

Research Article

Synthesis and Characterization of Semicrystalline Polyimides Containing Bridged Linkages

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A series of polyimides (PI) containing bridged linkages were prepared successfully through a three-step technique. The results indicated that the glass transition temperature (T_g) of polyimides was affected by flexibility of polymer chain and the intermolecular interactions. ODA-TPER-based polyimide possesses the lowest T_g , which was 214°C. All polyimides had semicrystalline characteristics, and ODA-TPER-based PI exhibited the lowest melting temperature (T_m) at 316°C. The polyimides had high weight loss temperatures, which indicated that bridged linkages can reduce the softening temperature, meanwhile keeping excellent thermal stability.

1. Introduction

Polyimides (PI), as a kind of high-performance aromatic polymers, have found various applications in the aerospace and electronics industries, due to their excellent thermal stability and good mechanical and electrical properties [1–6]. But common polyimides, synthesized by pyromellitic dianhydride and diaminodiphenyl ether, could easily form charge-transfer complex among monomeric units to enhance the intermolecular force, which makes the polyimide features high glass transition temperature (T_g) and high melting temperature (T_m). Sometimes, the T_g and T_m cannot even be observed before the decomposition temperature (T_d) is achieved [7–10]. This problem narrows the processing temperature range and influences the processability and applications of polyimides. An alternative strategy is to make structural changes based on the understanding that the superior performance of polyimide materials is mainly attributed to the structures of polymer chains. Very tiny changes in the chemical structures of the reaction monomers

may have critical effects on the overall properties of the resulting PI [11–14]. For instance, introducing flexible links, bulky substituents, fluorinated groups, and copolymerization can improve the processability of polyimides without sacrificing the excellent thermal stability [15–24]. Among these approaches, introduction of bridged linkages into anhydride structure has been considered to be the most efficient one, which can not only provide broader processing temperature range but also retain thermal stability [25, 26].

The presence of crystalline components in materials has obvious influence on the properties of polymer [27, 28]. Semicrystalline polymers can be processed via a variety of processing methods. At the same time, crystalline regions play an important role like physical crosslinking does, maintaining polymer mechanical properties at certain level, even above its T_g . Thus, research on the crystalline polyimide is highly valuable [29, 30].

In this article, the semicrystalline polyimides containing bridged linkages were synthesized using different monomers, and their properties were characterized.

