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Modified Poly(*p*-phenylene benzoxazole) with Improved Thermal Property

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Poly(*p*-phenylene benzoxazole) (PBO) with superior thermal property were widely used in many key areas. With the development of PBO application, higher thermal stability is required. In this contribution, modified PBO, containing different content of pyridine in the macromolecular chains, were prepared *via* direct polycondensation of salt monomer mixtures in poly(phosphoric acid). The salt monomer mixtures were synthesized by salification of 1,3-diamino-4,6-dihydroxybenzene dihydrochloride (DAR), terephthalic acid (TPA), 2,6-pyridinedicarboxylic acid (PDA) and 2,3,5,6-tetraaminopyridine (TAP). The obtained copolymers were characterized by Fourier transform infrared, elementary analysis, X-ray diffraction and thermogravimetric analysis. It can be found that PBO based copolymers modified with low dosage of PDA and TAP exhibit improved thermal property, whose thermal decomposition temperature with 10 % weight loss can reach 620 °C in air atmosphere.

Keywords: Copolymer, 4,6-Diaminoresorcinol, Modified poly(*p*-phenylene benzoxazole), Thermal stability.

INTRODUCTION

It is known that aromatic poly(*p*-phenylene benzobisoxazole) (PBO) has attracted extensive attention due to its excellent properties in chemical resistance, flame retardance, thermal and oxidative stability, specific strength and modulus, cut and abrasion resistance [1,2]. Significant advances have been made in development of these high-performance fibres over the past 30 years and remarkable progress has also been made in the production of so-called super organic fibre [2,3]. With development of PBO technology, lots of work focused on PBO application extension and property improvement [4-7]. Thus, kinds of modified PBO with desired properties has been developed, including improvement of photophysical property, compressive property, surface property, *etc*. [8-13]. Besides, some benzoxazole based rigid rod copolymers were prepared by introducing some unique units into polymer chains, which are expected to show more excellent properties [3,8,12]. Moreover, thermal stability is recognized as an most important property of PBO, hence, high performance material with higher thermal degradation temperature is highly pursued.

In general, PBO based aromatic heterocycle rigid rod copolymers were prepared by condensation copolymerization of 4,6-diaminoresorcinol dihydrochloride (DAR) and terephthalic acid (TPA) with another monomer. However, the polymerization procedure is complicated and long time is also required [14-18]. Many efforts were underway to improve the experimental operation [19], and in our previous studies, a novel benzoxazole based rigid rod polymer poly(2,6-pyridinylene benzobisoxazole) (PPBO) containing pyridine unit in molecular chains was successfully synthesized *via* direct polycondensation of salt monomer as 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid (DAR-PDA) in shorter time [20]. Although, no similar method is underway to synthesize aromatic copolymer.

Herein, salt monomer mixtures instead of isolated DAR and terephthalic acid (TPA) are employed to directly synthesize PBO based aromatic copolymer. The monomer mixtures are constitutive of salt monomers as 4,6-diaminoresorcinol-terephthalic acid (DAR-TPA), 4,6-diaminoresorcinol-2,6-pyridinedicarboxylic acid (DAR-PDA) and 2,3,5,6-tetraaminopyridine-terephthalic acid (TAP-TPA). In this way, PDA and TAP structures are introduced into the copolymer chains, which are expected to significantly enhance thermal degradation property of the modified PBOs.

EXPERIMENTAL

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The elemental analysis was determined with a CE Instruments EA-1110 elemental analyzer. X-ray diffraction (XRD) patterns were recorded by monitoring the diffractions in the range 5-60° with the scan speed 1° min^{-1} on a TTRAX3 diffractometer. CuK_{α} radiation source was operated at 40 kV and a current of

200 mA. Themogravimetric analysis (TGA) was performed on a TA SDT Q600 instrument in air atmosphere at a heating rate of 10 °C min^{-1} in the range 0 to 800 °C for analysis of weight loss and decomposition of modified PBO. Decomposition temperature (T_d) is defined as the temperature at 10 wt % weight loss. Molecular mass was determined by intrinsic viscosity, which was measured with ubbelohde viscometer at 30 ± 0.1 °C by dissolving modified PBO in methane sulfonic acid (MSA).

