Polymer Bulletin 38, 273–277 (1997)

Polymer Bulletin

Poly(2,6-dihydroxy-1,4-oxyphenylene)

Synthesis of a new poly(phenylene oxide) derivative

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Received: 20 November 1996/Accepted: 28 November 1996

Summary

A new poly(phenylene ether) derivative, poly(2,6-dihydroxy-1,4-oxyphenylene), was synthesized by demethylation of poly(2,6-dimethoxy-1,4-oxyphenylene) with an excess of boron tribromide in methylene chloride. The resulting polymer was soluble in *N*,*N*-dimethylformaide, dimethyl sulfoxide, and acetone, however, insoluble in chloroform, methanol, and benzene. NMR and IR analyses showed that the extent of the demethylation was 93 % and the polymer was composed of 2,6-dihydroxy-1,4-oxyphenylene unit. The polymer was stable below 300 ℃ under nitrogen.

Introduction

Polymer alloys from poly(2-6-dimethyl-1,4-oxyphenylene) (PPO) and polystyrene are important engineering thermoplastics (1). The alloys provide a desired combination of physical properties and processability of the two polymers since PPO is miscible with polystyrene over the complete composition range. PPO is industrially manufactured by oxidative polymerization of 2,6-dimethylphenol using a copper/amine catalyst system (2-4).

Polymerization catalyzed by enzymes ("enzymatic polymerizations") have received much attention as a new methodology for polymer syntheses. Specific enzymatic catalysis is expected to synthesize polymers with high selectivity and/or novel structures (5). Very recently, we have developed a novel synthetic pathway to a poly(phenylene oxide) by a laccase-catalyzed oxidative polymerization of syringic acid (3,5-dimethoxy-4-hydroxybenzoic acid) (6). The polymerization is a new type of the oxidative polymerization involving elimination of carbon dioxide and hydrogen from the monomer, yielding poly(2,6-dimethoxy-1,4-oxyphenylene) (**1**). This study deals with synthesis of a new poly(phenylene oxide) derivative, poly(2,6-dihydroxy-1,4-oxyphenylene) (**2**) from **1**.

Results and discussion

In this study, synthesis of **2** was attempted by the treatment of **1** with boron tribromide (7). Although **1** has been prepared by oxidative polymerization of 2,6-dimethoxyphenol using the copper/amine catalyst at low temperature or by electrolysis (4),

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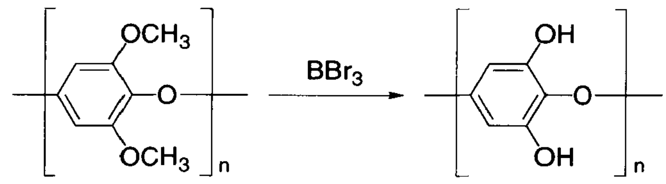

1 **2**

synthesis of poly(2,6-dihydroxy-1,4-oxyphenylene) (**2**) has not be achieved yet to our knowledge.

The reaction of **1** with boron tribromide was performed in methylene chloride. During the reaction, light brown precipitates were formed. The resulting polymer was soluble in *N*,*N*-dimethylformaide (DMF), dimethyl sulfoxide (DMSO), and acetone, however, insoluble in chloroform, methanol, and water. The starting polymer was readily soluble in chloroform, therefore, the treatment of **1** with boron tribromide produced the polymeric material with different solubility.

The structural analysis of the polymer was made by using ^{1}H NMR and IR spectrometers. Figure 1 shows ^{1}H NMR charts of the product before and after the reaction. There are two main peaks (A and B) at δ 6.2 and 3.6 in the chart of **1** (Figure 1(A)), which are due to phenyl and methyl protons of 2,6-dimethoxy-1,4-oxyphenylene unit, respectively. These peaks, on the other hand, became smaller in the chart of the demethylated sample (Figure 1(B)), and two large peaks newly appeared at δ 9.2 and 5.9 (peaks C and D), ascribable to phenolic hydroxyl and phenyl protons of 2,6-dihydroxy-1,4-oxyphenylene unit, respectively. The extent of demethylation was calculated from the integrated areas of peaks A and D as 93 %.

Polymer **1** has characteristic peaks at 2940 and 1218 cm^{-1} in its IR spectrum. These are ascribed to C-H vibration of methyl group and C-O vibration of methyl ether, respectively. In the spectrum of **2**, on the other hand, these peaks almost disappeared and a new broad peak centered at 3400 cm^{-1} due to the phenolic O-H bond appeared. These data indicate that the demethylation of **1** produced the polymer mainly consisting of 2,6-dihydroxy-1,4-oxyphenylene unit.

