), 6.69 (d, J=8 Hz, 2H; Ar H), 4.70 (s, 4H; NH$_2$), 1.38 (s, 18H); ^{13}C NMR (101 MHz, CDCl$_3$, δ): 143.03 (Ar C), 133.81 (Ar C), 132.42 (Ar C), 125.11 (Ar C), 125.06 (Ar C), 118.15 (Ar C), 34.34 (C), 29.61 (CH$_3$). HRMS (ESI, m/z): [M+H]$^+$ calcd for C$_{20}$H$_{29}$N$_2$, 297.2331; found, 297.2325.

Polymer synthesis

All the polyimides were synthesized by one-pot polycondensation and a typical procedure displayed as follows (e.g., **4b 1**-BPDA). A 50 mL three necked flask with a nitrogen inlet and a mechanical stirring was charged with 500 mg (1.687 mmol) **1**, 15 mL m-cresol, 496.2 mg (1.687 mmol) BPDA and two drops of isoquinoline under N$_2$ atmosphere. The mixture was stirred and smoothly heated to 85 °C until the solids dissolved completely, and further kept stirring at this temperature for 12 h. Then the temperature of the reaction mixture was processed with the following heating programs, at 100 °C for 0.5 h, 120 °C for 12 h, 150 °C for 12 h and 220 °C for 12 h. After cooling to room temperature, the resulting viscous mixture was diluted by 20 mL CHCl$_3$ under the stirring. Finally, the transparent polyimide solution was poured slowly into 500 mL vigorously stirred methanol to afford a fiber-like precipitate. After filtration, the precipitated polyimide was washed with methanol repeatedly, collected and dried under vacuum at 100 °C for 24 h. For further purification, the polyimide **4b** was reprecipitated twice from DMAc into methanol. Yield is 890 mg (95 %).

4b (1-BPDA)

Yield: 95 %. IR (solution casting film, cm^{-1}): ν=3,648 (−NH or H$_2$O), 3,485 (−NH or H$_2$O), 3,037, 2,964 (CH$_2$-H), 1,779

(C = O), 1,721 (C = O), 1,621, 1,489, 1,369 (C-N), 1,261, 1,215, 1,100, 865, 824, 746, 701, 635, 498. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.56 (m, 4H; Ar H), 8.24 (s, 2H; Ar H), 7.95 (s, 2H; Ar H), 7.78 (s, 2H; Ar H), 7.60 (s, 2H; Ar H), 1.43 (s, 18H; CH$_3$) ppm. ELEM. ANAL. Calcd. for (C$_{36}$H$_{30}$N$_2$O$_4$)$_n$: C, 77.96 %; H, 5.45; N, 5.05 %. Found: C, 77.18; H, 5.57; N, 5.00 %.

4d (1-OPDA)

Yield: 97 %. FTIR (solution casting film, cm^{-1}): 3,489 (−NH or H$_2$O), 3,067, 2,964 (CH$_2$-H), 1,780 (C=O), 1,724 (C = O), 1,609, 1,475, 1,369 (C-N), 1,275, 1,101, 956, 866, 810, 751, 696, 634, 575, 497. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.13 (s, 2H; Ar H), 7.84 (s, 2H; Ar H), 7.79–7.62 (m, 6H; Ar H), 7.49 (s, 2H; Ar H), 1.33 (s, 18H; CH$_3$) ppm. ELEM. ANAL. Calcd. for (C$_{36}$H$_{30}$N$_2$O$_5$)$_n$: C, 75.77; H, 5.30; N, 4.91 %. Found: C, 75.05; H, 5.36; N, 4.91 %.

4e (1-6FDA)

Yield: 98 %. FTIR (solution casting film, cm^{-1}): 3,651 (−NH or H$_2$O), 3,497 (−NH or H$_2$O), 2,964 (CH$_2$-H), 1,788 (C = O), 1,729 (C = O), 1,625, 1,488, 1,370 (C-N), 1,258, 1,193, 1,146, 1,104, 1,021, 985, 866, 815, 724, 712, 636, 572, 498. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.22 (d, J=7 Hz, 2H; Ar H), 7.98 (s, 2H; Ar H), 7.91 (d, J=8 Hz, 2H; Ar H), 7.84 (s, 2H; Ar H), 7.67 (s, 2H; Ar H), 7.53 (s, 2H; Ar H), 1.32 (s, 18H; CH$_3$) ppm. ELEM. ANAL. Calcd. for (C$_{39}$H$_{30}$F$_6$N$_2$O$_4$)$_n$: C, 66.47; H, 4.29; N, 3.98 %. Found: C, 66.41; H, 4.64; N, 3.80 %.