4,6-Diaminoresorcinol dihydrochloride (DAR·2HCl) was prepared from resorcinol *via* diacylation, oximation, Beckmann rearrangement and hydrolysis processes [21]. 2,3,5,6-Tetraaminopyridine hydrochloride (TAP·3HCl·H_2O) was synthesized *via* 2,6-diaminopyridine nitration, subsequent 2,6-diamino-3,5- dinitropyridine (DADNP) reduction and final hydrogenation [22]. Homo-PBO was synthesized *via* condensation polymerization of 4,6-diamino-1,3-benzenediol- terephthalic acid (DAR-TPA) salt monomer. 2,6-Pyridinedicarboxylic acid (PDA, ≥ 99.0 %), poly(phosphoric acid) (PPA, P_2O_5 content ≥ 80.0 %), P_2O_5 (≥ 98.0 %), $SnCl_2$ (≥ 98.0) and NaOH (≥ 96.0) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received.

Synthesis of DAR-TPA and DAR-PDA based salt monomer mixture: Into a 1000 mL flask, equipped with a mechanical stirrer and a nitrogen inlet/outlet, were placed 400 mL water and DAR·2HCl (4.26 g, 0.02 mol) was added. One equimolar total amount of terephthalic acid and 2,6-pyridinedicarboxylic acid (TPA + PDA, 0.02 mol) dissolved in aqueous solution of NaOH (0.04 mol) was slowly added. Afterwards, the mixture was heated to 90 °C for 10 min and the salt monomer mixture solid precipitated, then the product was collected in nitrogen atmosphere. Finally, the product was dried under vacuum at 60 °C for 48 h.

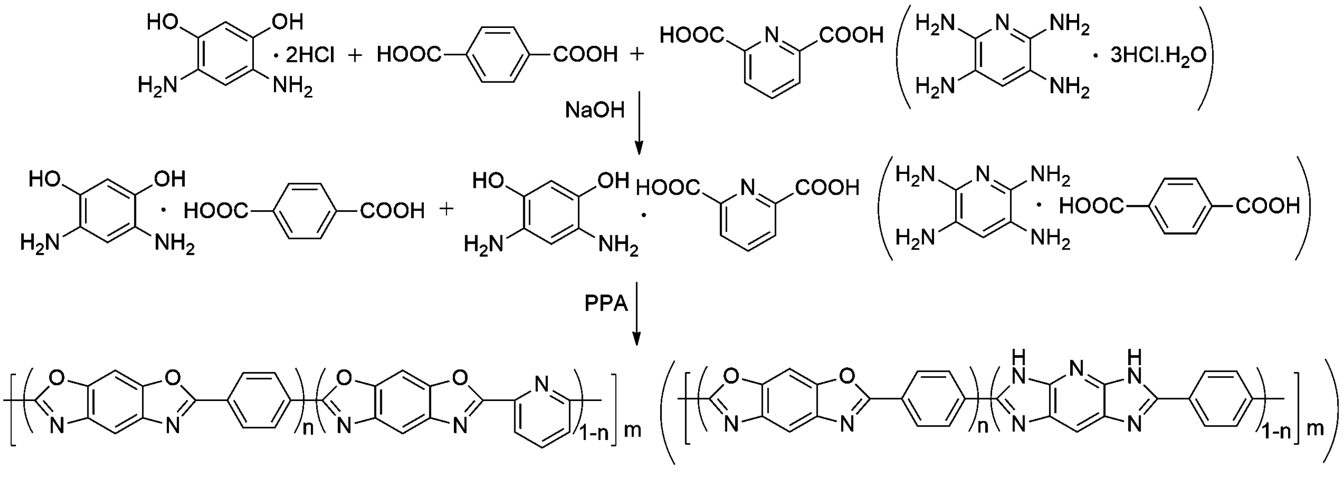
Synthesis of DAR-TPA and TAP-TPA based salt monomer mixture: Into a 1000 mL flask, equipped with a mechanical stirrer and a nitrogen inlet/outlet, were placed 400 mL water. DAR·2HCl and TAP·3HCl·H_2O (total, 0.02 mol) was added. One equimolar amount of terephthalic acid (TPA, 0.02 mol) dissolved in NaOH (0.04 mol) aqueous solution was slowly added. Afterwards, the mixture was heated to 90 °C for 10 min, then salt mixture solid precipitated. Finally, the product was collected in nitrogen atmosphere and dried under vacuum.