In order to improve the ratio of demethylation (93%), the reaction was carried out for a longer time or at a higher temperature (40 °C, a reflux temperature of the solvent), resulting in the similar results. This may be due to the precipitate formation during the reaction.

Recently, matrix-assisted laser desorption/ionization - time of flight mass spectroscopy (MALDI-TOF MS) has been used to determine the absolute molecular weight of not only biomolecules but also synthetic polymers (8-10). In this study, molecular weight of polymers **1** and **2** was measured by MALDI-TOF MS. The values of **1** and **2** were 1.0×10^4 and 8.2×10^3, respectively. The latter was close to the calculated value from **1** (8.6×10^3). These data indicate that the ether linkage of poly(1,4-oxyphenylene unit) was not cleaved during the demethylation.

Thermal properties of the product were evaluated by using differential scanning calorimetry (DSC) and thermogravimetry (TG). The measurement was performed under nitrogen. DSC analysis showed that the present polymer has no clear glass transition

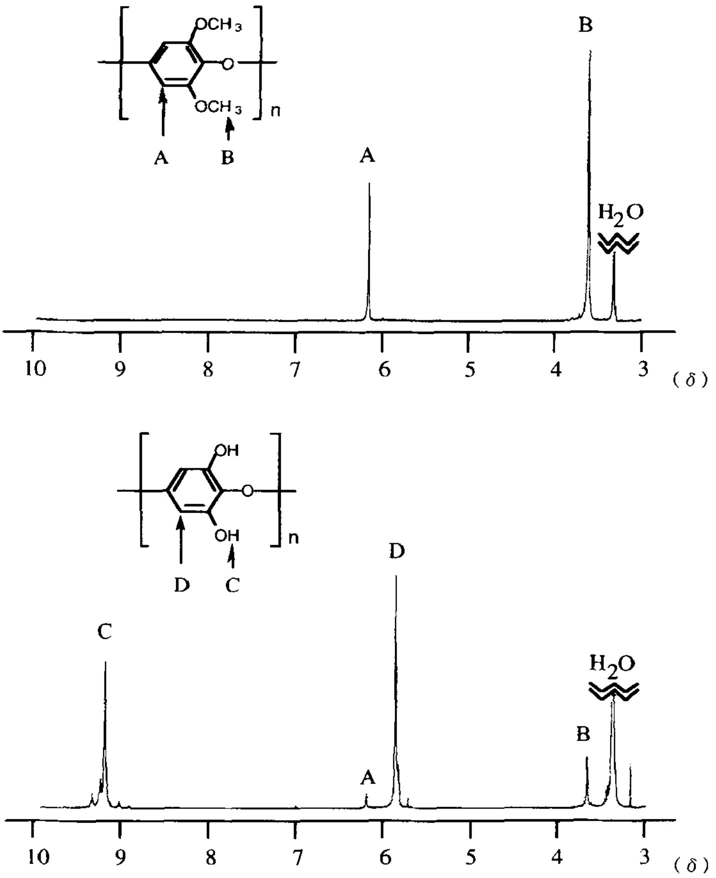

Figure 1 ^{1}H NMR spectra of (A) poly(2,6-dimethoxy-1,4-oxyphenylene) (**1**) and (B) poly(2,6-dihydroxy-1,4-oxyphenylene) (**2**) in DMSO-d_6.

temperature and melting point below 300 °C. Figure 2(A) shows the TG trace of **2**. The polymer was stable below 300 °C (5 weight-% loss of the polymer = 299 °C), and 31 % of the polymer remained at 1000 °C.

As a possible application, a polyaromatics gel was prepared by the reaction of **2** with isophthaloyl chloride in the presence of triethylamine. During the reaction, precipitates were formed, which were insoluble in common organic solvents. In the IR spectrum of the gel, the broad peak centered at 3400 cm^{-1} ascribed to the phenolic O-H bond became smaller than that of **2**, and a new strong peak at 1751 cm^{-1} due to the ester group appeared. These results that the phenolic group in **2** was partly reacted with isophthaloyl chloride to form the aromatic ester linkage during the gelation reaction. TG analysis showed that the thermal stability of the gel under nitrogen was improved, in comparison with that of **2** (Figure 2(B)).

