

Synthesis and properties of thermoplastic polyetherimide resins modified by 1,4-bis(2,3-dicarboxyphenoxy)-2-*tert*-butylbenzene dianhydride (3,3'-TBHQDA)

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ABSTRACT

In order to prepare thermoplastic polyimide (PI) resins with good comprehensive performances, the modification of thermoplastic polyetherimides (PEIs) by 1,4-bis(2,3-dicarboxyphenoxy)-2-*tert*-butylbenzene dianhydride (3,3'-TBHQDA) was systematically investigated. The PEI-a-x and PEI-b-x series of polyetherimides were synthesized by chemical imidization of the diamine monomer *m*-phenylenediamine (*m*-PDA) with different contents of 1,4-bis (3,4-dicarboxyphenoxy)-2-*tert*-butylbenzene dianhydride (4,4'-TBHQDA) and 3,3'-TBHQDA or 4,4'-(4,4'-isopropylidenediphenoxyl) bis(phthalic anhydride) (4,4'-BPADA) and 3,3'-TBHQDA. These PEIs had glass transition temperatures (T_g) in the range of 217–264 °C, low melt viscosities of 79–2367 Pa s, good transmittances of 87–88 % at 450 nm, and displayed good mechanical properties with tensile modulus of 2.8–3.2 GPa, tensile strengths of 89.6–118.4 MPa, and elongations at break of 3.9–6.4 %. The introduction of 3,3'-TBHQDA successfully improved thermal properties and melt processability of the PEIs. Among them, PEI-a-50 and PEI-b-50 displayed better comprehensive performances in PEI-a-x and PEI-b-x series, respectively, with moderate T_g (256 and 249 °C, respectively), extremely low melt viscosities (161 and 297 Pa s at 400 °C, respectively), high transmittances at 450 nm (87 %), and good mechanical properties (tensile modulus of 3.1 and 2.8 GPa, tensile strengths of 105.6 and 106.3 MPa, respectively).

1. Introduction

Among many special engineering plastics, polyimides (PIs) are regarded as one of the most promising engineering plastics in the 21st century due to their excellent high- and low-temperature resistance, dielectric properties, and mechanical properties, which are widely used in aerospace, semiconductors, microelectronics, and other material fields [1–3]. Especially in recent years, with the development and application of thin-walled devices, fiber optic connectors, bearings, and other precision components, higher requirements have been placed on the performance of PIs [4–6]. In general, PIs are difficult to melt during the application process due to the strong intermolecular forces caused by the rigid molecular structure and regular molecular configuration, especially difficult to be processed by injection and extrusion [7]. Meanwhile, how to strike a balance between higher service temperature and excellent melt processability to prepare polymers with better

comprehensive performances is still a problem to be solved for PIs in engineering plastics applications [8,9].

The PIs with flexible units, asymmetric structures, and bulky side groups usually exhibit good melt flowability due to the better flexibility of molecular chains and weaker intermolecular forces [10–12]. However, the introduction of these structures was usually adverse to the glass transition temperatures (T_g) of PIs. At present, there are various commercial thermoplastic polyimides (TPI) on the market. Among them, Ultem resins derived from 4,4'-(4,4'-isopropylidenediphenoxyl) bis(phthalic anhydride) (4,4'-BPADA) and *m*-phenylenediamine (*m*-PDA) has become one of the most widely used TPI material due to its excellent processability, with a minimum melt viscosity of less than 1000 Pa s. However, it had poor heat resistance ($T_g = 217$ °C) due to the presence of flexible ether bonds and isopropylidene group in 4,4'-BPADA [13]. For the study of 4,4'-BPADA, the introduction of a small amount of rigid dianhydride 4,4'-(hexafluoroisopropylidene)diphthalic anhydride

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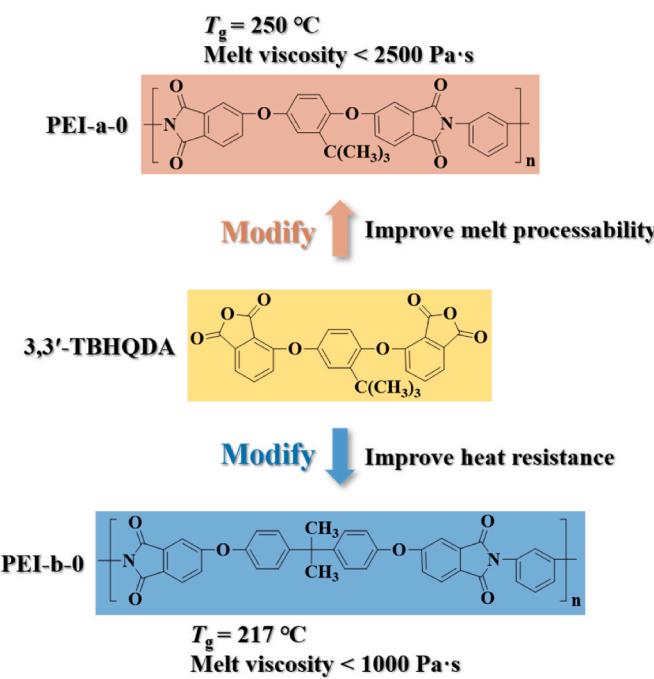


Fig. 1. Structural design of PEIs.

(6FDA) in the polymer with 2,2'-bis(trifluoromethyl)benzidine (TFMB) as diamine, can make it had a melt viscosity of about 630 Pa s and *T_g* of 230 °C [14]. Unfortunately, the heat resistance does not change much compared with the polymer without 6FDA in this study. In addition, the *m*-PDA in the Ultem structure was replaced by *p*-phenylenediamine (*p*-PDA) polymerized with 4,4'-BPADA, which achieved a minimum melt viscosity of 3970 Pa s and a *T_g* of 233 °C [15]. Although the heat resistance was improved compared with the Ultem structure, it still needs to be further adjusted to a higher level. Furthermore, its melt processability was significantly reduced, which should be improved.

