



Synthesis and characterizations of novel phosphorous–nitrogen containing poly(ether sulfone)s

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ABSTRACT

The synthesis of novel phosphorus–nitrogen synergism aromatic poly(ether sulfone)s was carried out successfully by using phosphorus-containing and nitrogen-containing biphenol-like monomers, 1,1'-bis(4-hydroxyphenyl)-methylene-bispheny-1-oxophosphine oxide (DOPO-PhOH) and 1,2-dihydro-4-(4-hydroxyphenyl)phthalazin-1(2H)-one (DHPZ), in the usual synthesis procedure. Polymers with sufficient molecular weights could be obtained. The structure of the phosphorus–nitrogen containing poly(ether sulfone)s was characterized by means of Fourier transform infrared spectra (FTIR) and nuclear magnetic resonance spectroscopy (^1H NMR, ^{31}P NMR). The influence of monomer ratio on their thermal stability was also investigated by adjusting the proportion of DOPO-PhOH/DHPZ (mol/mol) from 80/20 to 20/80. The molecular weight and glass-transition temperatures (T_g 's) of the polymers increased with increasing content of the DHPZ monomer. The high thermal stabilities were depended on the different proportion of diol type incorporated.

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1. Introduction

Due to the outstanding properties, aromatic polyethers such as poly(ether sulfone)s are commonly used for high-performance applications such as toughness modifiers in curable resin mixtures and advanced injection-moulded engineering parts. However, these polymers show rather low intrinsic fire risk [1–4]. Their increasing use present the challenge of developing flame retarded poly(ether sulfone)s for high-performance engineering plastics and composites.

Several advantages of phosphorus being utilized as a flame-retardant element are demonstrated. High flame-retardant efficiency, less production of corrosive and toxic gases in flames, and less destruction to the earth's environment are the noteworthy benefits of polymers with phosphorus-containing groups in the chemical backbone [5–7]. Thus, the synthesis of polymers that contain phosphorus in the main chain or side chain attracts the interest of polymer specialists [8,9]. Recently, it was proposed to incorporate phosphorus-containing diols into the polymer to further improve the fire behavior of poly(ether sulfone). One of the compounds that has attracted increasing attention is 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives. The use of DOPO derivatives, as represented phosphorus-containing diol, to improve the thermostability and

flame resistance of polymers was already known from literatures [10–13]. However, due to the unstable of the large phosphorus-containing ring and low activated aromatic diols, only oligomers or cyclic by-products were obtained [14].

As we know, the nitrogen containing compounds, producing incombustible gases without toxic smoke or fog under degradation at high temperature, are also considered to be environment-friendly flame retardants [15]. In fact, phosphorus and nitrogen have been proved to display a synergy action. It was found that upon intense heating phosphorus–nitrogen containing combinations may produce stable P–N products which remain in the char and contribute to the fire retardancy. Some phosphorus–nitrogen containing fire retardants have been investigated for polymers [16–20]. We have found that 1,2-dihydro-4-(4-hydroxyphenyl)phthalazin-1(2H)-one (DHPZ), with the N–N bond in the heterocyclic ring, behaves like a bisphenol monomer in reactions with activated aromatic dihalides to make high molecule weight poly(ether)s via a nucleophilic substitution reaction [21,22].

In the project presented in this paper, a series of novel phosphorus–nitrogen containing poly(ether sulfone)s were synthesized with different molar ratios of DOPO-PhOH and DHPZ as biphenol-like monomers. It is our aim to prove the ability of these different biphenol-like monomers to form high molecular weight poly(ether sulfone)s by polycondensation with the respective dihalogen-substituted aromatics, and the influence of phosphorus and nitrogen-containing monomer ratio on their thermal stability was investigated by adjusting the proportion of DOPO-PhOH and DHPZ.