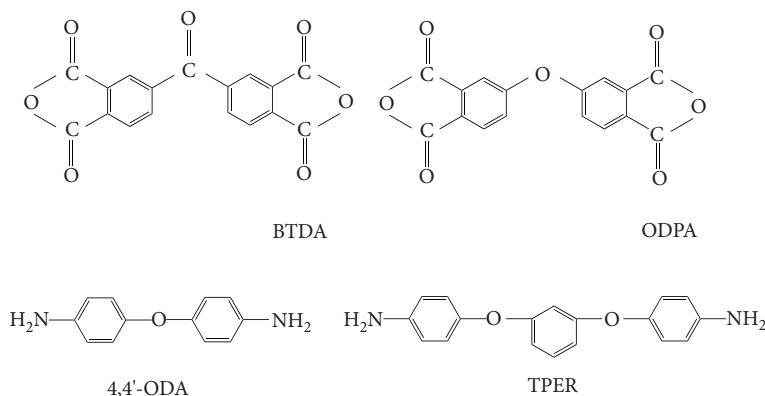
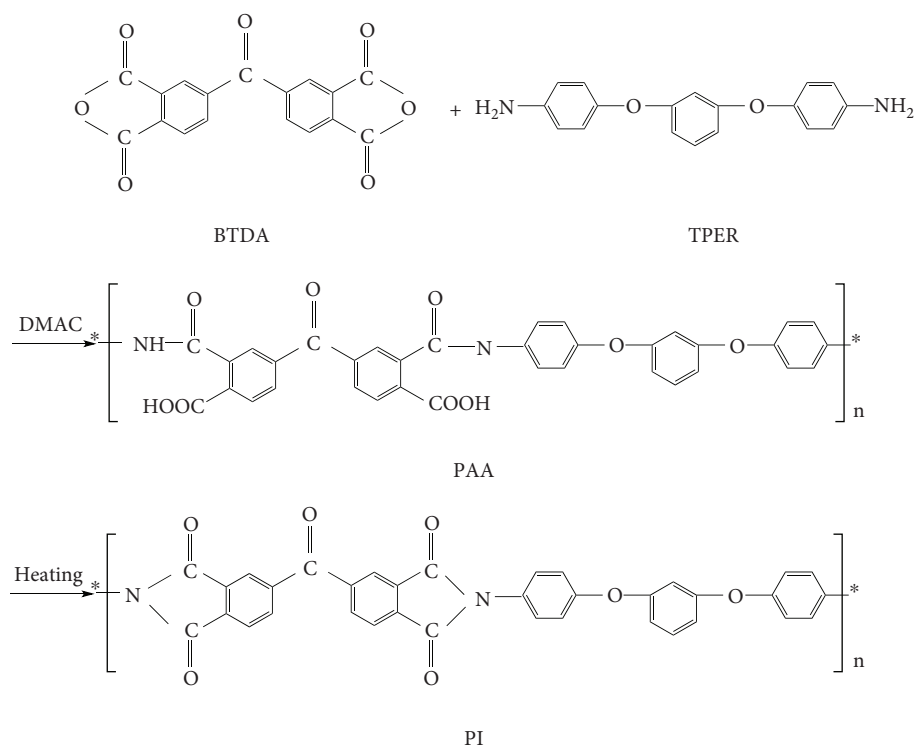


FIGURE 1: Chemical structure of monomers used for polyimide synthesis.



SCHEME 1: Preparation of BTDA-TPER PI.

2. Experimental

2.1. Starting Materials. 1,3-Bis(4-aminophenoxy)benzene (TPER) was synthesized in our laboratory. Benzophenonetetracarboxylic dianhydride (BTDA), oxydiphthalic anhydride (ODPA), 4,4'-diaminodiphenyl (ODA) were obtained from Sinopharm Chemical Reagent Co. Ltd. and used after recrystallization. N,N'-dimethylacetamide (DMAc), methanol, and xylene were received from Tianjin Kermel Chemical Reagent Co. Ltd.

2.2. Polyimide Synthesis. Chemical structures of monomers used for polyimide synthesis were shown in Figure 1. The polyimide powder was synthesized from the diamine and

dianhydride via a three-step technique. The synthesis of PI1 (BTDA-TPER) was used as an example to illustrate the procedure of polyimide synthesis as shown in Scheme 1. The first step is called poly(amide acid)-forming reaction. A three-neck flask equipped with a mechanical stirrer, a thermometer, and a water separator was used as the reaction vessel. TPER was added to the reaction vessel, followed by the addition of DMAc to achieve a 15% solid concentration. After the solution was stirred for 30 minutes, BTDA was added gradually in 2 h and then kept stirred for another 1 h to obtain poly(amide acid) (PAA). The second step goes through the solution imidization process, where xylene was added to the as-produced PAA mixture, which was heated to 140°C for 4 h to remove water. After cooling down, methanol was

TABLE 1: Thermal properties of synthesized polyimides.

	Monomer content (Mol)	T_g (°C)	T_m (°C)
BTDA-TPER	1.02 : 1	240	370 424
BTDA-ODA	1.02 : 1	279	413
ODPA-TPER	1.02 : 1	214	316
ODPA-ODA	1.02 : 1	259	367