4f (1-BPADA)

Yield: 92 %. FTIR (solution casting film, cm^{-1}): 3,486 (−NH or H$_2$O), 3,037, 2,967 (CH$_2$-H), 2,688 (CH$_2$-H), 2,346, 1,902, 1,779 (C = O), 1,725 (C = O), 1,602, 1,480, 1,368 (C-N), 1,276, 1,239, 1,172, 1,100, 1,015, 953, 853, 752, 697, 635, 548, 498. 1H NMR (400 MHz, DMSO-d_6, δ): 7.99 (s, 2H; Ar H), 7.81 (s, 2H; Ar H), 7.63 (s, 2H; Ar H), 7.39 (s, 8H; Ar H), 7.16 (s, 6H; Ar H), 1.72 (s, 6H; Ar H), 1.28 (s, 18H; CH$_3$) ppm. ELEM. ANAL. Calcd. for (C$_{51}$H$_{44}$N$_2$O$_6$)n: C, 78.44; H, 5.68; N, 3.59 %. Found: C, 78.39; H, 5.82; N, 3.55 %.

Results and discussion

Monomer synthesis

The diamine monomer **1** was synthesized according to a previous report and the detailed synthetic route was outlined in Scheme 1 [32]. Firstly, an iodine substituted intermediate **2**

Scheme 1 Synthesis of the rigid diamine 1
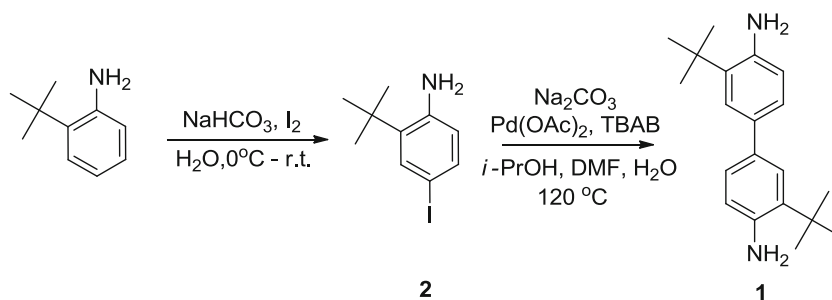
was prepared through the electrophilic substitution of 2-*tert*-butylaniline with I_2 on the mild reaction condition. Then, the compatible reaction condition was adopted in the Ullmann coupling reaction of intermediate **2** itself to synthesize diamine **1** due to the existence of sensitive amino groups [33]. That is, $Pd(OAc)_2$ was used directly and reduced in situ into