In conclusion, poly(2,6-dihydroxy-1,4-oxyphenylene) was first synthesized by the reaction of poly(2,6-dimethoxy-1,4-oxyphenylene) with boron tribromide. More than

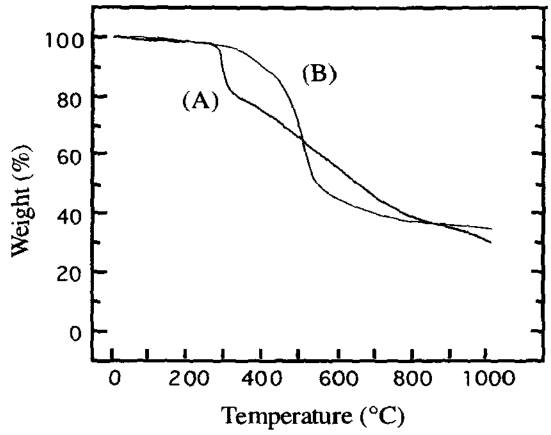

Figure 2 TG traces of (A) poly(2,6-dihydroxy-1,4-oxyphenylene) (**2**) and of (B) the polyaromatics gel from **2** and isophthaloyl chloride. The measurement was performed at a heating rate of 10 °C/min under nitrogen.

90 % of the methoxy group in the starting polymer was converted into the phenolic group. The resulting polymer is useful as a starting material for synthesis of functional polymers since it has a reactive phenolic group and a poly(phenylene oxide) backbone having high thermal stability and chemical resistance. Further investigations on the synthesis of novel polymeric materials based on **2** are under way in our laboratory.

Experimental part

Materials

Poly(2,6-dimethoxy-1,4-oxyphenylene) (**1**) was prepared by laccase-catalyzed polymerization of syringic acid in a mixture of acetone, chlorofrom, and acetate buffer (pH 5) (25 : 37.5 : 37.5 vol-%) at room temperature for 24 h under air (6). Methylene chloride solution of boron tribromide (1.0 M) was purchased from Aldrich Chemical Co. Other reagents and solvents were used without further purification.

Synthesis of poly(2,6-dihydroxy-1,4-oxyphenylene) (2)

A boron tribromide solution (38 mL, 38 mmol) was added dropwise to **1** (2.0 g, 13.4 mmol of polymer unit) in 80 mL of methylene chloride at -78 °C. The mixture was kept under gentle stirred overnight and poured into a large amount of ice water. Then, the precipitate was collected by filtration. After reprecipitation (acetone as good solvent, chloroform as poor solvent), the polymeric materials were collected and dried in vacuo to give 1.66 g of **2** (yield 100 %).

$C_{6.14}H_{4.28}O_3 \cdot 1.1H_2O$	Calc.	C	50.54	H	4.45
	Found	C	50.47	H	4.30

^{13}C NMR (acetone-d_6): δ 156.7 (C4 of **1**), 156.5 (C4 of **2**), 152.6 (C2 of **1**), 151.3 (C2 of **2**), 125.6 (C1 of **1**), 124.8 (C1 of **2**), 95.2 (C3 of **2**), 92.8 (C3 of **2**), 55.6 (OMe of **1**).

IR (KBr): 3400 (υ O-H), 1620, 1515, 1450 (υ C=C of Ar), 1175 (υ C(Ar)-O-C(Ar)), 1054 cm^{-1} (υ C-OH).

Synthesis of polyaromatics gel

To a mixture of polymer **2** (0.050 g, 0.396 mmol polymer unit), 0.14 g of triethylamine (0.140 g, 1.38 mmol), and 10 mL of acetone was dropwise added isophthaloyl chloride (0.161 g, 0.793 mmol) in 10 mL of acetone at 0 °C, and then the mixture was heated at reflux temperature for 2 h. The reaction mixture was poured into a large amount of ice water and the precipitate was collected by filtration. The residue was washed with water and subsequently acetone, followed by drying in vacuo to give 0.109 g of the gel.

Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer. IR spectra were recorded on Shimadzu IR-460 spectrometer. Mass measurement of polymers was carried out using a Bruker Protein TOF™ mass spectrometer, equipped with a 337 nm nitrogen laser. Molecular weight was recorded using dithranol as matrix in a linear mode. TG analysis was performed using a Seiko SSC/5200 apparatus for thermogravimetry / differential thermal analysis at a heating rate of 10 °C/min in a gas flow rate of 300 mL/min. DSC measurement was made at a 10 °C/min heating rate under nitrogen using a Seiko SSC/5200 differential scanning calorimeter calibrated with an indium reference standard.

Acknowledgement

This work was partly supported by a Grant-in-Aid for Specially Promoted Research (No. 08102002) from the Ministry of Education, Science, and Culture, Japan and by Proposal Based Advanced Industrial Technology R&D Program.

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