Synthesis of PBO based aromatic copolymer: Into a 100 mL reactor protected under nitrogen with a powerful and hastelloy made stirrer, were placed polyphosphoric acid (PPA; 83.69 % of P_2O_5), P_2O_5 and a small amount of tin powder. The reactor was closed and air was displaced by nitrogen by repeated evacuation and nitrogen blanketing. Then DAR-TPA & DAR-PDA or DAR-TPA & TAP-TPA based salt monomer mixture was added. Afterwards, the mixture was heated to 80 °C for 2 h, then heated further to 120 °C and stirred for 2 h more, following by further heating to 140 °C for 8 h and finally raised to 180 °C and held for 8 h. The product was completely washed in running hot water and then dried in vacuum.

RESULTS AND DISCUSSION

As well known, molecular structure plays important role on polymer property. Hence, a novel benzoxazole based aromatic rigid rod poly(2,6-pyridinylene benzobisoxazole) containing pyridine (PPBO) was prepared, which exhibits an excellent thermal decomposition temperature (T_d) of about 550 °C in air atmosphere. Although it is lower than that of homo-PBO, more final residues were left after decomposition [20]. Therefore, we presume that properties of PBO may be enhanced by introducing some unites into polymer chains.

Thus, as can be seem in **Scheme-I**, pyridine unit was introduced into PBO macromolecular chains *via* condensation polymerization of DAR-TPA & DAR-PDA or DAR-TPA & TAP-TPA salt monomer mixture. The pyridine content in copolymer depends on pyridine unites in salt monomer mixtures, which are prepared *via* salification of DAR, TPA, PDA and TAP, where the total amine has equal molar quantity as total acid. As reported, salt monomer method significantly shortens reaction time and improves molecular weight of the obtained copolymer [19,20]. As listed in Table-1, homo-PBO and PBO copolymers modified with 5 %, 10 % PDA and 2 %, 5 % TAP are prepared. More specifically, mole ratios of PDA:TPA are, respectively 5:95 and 10:90 for preparation of 5 % and 10 % PDA modified PBOs; similarly, mole ratios of TAP:DAR are, respectively 2:98 and 5:95 in 2 % and 5 % TAP modified copolymer.



Scheme-I: Strategy for synthesis of modified poly(*p*-phenylene benzoxazole) (PBO)

TABLE-1
SYNTHESIS AND PROPERTY OF MODIFIED PBO

Entry	Samples		Intrinsic viscosity (dL g^{-1})	Elemental analysis (wt. %): Calcd. (Found)			Decomposition temperature (T_d, °C)
				C	H	N	
1	Homo-PBO	0 %	11.2	71.80 (70.03)	2.56 (2.65)	11.96 (11.26)	581
2	PDA	5 %	16.9	71.53 (70.09)	2.44 (2.99)	12.25 (11.44)	618
3	PDA	10 %	13.1	71.26 (69.64)	2.52 (2.94)	12.55 (12.21)	620
4	TAP	2 %	11.6	71.71 (70.46)	2.55 (3.00)	12.33 (12.48)	597
5	TAP	5 %	12.9	71.59 (70.27)	2.54 (3.11)	12.88 (12.81)	576

To investigate chemical composition of obtained aromatic copolymer, FTIR and elemental analysis were conducted to probe their chemical structure. As FTIR spectra of TPA and PDA modified PBO shown in Fig. 1, band assignments at about 1625 cm^{-1} is attributed to the C=C stretching vibrations of aromatic rings, band at about 1670 and 1710 cm^{-1} are corresponding to C=N bonds in cyclic compounds, C-O stretching vibrations is located at 1055 cm^{-1}, which indicates the formation of the oxazole rings. Moreover, band at about 1548 cm^{-1} is the asymmetric stretching vibration of an unsaturated pyridine rings, bands around 735 cm^{-1} is corresponding to the out of plane bending vibrations of pyridine rings [23]. For PDA modified PBO shown in Fig. 1(a), as PDA content increases, intensity of bands at about 1548 and 735 cm^{-1} increases, which indicates the increases of PDA content in PBO copolymer. Similarly, for FTIR spectra of TAP modified PBO shown in Fig. 1(b), absorbance peak at about 1364 cm^{-1} is attributed to the C-N vibrations, which increases with increasing of TAP content in copolymers. Hence, PBO was successfully modified.

Besides, elemental analysis was performed on a dry basis of PDA and TAP modified PBO samples to further investigate their chemical structure and the results are summarized in Table-1. The result of element content of obtained copolymers is in coincidence with their calculated value. Moreover, with increase of PDA or TAP content, element content of N increases. It further indicates the successful synthesis of modified PBO and verifies their chemical composition.