Fig. 1 ^1H and ^{13}C NMR spectra of 3,3′-di-*tert*-butylbenzidine (1)
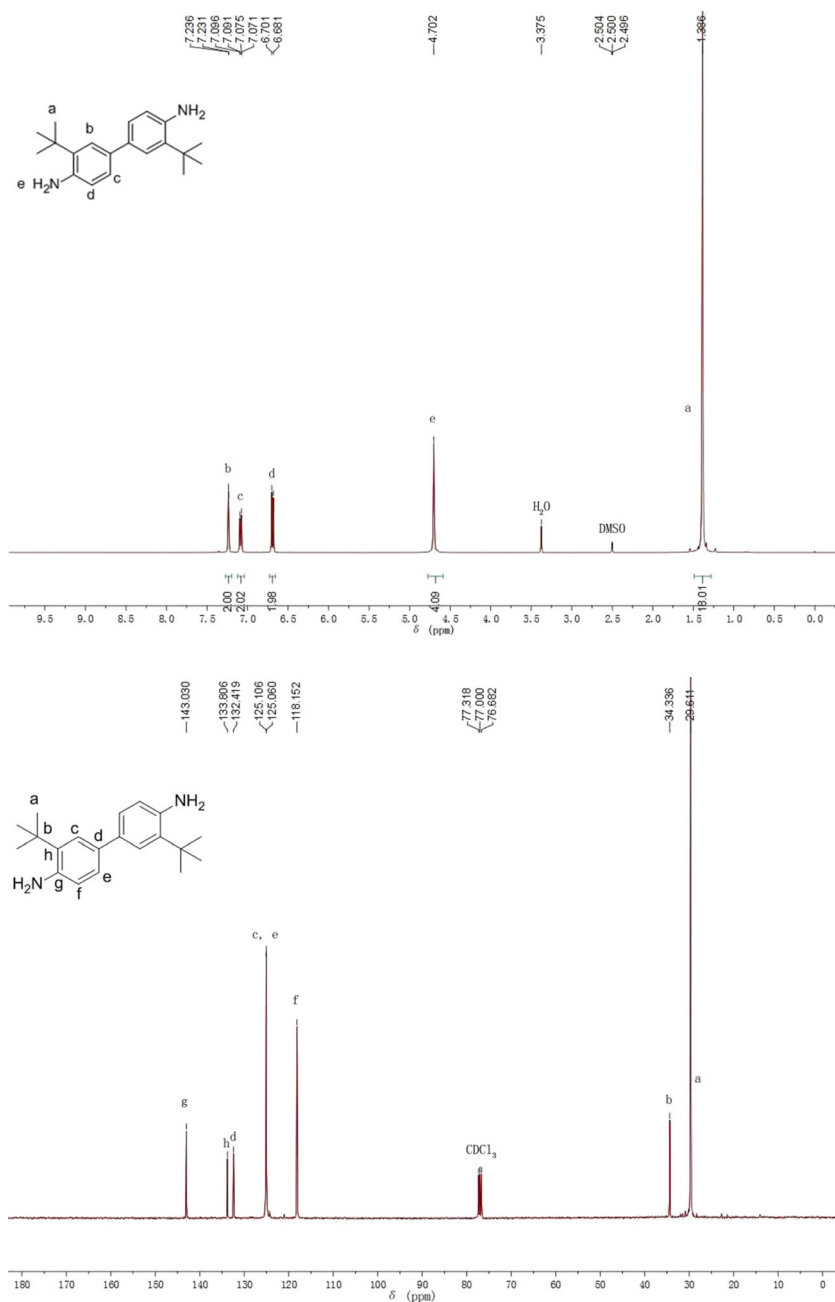
the palladium Pd(0) with catalytic activity by isopropanol among the Ullmann reaction process. Furthermore, the equivalent tetrabutylammonium bromide was added into the reaction mixture as a phase transfer catalyst to conduce to the reaction proceeding homogeneously. Finally the coupling product **1** was obtained through the oxidative addition and reductive elimination reactions. The chemical structure of the resulting diamine **1** was confirmed by ^{1}H NMR and ^{13}C NMR spectra (Fig. 1). The melting point of diamine **1** was observed at 137.0 °C from the DSC analysis curve as a sharp endothermic peak, which is higher than that of MBTBA (82.6 °C).

Polymer synthesis and characterization

The synthetic route of all polyimides is outlined in Scheme 2. In general, polyimides can be prepared from the polycondensation of a diamine and a dianhydride through either a two-step approach or a one-pot method [1]. Our previous research demonstrated that the reactivity of diamine was decreased heavily when the *tert*-butyl groups were introduced into the ortho-position of amino group in aromatic diamine due to the steric hindrance of large substituent groups [30, 31]. In the same way, the reactivity of diamine **1** was much less than that of benzidine so that a one-pot polycondensation in solution at a high temperature was adopted too in this study.

PMDA was first adopted to react with diamine **1** to synthesize polyimide because PMDA is the cheapest, smallest and most rigid aromatic dianhydride. We anticipated that the resulting polyimide may possess good solubility as well as high T_g due to the introduction of pendent *tert*-butyl groups into the polymer chains reducing the interaction among polyimide backbones as well as the rigid structure of PMDA and diamine **1**. Unfortunately, the reaction mixture became non-transparent and some light yellow powder appeared even with a solid content of 1 wt% when the reaction temperature was improved to 100 °C. In other words, the introduction of *tert*-butyl groups into benzidine is not enough to overcome the rigidity of PMDA and benzidine to produce a soluble polyimide. Then another relatively rigid aromatic dianhydride BPDA was selected to polymerize with diamine **1**. When the solid content was maintained lower than 6 wt%, the reactive mixture was kept transparent consistently in the whole polymerization process, i.e., under the following heating program: heated slowly to 85 °C and kept for 12 h, then at 100 °C for