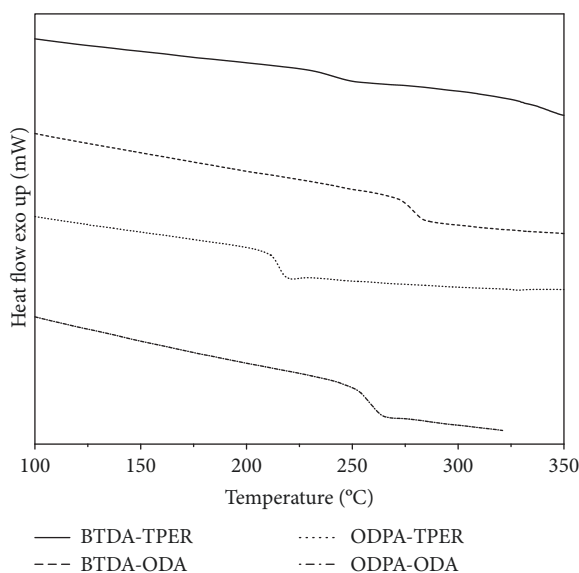


FIGURE 2: Glass transition curves of PI.

added, and the precipitated yellow polyimide powder was collected by filtration; this polyimide powder was partly imidized. And the last step will be the solid-phase thermal imidization to get fully imidized polyimide. In a forced air oven, the powder was kept at 100°C, 200°C, and 300°C for 1 h, respectively, to produce fully imidized polyimides as the final products. PI2 (BTDA-ODA), PI3 (ODPA-TPER), and PI4 (ODPA-ODA) were synthesized by the similar approach described above.

2.3. Characterization. Differential scanning calorimetry (DSC) measurement was performed on a TA Q1000-DSC under nitrogen atmosphere. Wide-angle X-ray diffraction (WAXRD) measurement was conducted on an X'Pert MPD PRO X-ray diffractometer. The X-ray diffractometer was operated at 40 kV and 35 mA using nickel-filtered Cu K α 1 radiation. Results were collected during a continuous scan at a speed of 0.1°/s and step of 0.02° between the angles of 5–70°. The morphology of the powder was characterized using a Quanta 200 environmental scanning electron microscope (SEM) of the FEI Company. The surfaces were sputter coated with a very thin layer of gold (approximately 15 nm thick) to prevent charging during imaging. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449C-type thermogravimetric analyzer at a heating rate of 5°C/min under nitrogen and air atmosphere, respectively.

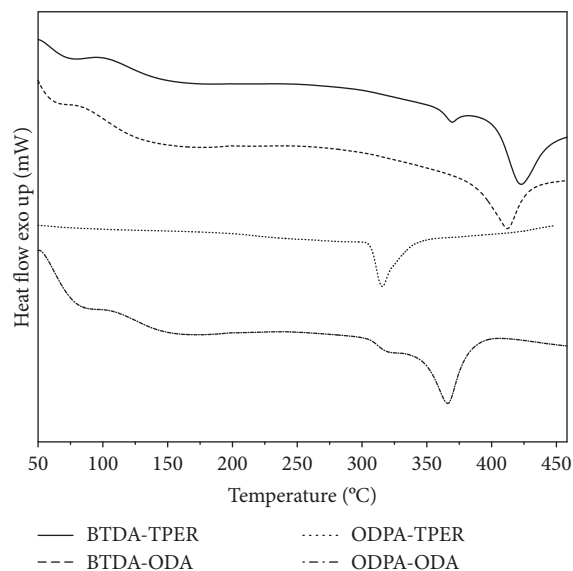


FIGURE 3: Melting curves of PI.

