Preparation and Characterization of Aromatic Polybenzoxazoles Copolymers Containing 2, 6-Naphthalene Units*

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A series of polybenzoxazoles (co)polymers bearing crankshaft units in the main chain was synthesized by the conventional solution polycondensation of 4, 6-diaminorescinc dicyanide, terephthalic acid (TA) and 2, 6-naphthalene dicarboxylic acid (NDA). All the copolymers show isotropic liquid crystal behavior in phosphoric acid (PPA) and methanesulfonylic acid (MSA). The polybenzoxazoles exhibit an excellent thermal resistance although the crankshaft monomer has been introduced into the polymer backbone. The temperature for the 5% weight loss of all the polymers is above 600 °C. The X-ray diffraction analysis results show that the series of the polymers has a high crystallinity. The introduction of NDA makes a slight decrease in the thermal resistance of the polymers. The maximum absorption peak in the UV-Vis spectra can be adjusted according to the amount of 2, 6-naphthalene units in the polymers, which indicates the potential application of the polymers as optoelectronic materials.

Keywords Polybenzoxazoles; Copolymer; Liquid crystal; Thermal resistance

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Introduction

The production of thermally stable organic polymers has attracted much attention of some scientists for the past 30 years[1]. Aromatic poly(benzoxazole) s (PBOs) are a class of heteroaromatic polymers characterized by a high thermal stability, excellent mechanical properties and outstanding environmental resistance, which are attributed to their unique extended rigid-rod like configuration[2,3]. However, they are soluble in strong concentrated acids such as methanesulfonic acid (MSA), trifluoromethanesulfonic acid and chlorosulfonic acid. The insolubility in common solvents and high melting temperature incur the difficulties for them to be processed. Therefore, a compromise is necessary between thermal stability and processability.

Many efforts have been made to improve the processability of the polymers with their thermal stability retained. The modifications include the introduction of non-coplanar monomers[4], the attachment of flexible side chains to the polymer main chain[5], and the preparation of the soluble precursor before cyclizing the intermediate structures[6].

An important structural modification which results in a parallel offset within the polymer backbone is the incorporation of 2, 6-difunctionalized naphthalene monomers. This class of monomers is also referred to as “crankshaft” monomers. A series of copolymers based on p-HBA/TA/HQ has melting temperature in the range of 420—500 °C. The melting temperature can be lowered by about 100 °C by replacing terephthalic acid (TA) with 2, 6-naphthalene dicarboxylic acid (NDA)[7].

The present paper covers some preliminary results on the synthesis and characterization of a series of PBO s copolymers whose general structure is presented in Scheme 1.

![Scheme 1: The structure of PBOs copolymers](image)

The objective of this paper is to investigate the
effect of introducing NDA on the thermal resistance, liquid crystal behavior and UV properties of the series of the polymers

Experimental

1■Materials

4, 6-Diaminorescino1 dihydrochloride (DAR) (1) was purchased from Acros and recrystallized from hot water/concentrated HCl before use. 1H NMR (D2O), δ 6.37 (s, 1H, A−r−H), 7.01 (s, 1H, A−r−H); elemental analyses (%), calc’d: C 33.80, H 4.73, N 13.15; found: C 33.61, H 4.72, N 12.94; MS, m/e: 233 (M+, 20%). Terephthalic acid (TA) (2) and 2, 6-naphthalenedicarboxylic acid (NDA) (3) were purchased from Acros and recrystallized from DMF before use. Elemental analyses of TA (calc’d, %): C 57.83, H 3.64; found (%): C 57.83, H 3.64; elemental analyses of NDA: calc’d (%): C 66.66, H 3.74; found (%): C 66.60, H 3.62.

2■Apparatus

The elemental analyses were performed with an Elemental Vario EL apparatus. The FTIR spectrum was recorded on a Nicolet IR-550 spectrophotometer. The 1H NMR was conducted on a Mercury 200 spectrometer. The thermogravimetric analysis was carried out with a TA SDT 2960 thermal analyzer at a heating rate of 10 °C/min under N2 atmosphere. The wide-angle X-ray diffraction measurements were performed at room temperature on a Shimadzu XRD-6000 X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV, 30 mA). The scanning rate was 2 °C/min over a 2θ range of 5°–40°. The inherent viscosity was measured with an Ubbelohde viscometer at 30 °C in MSA.

3■Polymer Synthesis

The typical polymer synthesis was conducted in a three-necked flask with a nitrogen inlet and a mechanical stirrer according to ref [2]. After the dehydrochlorination of compound I, performed at 90 °C for 40 h, controlled temperature program and long reaction time were adopted for the preparation of PBOs. The polymers were precipitated in water, and washed with water and methanol, then dried under vacuum at 80 °C for 24 hours. The yield is almost quantitative.