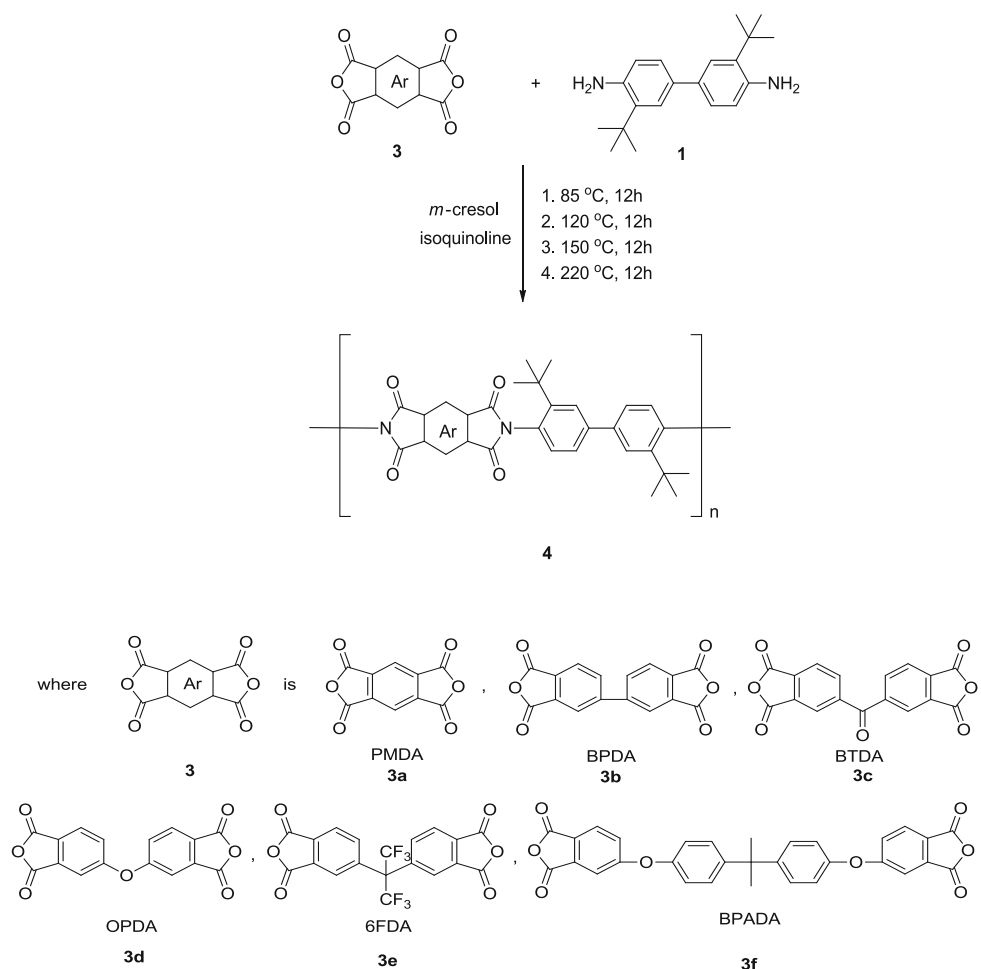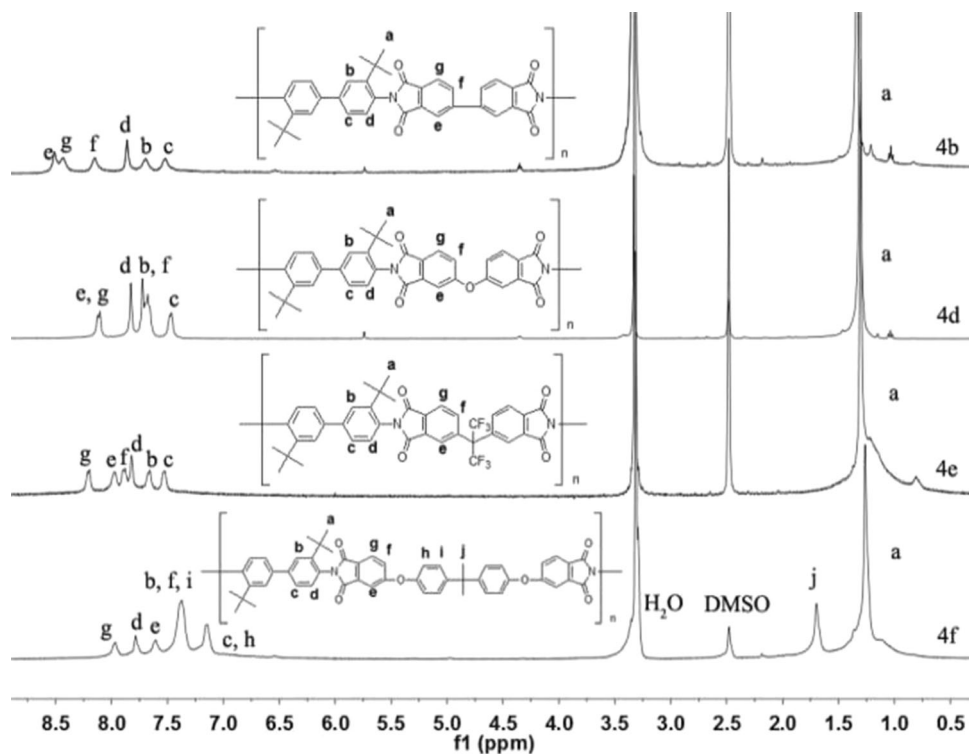**Scheme 2** Synthesis of the polyimides