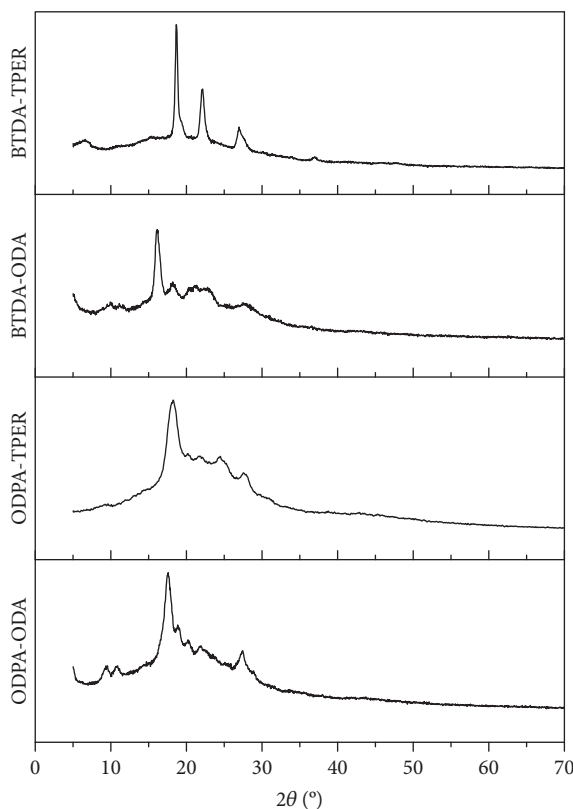


FIGURE 4: XRD patterns of polyimides.

3. Results and Discussion

The thermal properties of polyimides are shown in Table 1.

DSC experiments were conducted by heating the polyimides to 400°C at 10°C/min, holding for 1 min, quenching to 100°C, and reheating at 10°C/min to get the T_g

TABLE 2: XRD parameters of polyimides.

BTDA-TPER PI	2θ (°)	6.631	15.347	18.649	22.143	26.964	27.619	36.992
	d (Å)	13.3182	5.7688	4.7540	4.0112	3.3040	3.2241	2.4281
BTDA-ODA PI	2θ (°)	9.538	9.965	11.153	16.138	18.153	21.087	22.804
	d (Å)	9.2650	8.8687	7.9266	5.4878	4.8829	4.2096	3.8963
ODPA-TPER PI	2θ (°)	9.241	18.250	20.195	21.618	24.486	27.950	45.272
	d (Å)	9.5617	4.8571	4.3936	4.1075	3.6324	3.1896	2.0014
ODPA-ODA PI	2θ (°)	9.533	10.889	17.589	18.875	20.224	21.913	27.425
	d (Å)	9.2695	8.1185	5.0381	4.6976	4.3871	4.0528	3.2495

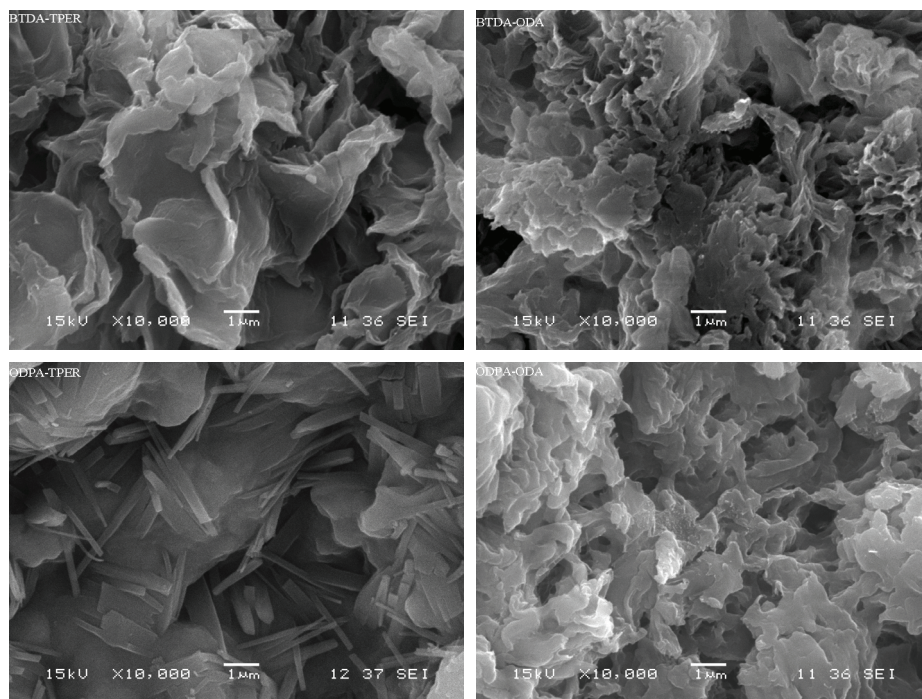


FIGURE 5: SEM images of polyimides.