In recent years, isomerization has attracted great attention as a method to improve the solubility, melt viscosity, and other properties of polymers. At the same time, isomers based on 4,4'-BPADA have been developed [16,17]. Recently, our group reported the polyetherimides (PEIs) derived from isomers of 4,4'-BPADA (4,4'-BPADA, 3,4'-(4,4'-isopropylidenediphenoxo) bis(phthalic anhydride) (3,4'-BPADA), 3,3'-(4,4'-isopropylidenediphenoxo) bis(phthalic anhydride) (3,3'-BPADA), and mixed isopropylidenebis(1,4-phenyleneoxy)bis(phthalic anhydride) (Mixed-BPADA)) [18,19]. It was found that compared with Ultem

derived from 4,4'-BPADA and *m*-PDA, the PEIs obtained by polymerization of 3,3'-BPADA and *m*-PDA or Mixed BPADA and *m*-PDA had lower melt viscosities (minimum melt viscosities of 435 and 325 Pa s) and better heat resistance (*T_{gs}* of 235 and 234 °C). In addition, our group reported the PEIs derived from isomeric dianhydrides (1,4-bis(3,4-dicarboxyphenoxy)-2-*tert*-butylbenzene dianhydride (4,4'-TBHQDA) and 1,4-bis(2,3-dicarboxyphenoxy)-2-*tert*-butylbenzene dianhydride (3,3'-TBHQDA)) with flexible ether bonds and *tert*-butyl group with large steric hindrance [20]. Among them, the polymer obtained from 3,3'-TBHQDA and *m*-PDA had a low melt viscosity of less than 100 Pa s and a *T_g* of more than 260 °C. Although the polymer obtained by 4,4'-TBHQDA and *m*-PDA had good heat resistance (*T_g* = 250 °C), the melt processability was poor with a minimum melt viscosity of less than 2500 Pa s. Up to now, the regulation of the performance of Ultem by a monomer with *tert*-butyl group and isomerization has not been investigated. From the perspective of the relationship between molecular structure design and polymer properties, 3,3'-TBHQDA with *tert*-butyl group and isomerism was introduced into the molecular chains of 4,4'-TBHQDA and 4,4'-BPADA with *m*-PDA as diamine to adjust the heat resistance and melt processability of the polymer, and to prepare thermoplastic polyimides with good comprehensive performances (Fig. 1).

In the work, PEI-a-x and PEI-b-x series polymers were prepared by introducing different contents of 3,3'-TBHQDA into 4,4'-TBHQDA or 4,4'-BPADA with *m*-PDA as diamine monomer. The properties of PEI-a-x series with *tert*-butyl group and PEI-b-x series with isopropylidene group were compared, and the modification effects of polymers with different contents of 3,3'-TBHQDA on the thermal properties, melt processability, optical properties, mechanical properties, and solubility of the two series of PEIs were systematically investigated.

2. Experimental

2.1. Materials

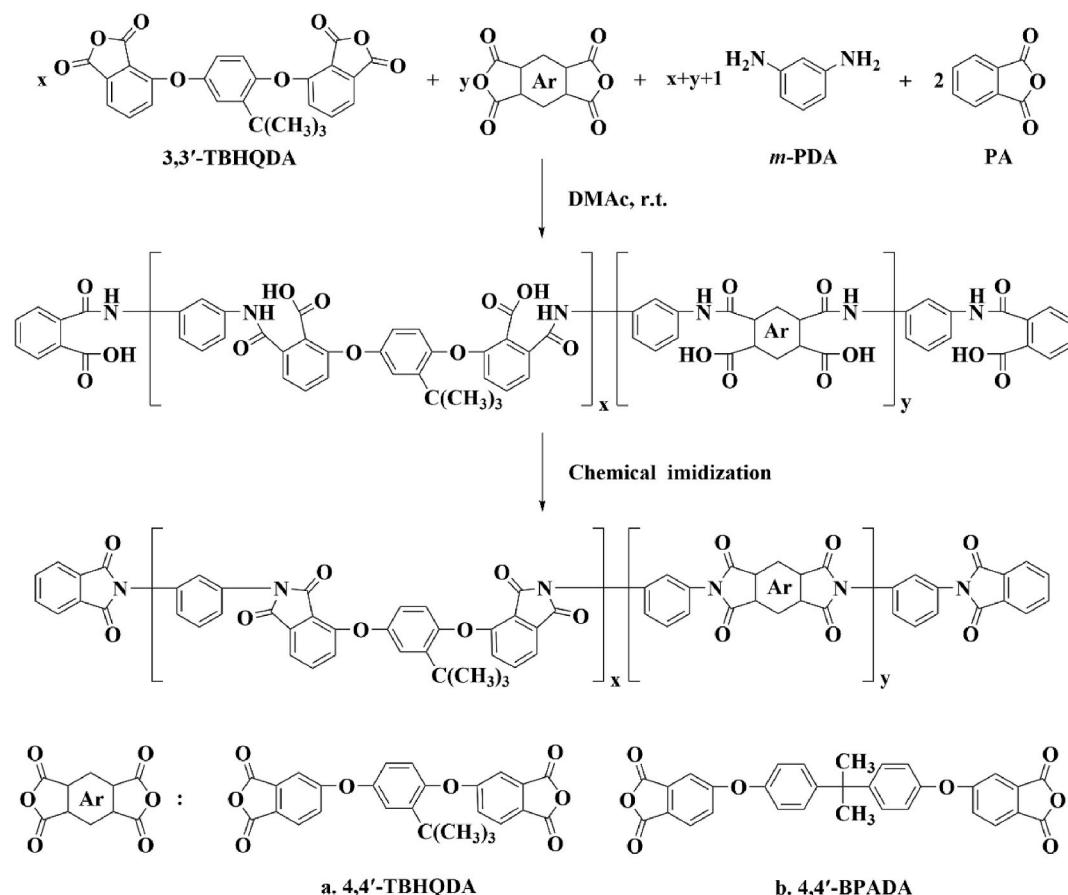
3,3'-TBHQDA and 4,4'-TBHQDA were synthesized according to the literature [20]. 4,4'-BPADA was obtained from Shanghai Guchuang Chemical New Material Co., Ltd., and *m*-PDA was purchased from Shanghai Macklin Biochemical Co., Ltd. Phthalic anhydride (PA), *N,N*-dimethylacetamide (DMAc), and pyridine (Py) were bought from Shanghai Aladdin Chemical Co., Ltd. Acetic anhydride (Ac₂O) was obtained from Shanghai Sinopharm Chemical Reagent Co., Ltd. All other reagents used in this study were commercially available.