Fig. 2 ¹H NMR spectra of the polyimides

0.5 h, 120 °C for 12 h, 150 °C for 12 h and 220 °C for 12 h. The viscosity of the homogeneous transparent solution increased smoothly during the polycondensation and finally some white fibre-like polyimide was obtained by precipitation in methanol. If the solid content was higher than 6 wt%, some

undesired light yellow powder would appear in the polymerization mixture at a time and no high molecular weight polyimide was produced. Other relatively flexible aromatic dianhydrides OPDA, 6FDA and BPADA were able to polymerize with diamine **1** smoothly under the similar procedure
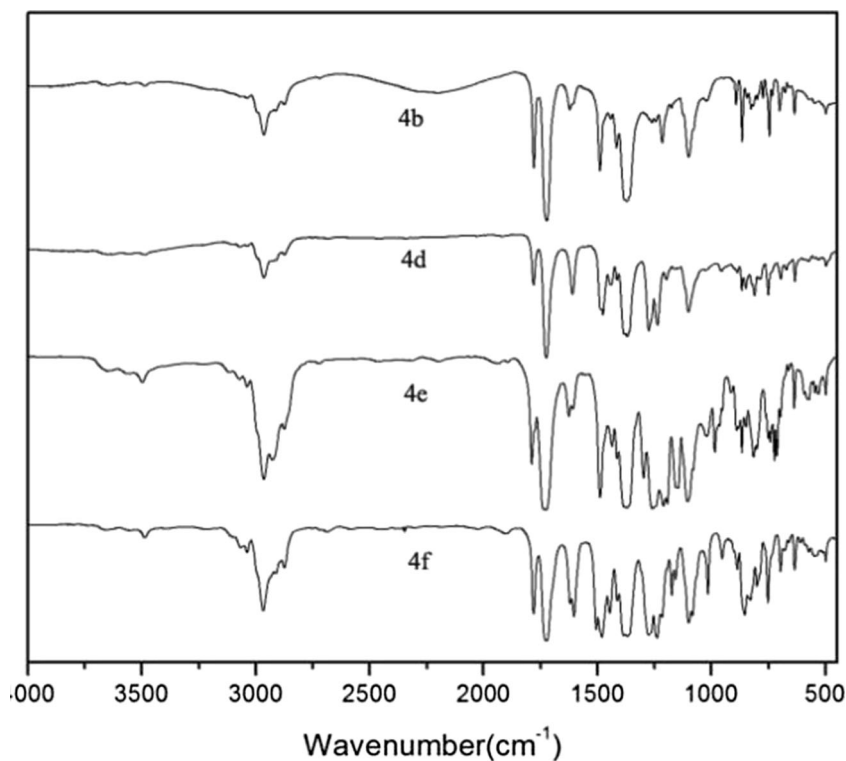
Fig. 3 FTIR spectra of the polyimides

Table 1 Characterization of the polyimides

Polyimides	M_n	PDI	T_g (°C)	T_5 (°C)
4a (1-PMDA)	-	-	-	-
4b (1-BPDA)	1.25×10^5	2.97	375.4	523.1
4c (1-BTDA)	-	-	-	-
4d (1-OPDA)	7.66×10^4	3.04	350.0	513.6
4e (1-6FDA)	1.01×10^5	2.59	336.8	508.5
4f (1-BPADA)	4.21×10^4	2.34	287.2	510.3

M_n number-average molecular weight; *PDI* polydispersity index; T_g glass transition temperature; T_5: temperature at 5 % weight loss, −: unsuccessfully synthesized

and produce some high molecular weight polyimides even when the solid content was larger than 6 wt%. Strangely, it was difficult to produce high molecular weight polyimide when the commonly used aromatic dianhydride BTDA was polymerizaed with diamine **1**. In the polymerization process of BTDA and diamine **1**, the reaction mixture seemed transparent consistently but its viscosity increased a little. After the polymerization finished and the mixture was cooled to room temperature, the whole polymerization system formed a gel. We conjectured that some chemical cross-linking occurred easily or the liquid - liquid phase separation appeared in the polymerization process [34–38].