To further understand the structure of modified PBO, viscosity of obtained aromatic polymer was measured with Ubbelohde viscometer to determine its intrinsic viscosity. As summarized in Table-1 and Fig. 2, homo-PBO and 5 % PDA, 10 % PDA, 2 % TAP, 5 % TAP modified PBO, respectively have intrinsic viscosity value of 11.2 (a), 16.9 (b), 13.1 (c), 11.6 (d), 12.9 dL g^{-1} (e), where higher value of intrinsic viscosity almost means higher molecular weight. In other words, small amount of PDA or TAP modified PBO has a higher intrinsic viscosity than homo-PBO, that is, introducing some PDA or TAP helps to improve condensation polymerization. Notably, 10 % PDA modified PBO exhibits lower intrinsic viscosity than the one of 5 %. Furthermore, homo-PPBO has an intrinsic viscosity value of 10.2 dL g^{-1} and 10 % TAP modified PBO has a viscosity value of 6.6 dL g^{-1}, which are both lower than homo-PBO (not shown). It implies that introduced monomer is not always beneficial for polycondensation and the dosage used plays an important role.

As we know, PBO based rigid-rod polymers tend to aggregate and orient themselves into much more ordered structures than typical flexible polymers. In order to further understand the crystallinity of this series of polymers, PDA modified PBO was characterized by X-ray diffractograms for example for further determining crystal structure of modified PBO, which was presented in Fig. 3. Clearly, two strong diffraction peaks of modified PBO at about 16.0° and 26.7° can be observed in the X-ray diffractograms of PBO based copolymers [8]. With increase of PDA content in copolymer,

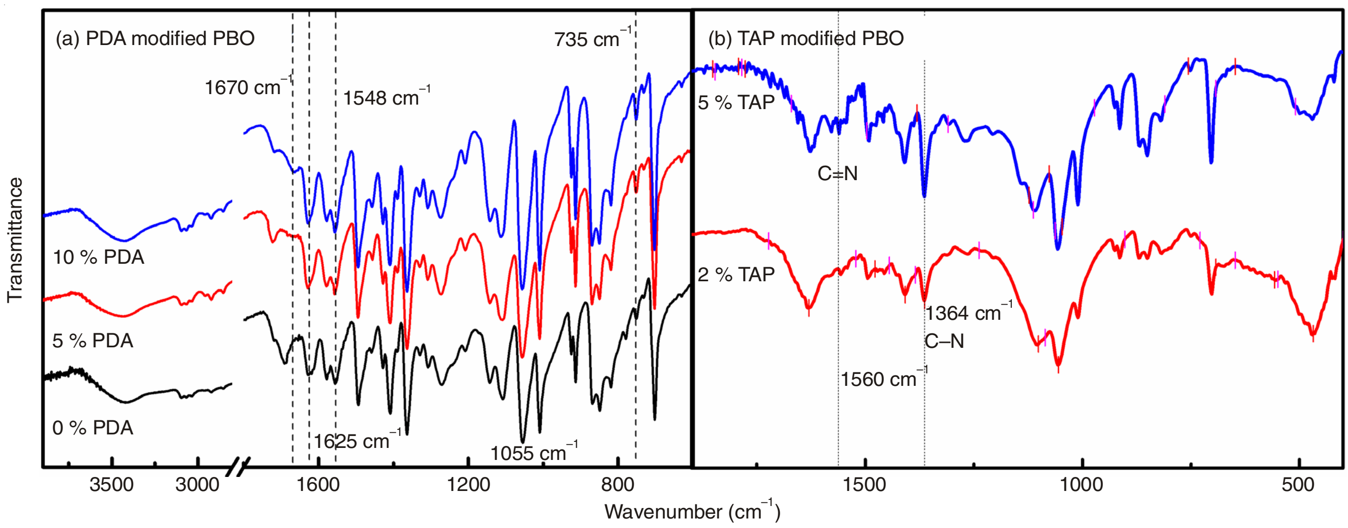


Fig. 1. FTIR spectra of 2,6-pyridinedicarboxylic acid (PDA) (a) and 2,3,5,6-tetraaminopyridine (TAP) (b) modified poly(*p*-phenylene benzoxazole) (PBO)