2.2. Characterization

The ¹H NMR spectra of PEI films was characterized by Bruker AVANCE III at 400 MHz using chloroform-*d* (CDCl₃) as solvent and tetramethylsilane as internal standard. Fourier transform infrared spectra (ATR-FTIR) were measured on Thermo Nicolet 6700 FT-IR spectrometer using PEI films within the scanning range of 4000–400 cm⁻¹ for an average of 32 scans. The wide-angle X-ray diffraction (WAXD) of PEI films was recorded on a Bruker D8 Advance Davinci diffractometer, with Cu K α radiation within the range of 5–50°, operated at 40 KV and 40 mA. The inherent viscosities of polymers were obtained by the Ubbelohde viscometer at 30 ± 0.1 °C, and the concentration was 0.5 g/dL in DMAc. The molecular weights and polymer dispersion index (PDI) of the polyetherimides were measured on a Agilent 1260 Infinity II using chloroform (CHCl₃) as eluent at a flow rate of 1.0 mL/min and polystyrene as the calibration standard at 40 °C. The differential scanning calorimetry (DSC) was executed on a Mettler Toledo DSC instrument within the range of 50–350 °C at a heating rate of 20 °C/min under a nitrogen atmosphere (gas flow of 20 mL/min), and the temperature in the middle of the thermal transition from the second heating scan was viewed as *T_g*. The thermal stability of polyetherimide films was evaluated using Netzsch TG209F1 from 25 °C to 810 °C at a heating rate of 10 °C/min and a gas flow rate of 50 mL/min in nitrogen or air

Table 1
Dianhydride monomer ratios of PEIs.

PEIs	Feed ratio (4,4'-TBHQDA:3,3'-TBHQDA)	Feed ratio (4,4'-BPADA:3,3'-TBHQDA)
PEI-a-0	100:0	—
PEI-a-25	75:25	—
PEI-a-50	50:50	—
PEI-a-75	25:75	—
PEI-b-0	—	100:0
PEI-b-25	—	75:25
PEI-b-50	—	50:50
PEI-b-75	—	25:75
PEI-b-100	—	0:100



Scheme 1. Synthesis of PEIs.

atmosphere. The rheological properties of PEIs were performed on a TA Instrument Discovery HR-3 hybrid rheometer in an oscillation model at a heating rate of 4 °C/min and a frequency of 1 Hz in nitrogen. The UV-vis spectra of the polymers were recorded on a Lambda 1050+ UV-visible near-infrared spectrophotometer. The tensile properties of at least five film samples (50 mm long, 10 mm wide, and about 0.04 mm thick) were measured at room temperature at a crosshead speed of 5 mm/min on an Instron mode 5567 instrument. The solubility of the polymers was determined by immersing a series of film samples (10 mg) in various test tube solvents (1 mL) at room temperature.

2.3. Synthesis of polyetherimides

2.3.1. Synthesis of PEI-a-x and PEI-b-x

All the PEIs were synthesized via two-step method from *m*-PDA with 4,4'-TBHQDA and 3,3'-TBHQDA or 4,4'-BPADA and 3,3'-TBHQDA, respectively, with different feed ratios (Table 1).

The synthesis of PEI-a-50 was used as an example, DMAc (32.1051 g, 15 wt%) and *m*-PDA (1.0814 g, 10.0 mmol) were added to a 100 mL three-necked flask with a magnetic stirrer under a nitrogen atmosphere. After the diamine was completely dissolved, 4,4'-TBHQDA (2.3379 g, 5.1 mmol) and 3,3'-TBHQDA (2.3379 g, 5.1 mmol) were added to the mixture. The mixture was stirred overnight at room temperature to obtain a polyamic acid (PAA) solution, and then PA (0.1185 g, 0.8 mmol) was added to the PAA solution. After stirring at room temperature for 1.5 h, the solution was diluted by DMAc (18.8853 g) to 10 wt%. After stirring for 5 min until the mixture was uniform, Ac₂O (2.5523 g, 25.0 mmol) and Py (1.9775 g, 25.0 mmol) were added to the mixture, and the reacted at 80 °C for 2.5 h. After cooling to room temperature, the reaction solution was poured into ethanol solution slowly under stirring to obtain a precipitate. The precipitate was collected by filtration and

washed twice in boiling ethanol. Finally, the PEI-a-50 powder was obtained after drying at 120 °C for 6 h.

2.3.2. Polyetherimide films preparation

The powder of PEI was dissolved in DMAc to prepare a 10 wt% solution. After dissolving completely, a clarified and homogeneous polymer solution was obtained by filtration through a PTFE membrane syringe filter with a pore size of 0.45 µm. The solution was bar coated on a clean glass plate and heated at 80 °C for 2 h in an oven to allow slow evaporation of DMAc, subsequently casted film was further heated at 100, 150, 200, and 220 °C for 1 h at each temperature. After the whole system was cooled to room temperature, the film was stripped off the glass plate by immersion in water and further dried in an oven at 120 °C. The obtained film with approximately uniform thickness.

PEI-a-0 (cm⁻¹): 1778 (asym C=O str of imide ring), 1714 (sym C=O str of imide ring), 1346 (C-N str of imide), and 740 (imide ring deformation).