The chemical structure of all polyimides was first confirmed by ^{1}H NMR spectra (Fig. 2). The water peak appeared around 3.3 ppm in ^{1}H NMR spectra for all polyimides. It is likely that

the deuterated solvent (DMSO-d_6) contained a little water or the polyimide films absorbed a little water. The detailed ascription of other signals to the corresponding chemical structure of polyimides is demonstrated in Fig. 2. The FTIR spectra of all polyimides are shown in Fig. 3. All the characteristic peaks for polyimides could be observed at 2,964–2,967 cm^{-1} (for carbon-hydrogen bond in tert-butyl), 1,779–1,788 and 1,721–1,729 cm^{-1} (for imide carbonyl), 1,368–1,370 cm^{-1} (for carbon-nitrogen bond), 1,015–1,104 and 724–752 cm^{-1} (for imide-ring). The signal of amide carbonyl was not found around 1,650 cm^{-1}, indicating the imidization proceeded completely during the one-pot polycondensation. That is, the byproduct (H$_2$O) was removed rapidly from the reaction system by a nitrogen flow to destroy the equilibrium between water and the imide groups. The small peak around 3,500 cm^{-1} may be attributed to the polyimide chain end (amino groups) or a little water absorbed by the polyimide film.

The number-average molecular weights (M_n) of these polyimides are shown in Table 1. Some high molecular weight aromatic polyimides were still synthesized through a one-pot polycondensation, even though the reactivity of the rigid and hindered aromatic diamine **1** was relatively low. It can be seen from Table 1 that the molecular weights of these polyimides are related to the chemical structure of the aromatic dianhydrides used. The M_n of 1-BPADA polyimide was only 42,100 because of the lower reactivity of BPADA, but M_n of **1**-BPDA reached up to 125,000. The polydispersity indices (PDIs) of all the polyimides were about 2.34 - 3.04.
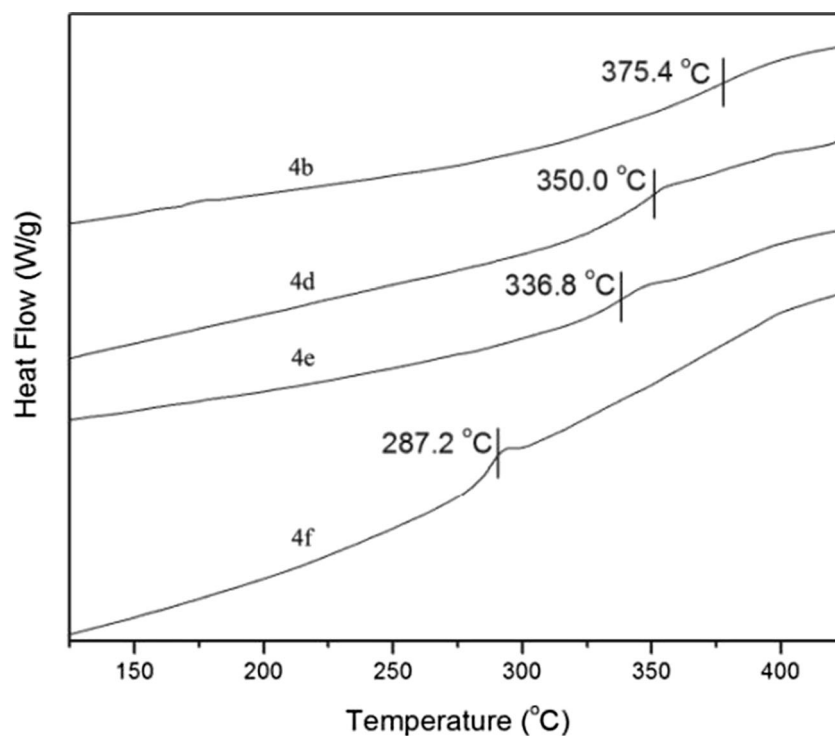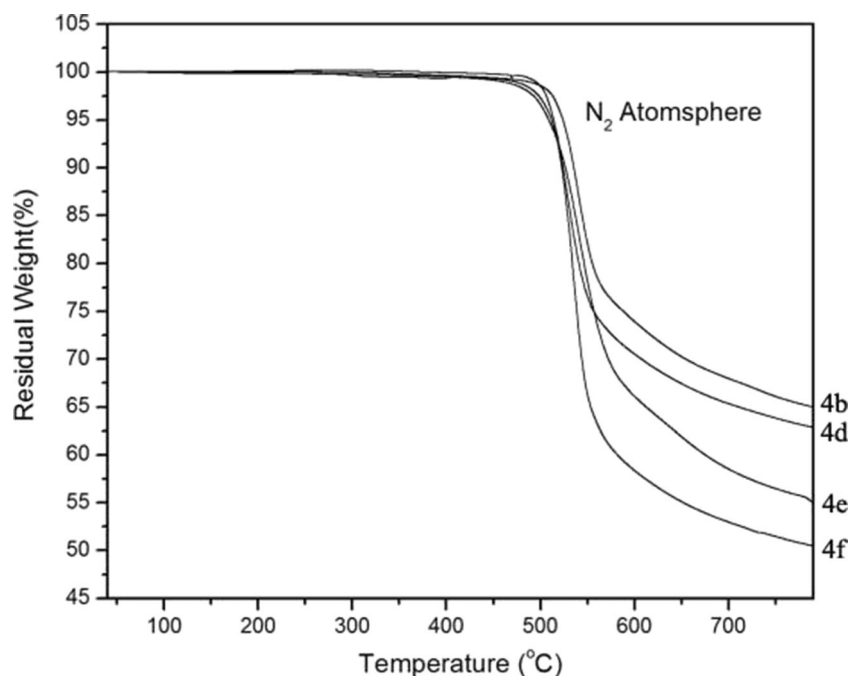
Fig. 4 DSC curves of the polyimides