(Figure 2). And T_m was obtained by heating the polyimides to 450°C at 10°C/min (Figure 3).

T_g is mainly affected by the flexibility of polymer chain and the intermolecular interaction. Because of the symmetry of the benzene ring and the rotation of the benzene ring around the C-X bond could be considered as free rotation, so the flexibility of polyimide only depends on the length of rigid chain and the valence angle of the C-X-C bond [31]. And the intermolecular interaction is dependent on the polarity of polar groups. Compared with 4,4'-ODA, TPER is more flexible. Since the valence angle of C-O-C is 123°, and the valence angle of C-CO-C is 127°, BTDA is slightly more flexible than ODPA. But the polarity of -CO- is stronger than that of -O-, so BTDA-based polyimide has stronger intermolecular interaction than ODPA-based polyimide. Affected by these two factors, ODPA-TPER-based polyimide showed the lowest T_g due to the most flexible chain, which was 214°C. And the BTDA-ODA-based polyimide showed the highest value at 279°C.

Regarding the melting temperature, T_m had more influencing factors than T_g ; it could also be influenced by the crystal perfection and the lamellar thickness. The values of T_m had similar trend to the T_g values. ODPA-TPER PI showed the lowest value, which was 316°C. BTDA-ODA PI showed the highest value, which was 413°C. In addition, BTDA-TPER PI showed two obvious T_m peaks; it was because the polyimide recrystallized after the first crystallization. And the recrystallization made the crystal more perfect than before, so the second T_m value was higher, which was 424°C.

It can be found from the T_g and T_m results that all of the four polyimides containing bridged linkages have measurable T_g and low T_m , so can be expected to be appropriate for many different types of processing methods, and have lower requirement for the equipment. At the same time, the T_g of the polyimides is high enough to be used at a high temperature without losing its mechanical properties and lower than the decomposition temperature, T_d , to make the polyimides suitable for processing.