PEI-a-25 (cm⁻¹): 1776 (asym C=O str of imide ring), 1714 (sym C=O str of imide ring), 1347 (C-N str of imide), and 740 (imide ring deformation).

PEI-a-50 (cm⁻¹): 1776 (asym C=O str of imide ring), 1714 (sym C=O str of imide ring), 1346 (C-N str of imide), and 738 (imide ring deformation).

PEI-a-75 (cm⁻¹): 1776 (asym C=O str of imide ring), 1714 (sym C=O str of imide ring), 1338 (C-N str of imide), and 738 (imide ring deformation).

PEI-b-0 (cm⁻¹): 1776 (asym C=O str of imide ring), 1712 (sym C=O str of imide ring), 1347 (C-N str of imide), and 740 (imide ring deformation).

PEI-b-25 (cm⁻¹): 1776 (asym C=O str of imide ring), 1714 (sym C=O str of imide ring), 1347 (C-N str of imide), and 740 (imide ring

Table 2
Inherent viscosities, molecular weights, and PDI of PEIs.

PEIs	$\eta_{\text{PEI}}^{\text{a}}$ (dL/g)	M_n^{b} (g/mol)	M_w^{b} (g/mol)	M_w/M_n^{b} (PDI) ^b
PEI-a-0	0.42	34500	61500	1.78
PEI-a-25	0.42	33700	57400	1.71
PEI-a-50	0.45	34900	59200	1.70
PEI-a-75	0.42	36500	63200	1.73
PEI-b-0	0.44	33800	58400	1.73
PEI-b-25	0.42	36900	62800	1.70
PEI-b-50	0.41	37200	63600	1.71
PEI-b-75	0.41	34700	58600	1.69
PEI-100	0.42	30300	51900	1.71

^a Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

^b Determined by GPC using CHCl₃ as the eluent at 40 °C.

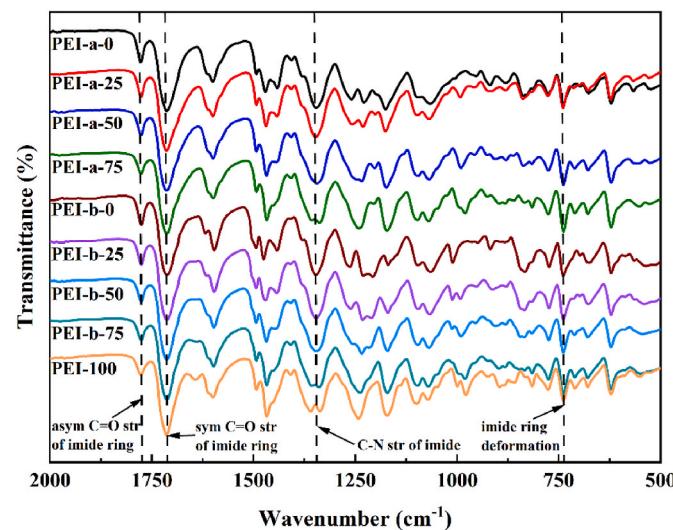


Fig. 2. FT-IR spectra of PEI films.

deformation).

PEI-b-50 (cm⁻¹): 1776 (asym C=O str of imide ring), 1714 (sym C=O str of imide ring), 1346 (C-N str of imide), and 740 (imide ring deformation).

PEI-b-75 (cm⁻¹): 1776 (asym C=O str of imide ring), 1714 (sym C=O str of imide ring), 1340 (C-N str of imide), and 738 (imide ring deformation).

PEI-100 (cm⁻¹): 1778 (asym C=O str of imide ring), 1714 (sym C=O str of imide ring), 1359 (C-N str of imide), and 738 (imide ring deformation).

3. Results and discussion

3.1. Synthesis and structure characterization of polyetherimide

The synthesis of PEIs is presented in [Scheme 1](#), the series of PEI-a-x and PEI-b-x were synthesized by chemical imidization of 4,4'-TBHQDA and 3,3'-TBHQDA or 4,4'-BPADA and 3,3'-TBHQDA with *m*-PDA, respectively, and PEIs were end-capped with PA. The inherent viscosities, molecular weights, and PDI of PEIs are listed in [Table 2](#). The inherent viscosities of PEIs were controlled from 0.41 to 0.45 dL/g in DMAc at 30 °C, which were sufficient for casting into flexible films. The molecular weights of PEIs were determined by gel permeation chromatography (GPC) in CHCl₃. They were in the range of 30300–37200 g/mol for M_n and 51900–63600 g/mol for M_w with M_w/M_n values of 1.69–1.78.

The chemical structures of PEIs were examined by FT-IR and ¹H NMR spectroscopy. The FT-IR spectra of the PEIs are shown in [Fig. 2](#). The characteristic bands around 1778 cm⁻¹ (asym C=O str of imide ring),

1714 cm⁻¹ (sym C=O str of imide ring), 1346 cm⁻¹ (C-N str of imide), and 740 cm⁻¹ (imide ring deformation) indicate that the polymers imidization were completed and PEIs were successfully obtained. Representative ¹H NMR spectra of PEIs (PEI-a-0, PEI-a-50, PEI-b-0, PEI-b-50, and PEI-100) are shown in [Fig. 3](#). Comparing the ¹H NMR spectra of PEI-a-0, PEI-a-50, and PEI-100 in [Fig. 3](#) (a), it was observed that the integral ratio of the H_a signal of *tert*-butyl group from 4,4'-TBHQDA and the H_b signal of *tert*-butyl group from 3,3'-TBHQDA in PEI-a-50 was about 9/9, which was basically consistent with the feed ratio of 3,3'-TBHQDA and 4,4'-TBHQDA (50/50). Furthermore, comparing the ¹H NMR spectra of PEI-b-0, PEI-b-50, and PEI-100 in [Fig. 3](#) (b), it was observed that the integral ratio of the H_b signal of *tert*-butyl group from 3,3'-TBHQDA and the H_c signal of isopropylidene group from 4,4'-BPADA in PEI-b-50 was about 9/6, which was also basically consistent with the feed ratio of 3,3'-TBHQDA and 4,4'-BPADA (50/50). The crystallinity of PEI films was determined by wide-angle X-ray diffraction (WAXD), the results are shown in [Fig. S1](#). It can be seen that the diffraction characteristic peaks of all PEI films exhibited broad peak shapes, which indicated that these were amorphous structures. The amorphous properties of these films can be attributed to the presence of *tert*-butyl group and rotational ether bonds with twisted conformation can disturb molecular stacking and reduce the interaction force between the polymer chains, thus preventing the crystallization of the polymers.