Fig. 5 TGA curves of the polyimides

Thermal properties

The thermal properties of the polyimides were studied by DSC and TGA under a nitrogen atmosphere. The DSC curves are displayed in Fig. 4 and the corresponding T_gs are also shown in Table 1.

As we anticipated, the polyimide prepared from **1**-BPDA had a high T_g (375.4 °C) due to the rigid structure of biphenyl in diamine and dianhydride. The T_g of the polyimide **1**-OPDA still reached 350.0 °C even if dianhydride OPDA contained a flexible ether bond. For dianhydride BPADA with two flexible ether bonds, the T_g of the resulting polyimide **1**-BPADA reached up to 287.2 °C as well, which is considerably higher than that of the commercial polyetherimide (Ultem PEI, T_g= 210–215 °C). We inferred that the introduction of pendent *tert*-butyl group hindered the polyimide chain torsion. The polyimide **1**-6FDA also had a relatively high T_g of 336.8 °C. Here, the rigid structure of diamine **1** is the key parameter to produce the polyimide with high T_gs if the difference of the molecular weights is ignored. The TGA curves of all polyimides are shown in Fig. 5. They were all stable up to 500 °C under the nitrogen atmosphere. In summary, the high T_g and excellent heat resistance of the polyimides will not be deteriorated by introducing the pendent *tert*-butyl group into the backbone.

Solubility

The solubility of the polyimides was determined at 10 mg/mL (polymer/solvent) and room temperature or 60 °C in various organic solvents. The results were summarized in Table 2.

Comparing with the results of our previous research [30, 31], the solubility of the resulting polyimides here decreased somewhat because of the linkage of -CH2- cut off from the diamine with tert-butyl groups. However, the polyimides made from diamine **1** with 6FDA, OPDA, and BPADA still displayed excellent solubility, and even soluble in common organic solvent with low boiling point, such as THF and CHCl₃. For the polyimide **1**-BPDA with the rigid structure and high T_g, it is still soluble in NMP, DMAc and *m*-cresol at 60 °C. If this polyimide solution is a two-fold reduction in concentration, it could also be soluble in DMAc and *m*-cresol at room temperature. It can be seen that the incorporation of pendent *tert*-butyl groups is enough to reduce the interaction of polyimide mainchains and kept the good solubility of these polyimides, even if the rigidity of diamnie is improved.

Table 2 Solubility of the polyimides

Solvents	4b (1-BPDA)	4d (1-OPDA)	4e (1-6FDA)	4f (1-BPADA)
m-cresol	(++)	++	++	++
DMAc	(++)	++	++	++
DMSO	(+)	++	++	++
DMF	(+)	(++)	++	++
THF	-	(+)	++	(++)
Toluene	-	(+)	(++)	(+)
CHCl₃	-	(+)	++	(++)
NMP	(++)	++	++	++

NMP N-methyl-2-pyrrolidone; *DMAc* N,N-dimethylacetamide; *DMF* N,N-dimethylformamide; *DMSO* dimethyl sulfoxide; *THF* tetrahydrofuran; *CHCl₃* trichloromethane

++: soluble at room temperature, (++): soluble at 60 °C, (+): partially soluble at 60 °C, −: insoluble

Table 3 Mechanical behaviors of the polyimide films

Polyimide	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
4b(1-BPDA)	138.5	3.37	7.2
4d(1-OPDA)	90.0	2.47	5.3
4e(1-6FDA)	108.2	2.83	5.2
4f(1-BPADA)	58.8	1.84	5.8

Therefore, these polyimides were processed easily by solution casting to prepare transparent and strong films.