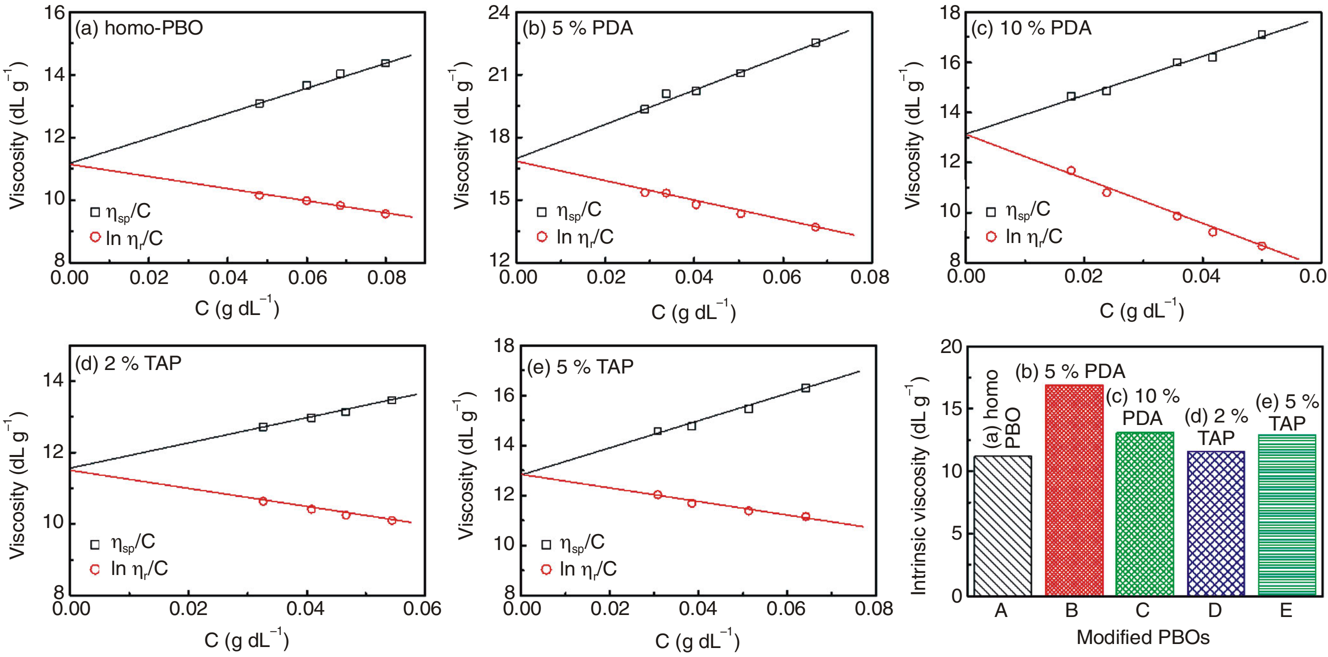


Fig. 2. Intrinsic viscosity of modified poly(*p*-phenylene benzoxazole) (PBO)

the peak intensity at about 16.0° decreases. Furthermore, when TPA is completely replaced by PDA, there is only one diffraction peak around 2θ = 26.7° for homo-PPBO (II). Thus, introduction of PDA may lower the orientation of modified PBO.

As known, PBO has an outstanding thermal stability, whose thermal decomposition temperature is highest in organic materials. With development of PBO application, polymer materials with higher thermal stability are required. Herein, PBO is modified by introducing PDA and TAP into polymer chains to investigate the effect on their thermal property. The basic data of decomposition of modified PBO is given in Table-1 and the corresponding TGA curves in atmospheric condition with a heating rate of 10°C min^{-1} is placed in Fig. 4. Hopefully, it can be observed that weight of all polymers drops dramatically between 600 and 700 °C, showing a high decomposition temperature (T_d is defined as 10 % weight lost temperature of

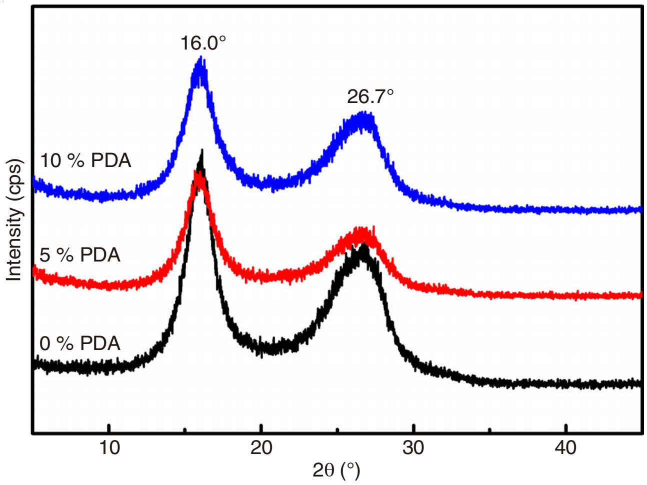


Fig. 3. XRD diffraction curves of 2,6-pyridinedicarboxylic acid (PDA) modified poly(*p*-phenylene benzoxazole) (PBO)