3.2. Thermal properties

The thermal properties of PEI films were evaluated by DSC and TGA. All the thermal properties of PEIs are summarized in [Table 3](#). T_g is considered as a basic performance index in material processing. The T_g s of the polymers were measured by DSC. As shown in [Fig. 4](#), all PEIs had significant thermal transition, the T_g s of PEI-a-x and PEI-b-x series were in the ranges of 250–264 °C and 217–264 °C, respectively. Among them, the PEI-a-x had higher T_g s than PEI-b-x series, the reason is that the *tert*-butyl group in PEI-a-x series derived from 4,4'-TBHQDA cause the hindrance effect of the polymer chains rotation and the movement of polymer chains can be hindered, which has a positive effect on T_g [21]. In contrast, the isopropylidene group in the PEI-b-x series derived from 4,4'-BPADA weakened intermolecular interaction [22]. In addition, for two series of PEIs, the T_g values increased with the content of the 3,3'-TBHQDA increased. For this phenomenon, it can be attributed to the gradual increase in the ratio of the 3-substituted phthalimide units in the dianhydrides, the restricted rotation around the bond between the bridge ether and the carbon in the phthalimide, require greater energy when moving, which contributed to the increase of T_g s [23].

The thermal stability and decomposition behavior of PEI films under nitrogen and air atmospheres were investigated through TGA. The TGA curves of PEI films are shown in [Fig. 5](#), all polymers showed good thermal stability. The 5 % weight loss temperatures ($T_{d5\%}$) of PEI-a-x series were observed in the range of 480–509 °C (N₂) and 479–508 °C (Air), respectively, and the $T_{d5\%}$ s of PEI-b-x series were observed in the range of 491–515 °C (N₂) and 488–514 °C (Air). Compared with PEI-a-x series, PEI-b-x series showed better thermal stability due to the higher ratio of phenyl group of 4,4'-BPADA [24]. Furthermore, with the content of the 3,3'-TBHQDA increased, there were not very large differences among the $T_{d5\%}$ s of PEI-a-x series and PEI-b-x series.

3.3. Melt processability

Melt processability is an important index to evaluate whether polymers can be used as engineering plastics. The complex viscosities (η^*) of PEIs at 300–400 °C were measured by rheometer. The melt composite viscosity data of PEIs are summarized in [Table 4](#), and the melt composite viscosity-temperature curve is plotted in [Fig. 6](#). The molecular weight of PEIs were controlled by adjusting the ratio of dianhydride to diamine monomer and end-capping with PA, the inherent viscosities in the range of 0.41–0.45 dL/g at a similar level ([Table 2](#)). Taking PEI-a-0, PEI-a-50,