Results and Discussion

The properties of all the polymers are shown in Table I. Usually, PBO polymerization is conducted in a liquid crystal phase in order to obtain a high molecular weight. The reason is that the polymer-condensation of PBO is a diffusion-limited process in the isotropic phase. The nematic mesophase can decrease the bulky viscosity and facilitate the end group diffusion, resulting in a much higher rate of polymerization.[8]

Generally, the concentration of PBO in polyphosphoric acid (PPA) is controlled between 10% and 13% (mass fraction). NDA is introduced into the polymer backbone. the solubility decreases and the oligomers will coagulate in PPA when the mass fraction is above 13%. So we cannot get any high molecular weight polymer except the mass fraction is below 10%. The inherent viscosity values, ranging from 2.90 to 4.63 dL/g, are indicative of moderate molecular weight. The color of the polymers turns into purple from bronze because of the enhancement of conjugation. In addition, all of the polymers are not soluble in common organic solvent except in MSA or PPA. It seems that NDA has little effect on the solubility and thermal resistance.

The temperature for the 5% weight loss of all the polymers is above 600 °C. PBO 1 has the highest thermal stability temperature. 675 °C. Even the temperature corresponding to 5% weight loss of PBO 5 is 628 °C though all of TA has been replaced by crankshaft mesogenic units. While all the polymers’ char yield at 700 °C is above 80%, they show the excellent resistance to thermal degradation. The thermal degradation temperature is linear with the NDA content, which is different from the “U” type curve reported in ref [3].

The FTIR spectra of all the synthesized PBOs are shown in Fig. 1. These polymers exhibit char-
characteristic absorptions at 1579, 1498 and 1058 cm\(^{-1}\). The weak absorptions at 1690 cm\(^{-1}\) and 3100 cm\(^{-1}\) suggest that there exist minor amounts of an intermediate. This is the reason why the elementary analysis values have a little difference with the calculated ones. Anyway, it was reported that the intermediate could be eliminated completely by annealing the kind of polymer at 300 °C for 8 h\(^{[9, 11]}\).

All the (co)polymers show lyotropic liquid crystal behavior in PPA or MSA at the mass fraction of 10% mass fraction. Figs 2(A)–(C) show the typical nematic schlieren textures of PBO1, PBO3 and PBO4 in PPA, respectively. The regular banded texture was found after the shear force had been removed, which means the molecular chain is rigid. If the same mass fraction samples were heated under polarized microscopy, it could be found that the isotropic temperature decreased with the increment of NDA. It could be attributed in part to the introduction of the crankshaft-like 2, 6-naphthyl units into the polymer backbone.

Fig 1 FTIR absorption spectra of the series of polymers
a. PBO1; b. PBO2; c. PBO3; d. PBO4; e. PBO5

Fig 2 Photomicrographs of the polymers in 10% (mass fraction) PPA solution by means of polarized microscopy
(A) PBO1; (B) PBO3; (C) PBO4; nematic textures; (D) PBO3; shear-induced banded texture

Fig 3 X-ray diffraction patterns of the series of polymers
a. PBO1; b. PBO2; c. PBO3; d. PBO4; e. PBO5
one. Gradually, the first diffraction peak in low angle shifts from 15.6° to 14.4°, which indicates that the crystal cell increases with the introduction of naphthalene units, while the location of the second diffraction peak remains unchanged, the strength increases. For sample PBO5, the strength of the second one is the same as that of the first one.

The UV-V is spectra of the series of polymers in MSA dilute solutions at room temperature are shown in Fig. 4. A maximum absorption peak is at 415 cm⁻¹ for PBO1, another weak shoulder peak is at 400 cm⁻¹. The third typical absorption peak is at 200 cm⁻¹. Gradually, the maximum absorption peak shifts to 450 cm⁻¹. The shoulder peak at 400 cm⁻¹ also shifts toward a high wavelength and the strength decreases. Furthermore, the two weaker absorption peaks at 385 and 240 cm⁻¹ appear while the peak at 200 cm⁻¹ disappears. So the location of the absorption peak in UV-V is spectra can be adjusted according to the amount of 2, 6-naphthalene units in the polymers. The potential application of the polymers will be reported in other papers.

Conclusion

A series of polybenzoxazoles containing 2, 6-naphthalene units in the polymer backbone was synthesized by solution polycondensation in PPA. All of the polymers show a lyotropic liquid crystal behavior in PPA and MSA. All the polybenzoxazoles exhibit an excellent thermal resistance. The X-ray diffraction analysis results show the series of polymers have a high crystallinity. The introduction of NDA slightly decreases the thermal resistance of the polymers. The UV-V is spectra show that the polymers can be used as the potential optoelectric materials.

References


molecules, 1994, 27, 1303.

Sci., 2004, accepted.


201, 42.


173, 589.