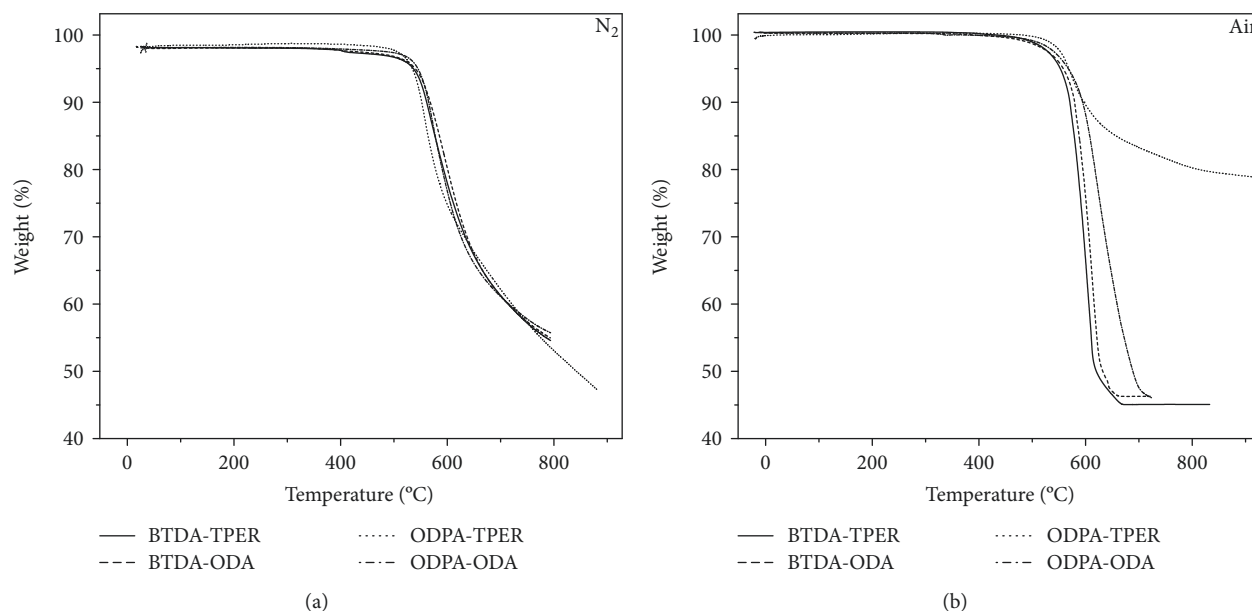


FIGURE 6: TGA curves of polyimide.

The XRD patterns and the corresponding parameters are given in Figure 4 and Table 2. In the XRD pattern, obvious diffraction peaks in crystalline fields and dispersion peaks in the amorphous region, which suggested different types of polyimides had semicrystalline phase, although they possess diffraction peaks at different positions. For example, BTDA-TPER PI exhibited three strong reflections at 18°, 22°, and 26°; BTDA-ODA PI showed peaks at 10°, 16°, 18°, and 21°; and ODA-TPER had a strong reflection peak at 18°. This phenomenon was because these four polyimides had different crystal structures due to the difference of their molecular chains.

The morphologies of polyimides were characterized by SEM (Figure 5). The result indicated that four polyimides showed various crystalline phases, that is, BTDA-TPER PI showed disorderly folds formed from thick-flake crystal structure, while BTDA-ODA PI looked like flowers which grew from thin flake crystal. ODA-TPER PI had a large amount of well-ordered thin flake crystal, and ODA-ODA PI displayed an irregular coral structure which formed from a flake crystal of different sizes and thicknesses. The morphologies of polymers depended upon the chain packing of polymer chains during the crystallization growth. And the chain packing was strongly influenced by the flexibility of polyimides. So the differences of flexibility of four polyimides gave them various crystalline phases and different T_m .

The weight loss temperatures of the polyimides under nitrogen and air atmospheres were measured by the TGA (Figure 6 and Table 3). It could be found from the results that polyimides showed excellent thermal stability; the 5% weight loss temperatures under nitrogen and air atmosphere were above 555°C and 530°C, respectively. But the differences of four polyimides were not distinctive. Compare two kinds of anhydride; the ketone that unites in the BTDA polyimides could decarbonylate to form a biphenyl structure and

TABLE 3: Weight loss temperatures of polyimides.

	$T_{5\%}$ (°C)		$T_{10\%}$ (°C)	
	N ₂	AIR	N ₂	AIR
BTDA-TPER PI	562	531	580	555
BTDA-ODA PI	566	531	588	560
ODPA-TPER PI	555	553	569	570
ODPA-ODA PI	567	541	583	569

maintain its thermal stability, so their weight loss temperatures are higher. And compare two diamines; TPER polyimides have ether bond between the benzene rings, which are a weakness to thermal stability, so their weight loss temperatures are lower.

4. Conclusion

In summary, four polyimide powders based on BTDA and ODA were prepared successfully through a three-step technique, and their properties were studied. The DSC results showed that all of the polyimides had measurable T_g and low T_m , affected by flexibility of the polymer chain and the intermolecular interaction, that is, ODA-TPER PI had the lowest T_g , which was 214°C. All of the polyimides had semicrystalline characters but various crystalline morphologies and different T_m , due to their different molecular structures, for instance, ODA-TPER PI exhibited the lowest T_m —316°C. At the same time, polyimides still retained high weight loss temperatures; all of their $T_{5\%}$ are above 550°C, which indicated that bridged linkages can reduce the T_g and T_m , meanwhile keeping excellent thermal stability.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The author declares that there are no conflicts of interest.

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