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2. Experimental

2.1. Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, from TCI, Tokyo, Japan), 4,4'-dihydroxybenzophenone (DHBP, from TCI, Tokyo, Japan) and 4,4'-difluorodiphenyl sulphone (DFDPS, from Apollo, Stockport, UK) were used as received. The potassium carbonate (Tianjin Basifu, China) was used as an initiator for nucleophilic condensation reaction. Phenolphthalein (Tianjin Kaitong Co., China), hydroxylamine hydrochloride (Chengdu Kelong Co., China) and hydrazine hydrate (Tianjin Kermel Co., China) were also used as received. The phosphorous monomer DOPO-PhOH and the nitrogenous monomer DHPZ were synthesized according to the literature [13,23]. The purity of both monomers was exceeding 99% as determined by means of HPLC after recrystallized procedure. N-methyl-2-pyrrolidone (NMP) and toluene were purified by distillation under reduced pressure and were stored over 4-Å molecular sieves. All other solvents were analytical grade and used without further purification.

2.2. Measurements

^1H NMR and ^{31}P NMR spectra were recorded on a JEOL-400 spectrometer using tetramethylsilane and H_3PO_4 as reference, respectively. Thin KBr pellets of monomer and polymers were employed to record IR spectra, at a resolution of 4 cm^{-1} , using Nicolet 380 (Nicolet, US). Elemental analyses were determined by a Perkin Elmer model 2400 CHN analyzer. Gel permeation chromatography (GPC) analyses were performed on a Waters 515 high-pressure liquid chromatograph equipped with 5- μm Phenol gel columns (linear, $4 \times 500\text{ \AA}$) arranged in series with chloroform as the solvent and with a UV detector at 254 nm. The glass-transition temperatures (T_g 's) were determined with differential scanning calorimetry (DSC) (TAQ10, US) in nitrogen atmosphere from 50 to $350\text{ }^\circ\text{C}$ at a scan rate of $10\text{ }^\circ\text{C}/\text{min}$. The T_g values were reported from the second scan after the first heating and quenching. T_g was taken from the midpoint of the change in the slope of the baseline. The weight-loss temperatures were obtained with DTG-60AH (Shimadzu, Japan) instrument at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ under a nitrogen flow (50 ml/min) and air flow (100 ml/min), respectively. The inherent viscosity (η_{inh}) values of the polymers were obtained with a calibrated Ubbelohde viscometer. Measurements were made in chloroform at $25\text{ }^\circ\text{C}$ at a concentration of 0.5 g/dL.

2.3. Synthesis of monomers

2.3.1. 1,1'-bis(4-hydroxyphenyl)-methylene-bisphosphine-1-oxophosphine oxide (DOPO-PhOH)

DOPO (4.32 g, 0.02 mol) and DHBP (2.14 g, 0.01 mol) were mixed together in a round-bottomed flask. The mixture was heated to $190\text{ }^\circ\text{C}$ and stirred for 3 h. The reaction mixture then became thick.

After being cooled to $100\text{ }^\circ\text{C}$, 10 ml toluene was added to the flask. The pale yellow precipitate was filtered and washed with toluene. The as-synthesized DOPO-PhOH was dissolved in boiling N,N-dimethylacetamide (DMAc) in nitrogen atmosphere, followed by filtration of the hot solution which was then precipitated in tetrahydrofuran (THF) and diethyl ether (Et_2O), filtered off and recrystallized two times to achieve high purity. The received white powder product was dried in vacuum to remove residual solvents. About 5 g refined DOPO-PhOH was obtained (80% yield), $\text{mp} > 300\text{ }^\circ\text{C}$. Purity: 100% (HPLC). FTIR (KBr cm^{-1}): 1181 and 924 (P–O–Ph), 1211 (P=O), 1580 (P–Ph), 3248 (–OH). ^1H NMR [400 MHz, dimethylsulfoxide- d_6 ($\text{DMSO-}d_6$), ppm]: 5.90 (d, 2H); 6.08–6.09 (d, 2H); 6.78–6.80 (d, 2H); 6.97–7.00 (m, 4H); 7.20–7.23 (m, 2H); 7.44–7.46 (m, 2H); 7.62–7.66 (m, 6H); 7.84–7.87 (m, 2H); 8.08 (s, 1H); 9.22–9.23 (d, 2H). Elem. Anal. Calcd. for $\text{C}_{37}\text{H}_{26}\text{O}_6\text{P}_2$, C (70.70%), H (4.17%); Found, C (70.67%), H (4.18%) (Scheme 1).