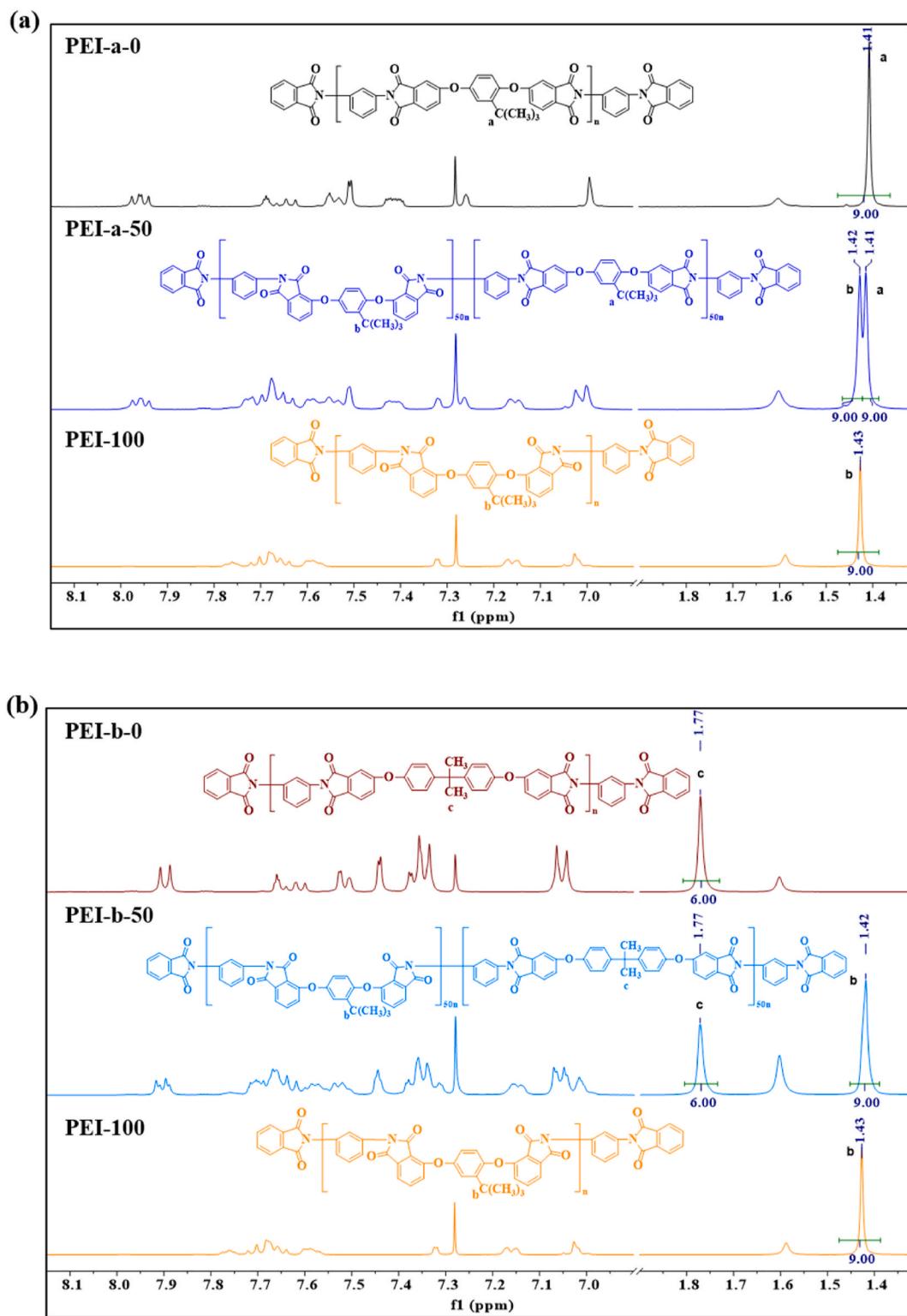


Fig. 3. ^1H NMR spectra of PEI films: (a) PEI-a-0, PEI-a-50, and PEI-100; (b) PEI-b-0, PEI-b-50, and PEI-100.

PEI-b-0, PEI-b-50, and PEI-100 as examples, the relationship between melt processability and polyimide structure was investigated. The melt viscosities of PEI-a-0, PEI-a-50, PEI-b-50, and PEI-100 decreased in different orders of magnitude with the increase of temperature. The difference was that the melt viscosity of PEI-b-0 reached the lowest value at 394 °C, showed a trend of decreasing first and then increasing with the increase of temperature. For this phenomenon, it may be the formation of the cross-linked structure of the imine ring and the

aromatic ring at high temperature [14]. Moreover, due to the lack of steric hindrance of *tert*-butyl group of PEI-b-0 molecular chains, which makes closer spacing between molecular chains and more prone to crosslinking reactions than other PEIs. With the increase of temperature, the decrease of melt viscosities of PEI-a-x series were faster than that of PEI-b-x series. Especially after 350 °C, the decrease rate of melt viscosities of PEI-b-x series gradually slowed down, while the decrease rate of melt viscosities of PEI-a-x series obviously accelerated. It may be that the

Table 3
Inherent viscosities and thermal properties of PEI films.

PEIs	T_g^a (°C)	$T_{d5\%}^b$ (°C)		RW ^c (%)
		N ₂	Air	
PEI-a-0	250	509	508	45
PEI-a-25	252	488	487	42
PEI-a-50	256	488	480	44
PEI-a-75	261	480	479	44
PEI-b-0	217	515	514	52
PEI-b-25	237	503	503	51
PEI-b-50	249	499	505	48
PEI-b-75	259	496	500	48
PEI-100	264	491	488	43

^a Obtained from DSC at a heating rate of 20 °C/min in nitrogen.

^b Obtained by TGA at a heating rate of 10 °C/min in nitrogen or air.

^c Residual weight (%) at 800 °C under nitrogen atmosphere.

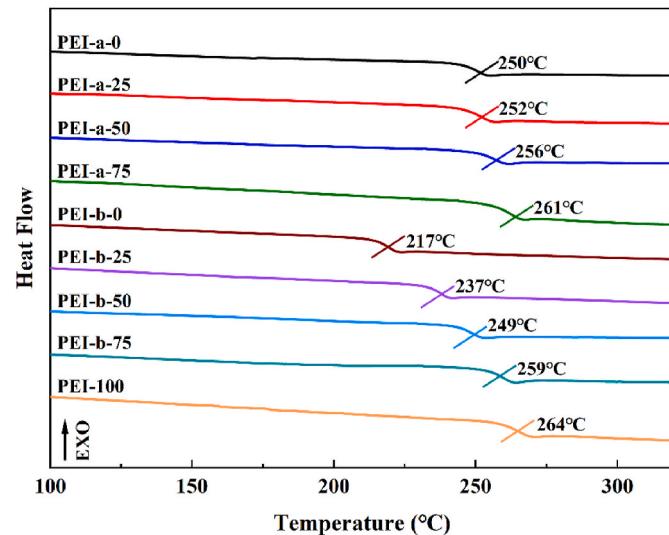


Fig. 4. DSC curves of PEI films.

tert-butyl group of the side chains of 4,4'-TBHQDA are easier to slip off the molecular chains than the isopropylidene group of the main chains of 4,4'-BPADA [19]. In addition, we found that the introduction of 3,3'-TBHQDA had a positive effect on the melt processability of PEIs. With the increase of 3,3'-TBHQDA content, the processing properties of both PEI-a-x and PEI-b-x series were greatly improved. When the addition of 3,3'-TBHQDA was 50 %, PEI-a-50 and PEI-b-50 had the lowest melt viscosities of 161 and 297 Pa·s at 400 °C, respectively. This was

attributed to the 3,3'-TBHQDA resulting in the loose packing of polymer chains and the intermolecular force to be reduced [25].

3.4. Optical properties

The optical properties of PEI films were evaluated by UV-visible spectroscopy and illustrated in Fig. 7. The cut-off wavelength and the transmittance data at different wavelengths of PEI films are listed in

Table 4
Melt complex viscosity of PEIs.