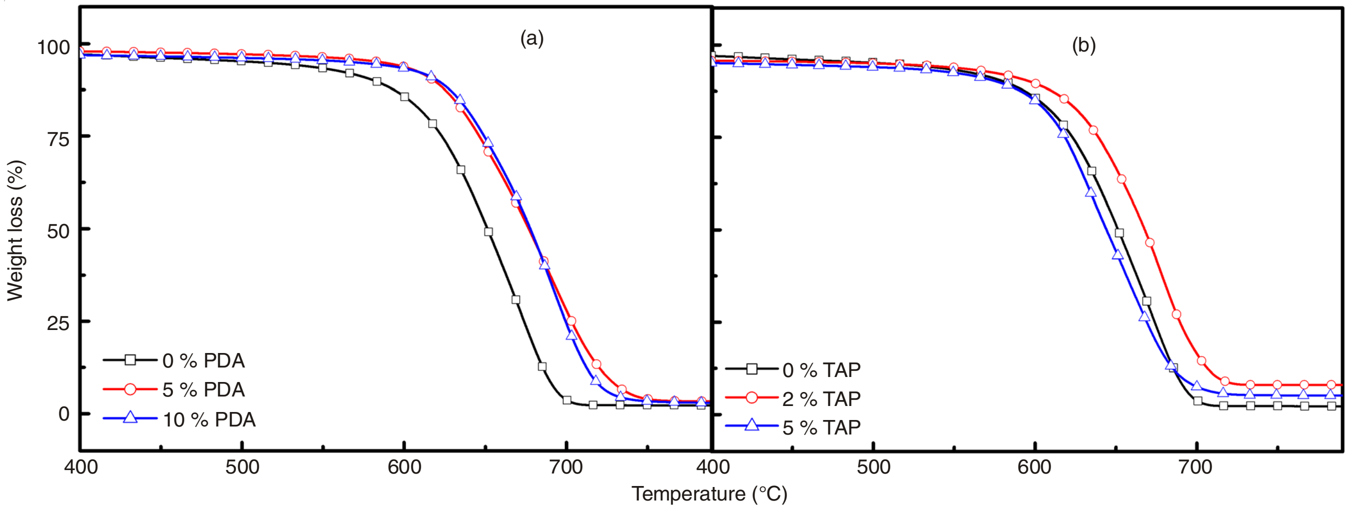


Fig. 4. TGA curves of 2,6-pyridinedicarboxylic acid (PDA) (a) and 2,3,5,6-tetraaminopyridine (TAP) (b) modified poly(*p*-phenylene benzoxazole) (PBO) under air condition with a heating rate of 10°C min^{-1}

all polymers). The high T_d of this kind of aromatic polymer is attributed to the highly conjugated system and great stiffness of PBO molecule, exhibiting two modes: the scission of the heterocyclic ring and the scission of the C-C single bond connecting to benzene ring [19]. More specifically, 5 %, 10 % content of PDA modified PBO, respectively exhibit decomposition temperature (T_d) of 618, 620 °C, which is much higher than the homo-PBO (581 °C). Moreover, 2 % TAP modified PBO exhibits T_d of 597 °C, whereas 5 % TAP modified PBO is only 576 °C. The result implies that small amount of PDA and TAP modification help to improve thermal stability of PBO based copolymer, which also provides an efficient method for thermal property improvement of PBO. On the other hand, T_d of homo-PPBO is only 550 °C [20] and 5 % TAP modified PBO possesses T_d of 576 °C, which is lower than homo-PBO (581 °C). Therefore, it is worth noting that modification with large dosage of PDA or TAP is not beneficial for thermal property improvement, which may even lower the thermal stability. Besides, in comparison with homo-PBO, modified PBO has more final residues left after decomposition. Degradation of modified PBO in air atmosphere is explained by thermo-oxidation mechanism [19]. In other words, two effects including oxidation and high-temperature degradation dominates the decomposition of polymer. Nitrogen element in modified PBO reduces their oxidation, resulting in more residues left.

Conclusion

In conclusion, PDA and TAP modified PBOs were successfully prepared by direct condensation copolymerization of their corresponding salt monomer mixtures. Moreover, modification of PBO with low dosage of PDA and TAP significantly improves thermal property of PBO, which provides an efficient method for thermal property improvement of aromatic polymers.

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