Mechanical behaviors

Polyimide films were obtained by casting the solutions (5 wt % polyimide in NMP) on the clean glass plates and dried under the programmed temperature. The mechanical behavior of these films was measured by a CMT-4104 tensile tester and the results are shown in Table 3. Their tensile strength and tensile modulus ranged from 58.8 to 138.5 MPa and 1.84 to 3.37 GPa, respectively. However, their elongations at break were only from 5.2 to 7.2 %. The relatively low elongations at break indicated that these polyimides were glassy polymers, because this is a typical brittle breakage of glassy polymer at the temperature far lower than their glass transition temperature. Especially for **4b**, this film exhibited higher tensile strength (138.5 MPa) and tensile modulus (3.37 GPa) with a elongation at break of 7.2 %, which was attributed to the rigid biphenyl backbone. On the other hand, the lower tensile

strength of **4f** was ascribed to its relatively low molecular weight (M_n=4.21×10^4).

X-ray diffraction data

The X-ray diffraction curves of the polyimide films were displayed in Supporting Information Fig. S1. Only one wide diffuse X-ray peak could be observed in each curve and further confirmed all of these polyimides are amorphous glassy polymers due to the incorporation of bulky *tert*-butyl decreasing the well ordered chain packing. In addition, the amorphous state also improved the solubility of polyimides.

UV–vis spectra

The UV–vis spectra of the polyimide films are shown in Fig. 6. The polyimide films were prepared from solution casting on quartz pieces at a concentration of 0.5 wt % in NMP and showed a high transmission above 90 % in a wavelength range of 400–700 nm. This can be ascribed to the *tert*-butyl moiety increased the intermolecular distance and decreased the interactions among polyimide chains to result in good optical transparency. Especially for the film of polyimide **4e** (**1**-6FDA), it has the most excellent optical transparency because of the lower polarization ability of the C-F bond weaken the chain-to-chain cohesive force. On the other hand, it seemed that the transparency of these films increased with the flexibility of the corresponding chemical structure of polyimides improved.

Fig. 6 UV–vis spectra of the polyimide films
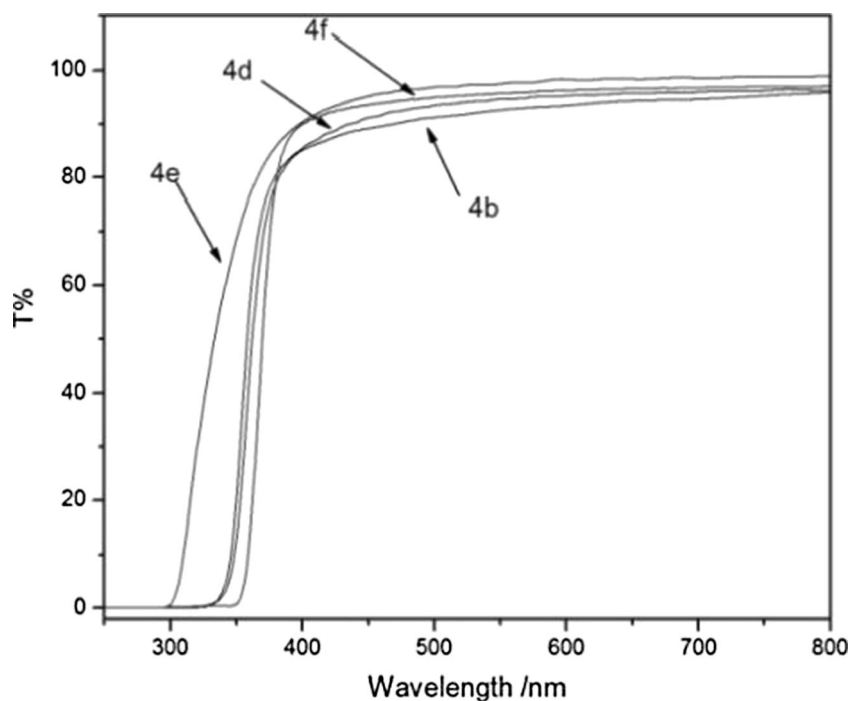
Conclusions

Some soluble polyimides with high T_gs were synthesized from the aromatic diamine **1** and various aromatic dianhydrides. Our results further confirm that the aromatic diamine containing two *tert*-butyl groups has lower reactivity, but soluble polyimides with high molecular weights are still produced by a one-pot polycondensation. The incorporation of pendent *tert*-butyl groups is enough to reduce the interaction of polyimide mainchains and keep the good solubility of these polyimides, even if the rigidity of the diamnie is improved. They can be processed easily by solution casting to prepare transparent, flexible, and tough films. These soluble polyimides with high T_gs are potential candidates for high performance polymer materials.

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