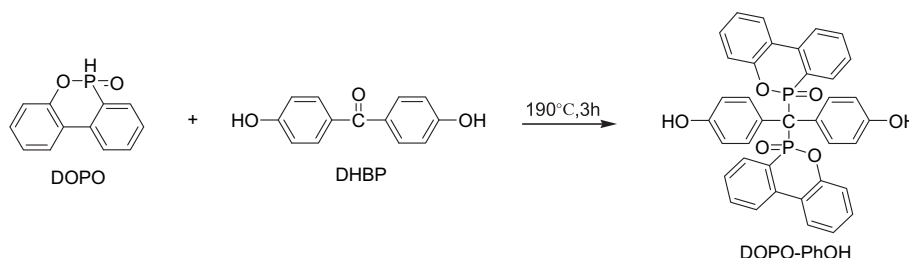
2.3.2. 1,2-Dihydro-4-(4-hydroxyphenyl)phthalazin-1(2H)-one (DHPZ)

2-(4-Hydroxybenzoyl)-benzoic acid [24] (24.2 g, 0.10 mol), DMAc (20 ml) and chlorobenzene (200 ml) were added into a three-necked flask equipped with a dropping funnel, and the mixture was heated to reflux. Then hydrazine hydrate (30 ml, 85 wt%) was carefully dropped into the mixture. The reaction was stopped in 2 h and was cooled to the room temperature. The precipitate was filtered and washed with anhydrous ethanol to obtain coarse compound. It was purified by recrystallization in DMAc and washed with anhydrous ethanol, then dried under vacuum at $120\text{ }^\circ\text{C}$ for 24 h. About 19 g refined DHPZ were obtained (79% yield). $\text{mp} > 300\text{ }^\circ\text{C}$. Purity: 100% (HPLC). FTIR (KBr cm^{-1}): 3221 (O–H), 1642 (C=O), 1354 (C–N) and 797 (N–H). ^1H NMR [400 MHz, $\text{DMSO-}d_6$, ppm]: 12.68 (s, 1H); 9.75 (s, 1H); 7.89–8.39 (d, 1H); 7.80–7.89 (m, 2H); 7.68–7.71 (d, 1H); 7.35–7.38 (d, 2H); 6.88–6.91 (d, 2H). Elem. Anal. Calcd. For $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$, C (70.58%), H (4.23%), N (11.76%); Found, C (70.55%), H (4.25%), N (11.73%) (Scheme 2).

2.4. Preparation of phosphorus–nitrogen containing poly(ether sulfone)s

Polymers were prepared from reacting various diols with DFDPS, as shown in Scheme 3. The polymerization procedures for preparing the poly(ether sulfone)s were similar. A typical example was as follows.

A 25 mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, a Dean–Stark trap, and a condenser was flushed with nitrogen and then charged with DOPO-PhOH (0.3771 g, 0.6 mmol), DHPZ (0.0913 g, 0.4 mmol), 4,4'-difluorodiphenyl sulphone (0.2542 g, 1 mmol), K_2CO_3 (0.2071 g, 1.5 mmol), N-methyl-2-pyrrolidone (NMP, 5 mL), and toluene (5 mL). The reaction mixture was heated to $150\text{ }^\circ\text{C}$ under nitrogen and kept at this temperature for 2 h to azeotrope off the resulting water with



Scheme 1. Synthesis of phosphorus-containing diol DOPO-PhOH.

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