PEIs	Melt complex viscosity [Pa·s] at			Minimum melt viscosity at temperature	Reference
	320 °C	350 °C	380 °C		
PEI-a-0	29653	12132	4233	2367 Pa·s at 400 °C	[20]
PEI-a-50	31061	6311	755	161 Pa·s at 400 °C	This work
PEI-b-0	6305	2110	935	842 Pa·s at 394 °C	[18]
PEI-b-50	13969	2994	770	297 Pa·s at 400 °C	This work
PEI-100	20602	3351	339	79 Pa·s at 400 °C	This work

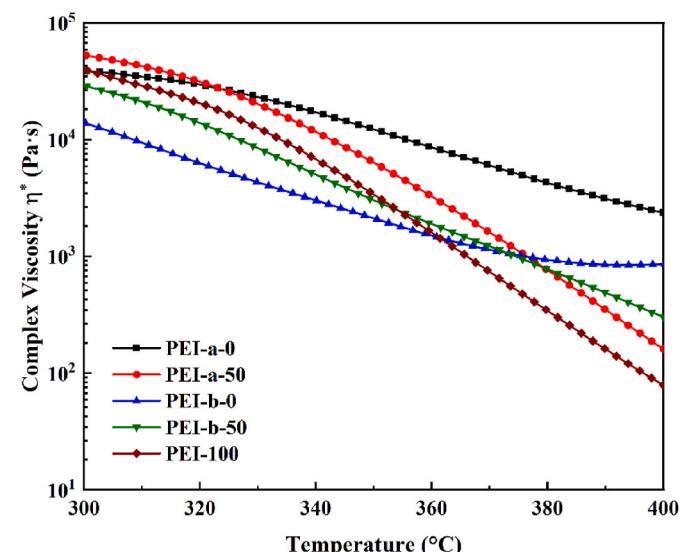


Fig. 6. Complex viscosity of PEIs as a function of temperature.

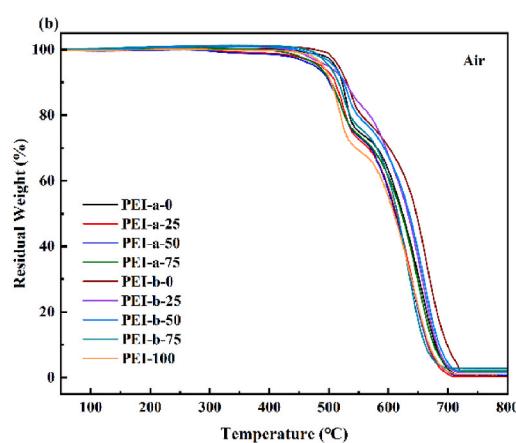
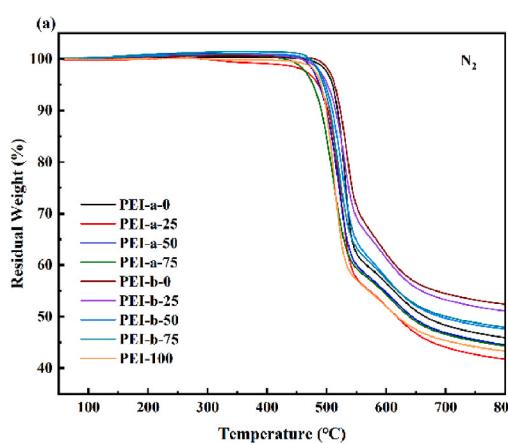


Fig. 5. TGA curves of PEI films: (a) in nitrogen; (b) in air.

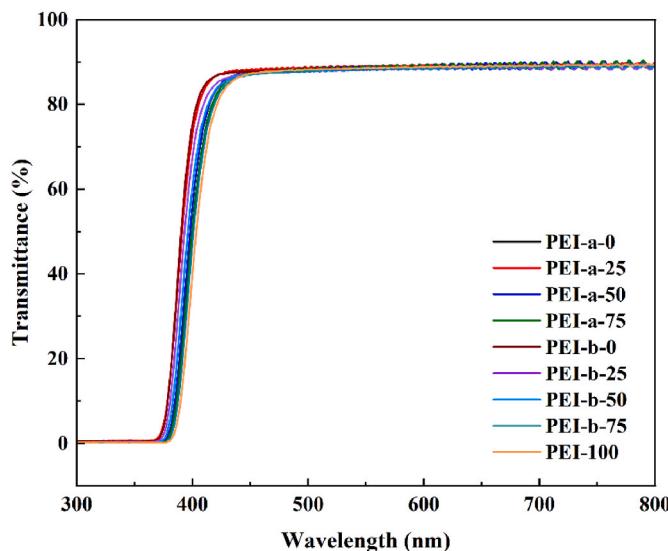


Fig. 7. UV-visible spectra of PEI films.

Table 5
Optical properties of PEI films.

PEIs	Thickness (μm)	λ_0 (nm) ^a	T_{400} (%) ^b	T_{450} (%) ^b	T_{500} (%) ^b
PEI-a-0	15	361	73	88	89
PEI-a-25	18	363	62	88	89
PEI-a-50	17	365	56	87	88
PEI-a-75	19	366	51	87	88
PEI-b-0	20	360	75	88	88
PEI-b-25	18	363	68	87	88
PEI-b-50	17	365	61	87	88
PEI-b-75	17	366	48	87	88
PEI-100	19	368	40	87	88

^a λ_0 : UV cut-off wavelength.

^b T_{400} , T_{450} , T_{500} : transmittance at 400, 450, and 500 nm, respectively.

Table 5. The photographs of PEI films are shown in Fig. 8, and all PEI films were colorless and transparent. The PEI-a-x and PEI-b-x series films had high transmittances at 450 nm (87–88 %) and 500 nm (88–89 %). The transmittances of the two series of PEI films at 400 nm were 40–73 % and 40–75 %, respectively. It can be seen that PEI-a-x and PEI-b-x series have similar optical properties. Moreover, the transmittances of PEI films at 400 nm decreased with the increase of 3,3'-TBHQDA content. For the PEI-a-x series, this was consistent with previous researches on other isomeric dianhydrides, and this phenomenon may be due to the

fact that 4,4'-TBHQDA reduces the conjugation effect of PEIs and effectively inhibits CTC compared with 3,3'-TBHQDA [20,26]. For the PEI-b-x series, which may be attributed to the lower electron affinity of 4,4'-BPADA when compared with 3,3'-TBHQDA and the presence of the isopropylidene group preventing the formation of CTC through steric hindrance [27,28]. Therefore, PEIs with a high content of 3,3'-TBHQDA are unfavorable for their optical properties, whereas the presence of moderate amounts of 4,4'-TBHQDA and 4,4'-BPADA in the polymer chains can ensure that PEIs have good optical properties along with good heat resistance (T_g) and low melt viscosity.

3.5. Mechanical properties

The mechanical properties of PEI films are outlined in Table 6. The PEI-a-x and PEI-b-x series films displayed good mechanical properties with tensile modulus of 2.8–3.2 GPa, tensile strengths of 89.6–118.4 MPa, and elongations at break of 3.9–6.4 %. Among them, there was no significant difference in mechanical properties between the PEI-a-x series derived from 4,4'-TBHQDA and the PEI-b-x series derived from 4,4'-BPADA. In addition, the tensile strengths and elongations at break of PEI-a-x and PEI-b-x series showed a decreasing trend with the increase of 3,3'-TBHQDA content. The reduced elongation at break of PEIs may be attributed to the introduction of 3,3'-TBHQDA which restricted the rotation of the molecular chains and reduced the flexibility of the molecular chains [29]. Additionally, compared with the planar molecular structure of 4,4'-TBHQDA and 4,4'-BPADA, the twisted molecular structure of 3,3'-TBHQDA made it difficult to form strong interchain interaction of the polymer chains, and thus the tensile strength

Table 6
Mechanical properties of PEI films.

PEIs	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PEI-a-0	3.2 ± 0.1	118.4 ± 2.5	6.4 ± 0.4
PEI-a-25	3.0 ± 0.1	116.8 ± 2.5	6.4 ± 0.2
PEI-a-50	3.1 ± 0.1	105.6 ± 1.3	4.5 ± 0.3
PEI-a-75	2.9 ± 0.2	95.3 ± 1.7	4.5 ± 0.3
PEI-b-0	3.1 ± 0.1	112.3 ± 2.2	6.0 ± 0.2
PEI-b-25	3.1 ± 0.1	111.7 ± 1.3	5.9 ± 0.4
PEI-b-50	2.8 ± 0.1	106.3 ± 8.9	5.9 ± 0.9
PEI-b-75	2.9 ± 0.1	105.9 ± 0.6	5.0 ± 0.2
PEI-100	2.9 ± 0.1	89.6 ± 1.7	3.9 ± 0.1



Fig. 8. Photographs of PEI films.

Table 7
Solubility of PEI films.

PEIs	Solvents ^a						
	NMP	DMF	DMAc	DMSO	THF	<i>m</i> -cresol	CHCl ₃
PEI-a-0	++	+	++	+	-	++	++
PEI-a-25	++	+	++	+	+-	++	++
PEI-a-50	++	++	++	+	+-	++	++
PEI-a-75	++	++	++	+	+-	++	++
PEI-b-0	++	+	++	+	-	++	++
PEI-b-25	++	+	++	+	+-	++	++
PEI-b-50	++	+	++	+	+-	++	++
PEI-b-75	++	++	++	+	+-	++	++
PEI-100	++	++	++	++	++	++	++

^a The qualitative solubility was tested with 10 mg samples in 1 mL solvent. Abbreviations: ++, soluble at room temperature; +, soluble on heating; +- partially soluble on heating; -, insoluble. NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; CHCl₃, trichloromethane.

decreased with the increase of the content of 3,3'-TBHQDA [30].

3.6. Solubility

The solubility of PEI-a-x and PEI-b-x series films in various organic solvents, and the results are summarized in Table 7. All the PEI films showed excellent solubility in NMP, DMAc, *m*-cresol, and CHCl₃, and exhibited good solubility in DMF and DMSO when heated. As for THF, all PEI films except PEI-100 showed poor solubility. It was found that the PEI-a-x and PEI-b-x series had similar solubility. Moreover, with the increase of 3,3'-TBHQDA, the solubility of PEI-a-x and PEI-b-x series had improved. This is because with the increase of 3,3'-TBHQDA content, the polymers had more twisted molecular structure, which hinder the stacking of polymer molecular chains and reduce the interaction force between molecular chains, thereby improving solubility [18].

4. Conclusion

PIs based on the 4,4'-TBHQDA and 4,4'-BPADA series were modified by introducing 3,3'-TBHQDA into the polymer chains, and two series of thermoplastic polyetherimide resins, PEI-a-x and PEI-b-x, with good comprehensive performances were prepared by a two-step chemical imidization method. All PEIs showed *T_g*s of 217–264 °C, minimum melt viscosities of 79–2367 Pa s, 87–88 % transmittances at 450 nm, good mechanical properties and solubility. Among them, with the increase of 3,3'-TBHQDA content, the heat resistance and melt processability of PEI-a-x and PEI-b-x series were well improved. The experimental results show that the two series of PEIs had the best comprehensive performances when the content of 3,3'-TBHQDA was 50 %. The PEI-a-50 and PEI-b-50 with moderate *T_g*s (256 and 249 °C), excellent melt processability (161 and 297 Pa s at 400 °C), and good transmittances at 450 nm (87 %). Moreover, the polymers had good mechanical properties (tensile modulus of 3.1 and 2.8 GPa, tensile strength of 105.6 and 106.3 MPa) and excellent solubility. These PEIs showed considerable application prospects in the field of engineering plastics with high heat resistance and melt processing.

CRediT authorship contribution statement

Jie Li: Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. **Nafeesa Mushtaq:** Supervision. **Xingzhong Fang:** Supervision, Funding acquisition. **Guofei Chen:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2024.127024>.

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