

Synthesis of poly(phenylene oxide) – aromatic polyester multiblock copolymers

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Summary

Poly(phenylene oxide) (PPO) - aromatic polyester multiblock copolymers were synthesized by polycondensation of bisphenol-A / isophthalic acid or *m*- and *p*-hydroxybenzoic acids in the presence of PPO having a carboxylic acid at one end and a phenolic hydroxy group at the other using triphenylphosphine / hexachloroethane as coupling agent. TG analysis showed that the multiblock copolymer showed relatively high thermal stability.

Introduction

Tailor-made block and graft copolymers have received much attention as novel polymeric materials with multi-components (1). End-functional engineering plastics are often used for preparation of block and graft copolymers consisting of such polymers. These multi-component engineering plastics are expected to possess unique properties which is not otherwise shown by homopolymers.

Poly(2,6-dimethyl-1,4-oxyphenylene) (poly(phenylene oxide), PPO) is a linear amorphous thermoplastics (2). PPO was first prepared by oxidative coupling of 2,6-dimethylphenol monomer using a copper/amine catalyst system (3,4). The commercially available PPO is synthesized by this process to give monofunctional PPO having a free phenolic hydroxy group at one end. Blended materials of PPO and polystyrene show excellent physical and impact properties, therefore, widely used in industrial fields. Aromatic polyesters, typically poly(ethylene terephthalate) and poly(1, 4-butylene terephthalate), are crystalline engineering thermoplastics showing high thermal stability (5).

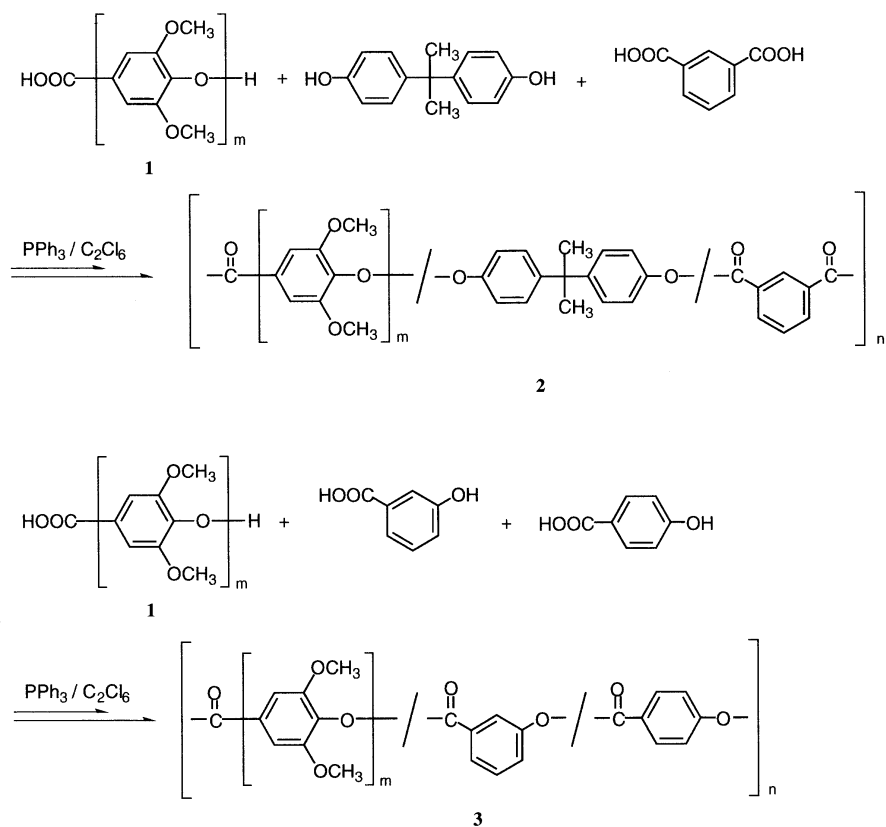
Polymerization catalyzed by an enzyme (“enzymatic polymerization”) provides a new methodology for polymer syntheses (6,7). Recently, syntheses of new polyaromatics using oxidoreductase catalyst have been developed. Peroxidases or oxidases induced an oxidative polymerization of phenol derivatives, yielding a new class of polyphenols. Furthermore, this enzymatic process is expected to be an alternative way for preparation of phenol polymers without using toxic formaldehyde, which is a monomer component for production of conventional phenolic resins (phenol-formaldehyde resins).

Very recently, we have found that 4-hydroxybenzoic acids, 3,5-dimethoxy-4-

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hydroxybenzoic acid (syringic acid) and 3,5-dimethyl-4-hydroxybenzoic acid, were oxidatively polymerized by laccase and peroxidase as catalyst (8,9). The polymerization involved elimination of not only hydrogen but also carbon dioxide to give PPO derivatives having a phenolic group at one end and a carboxylic acid group at the other. These polymers have heterogeneous two functional groups at the chain ends, and hence, will be useful as prepolymer for preparation of new functional polymeric materials containing PPO unit. This study deals with synthesis of PPO - aromatic polyester multiblock copolymer by using the enzymatically synthesized PPO from syringic acid (Scheme 1).



Scheme 1

Results and discussion

PPO having a phenolic group at one end and a carboxylic acid group at the other (**1**) was synthesized by laccase-catalyzed oxidative polymerization of syringic acid in an aqueous acetone. The degree of polymerization of **1** was determined by ¹H NMR spectroscopy as 13.5 (M_n = 1900).

In this study, PPO - aromatic polyester multiblock copolymers were synthesized by using **1** as monomer component in the presence of a mixture of triphenylphosphine and hexachloroethane, which is known to be an effective coupling agent for polycondensation

of an aromatic dicarboxylic acid / glycol or aromatic oxyacid (10).

In the copolymerization of **1**, bisphenol-A, and isophthalic acid, copolymer **2** was obtained in 67 % yield. The copolymer was isolated as acetone-insoluble part. In the size exclusion chromatographic (SEC) chart of **2**, the peak of **1** disappeared completely and a new peak appeared at lower elution volume. The molecular weight and polydispersity was 7800 and 1.3, respectively. The copolymerization of **1**, *m*- and *p*-hydroxybenzoic acids produced copolymer **3** having molecular of 7400 in 53 % yield. The structure of the copolymer was confirmed by ¹H and IR spectroscopies (see Experimental part). The PPO contents (repeating unit ratios) in copolymers **2** and **3** were determined by ¹H NMR as 51 and 61 %, respectively. The copolymer was almost soluble in chloroform, *N,N*-dimethylformamide (DMF), and pyridine, and insoluble in acetone, diethyl ether, acetone, and toluene.

Thermal properties of the present copolymers were evaluated by using differential scanning calorimetry (DSC) and thermogravimetry (TG). Figure 1 shows DSC traces (second scan) of **1-3** measured under nitrogen. In all samples, one shoulder due to the glass transition of PPO segment was clearly observed and there was no melting point below 300 °C. Glass transition temperatures of copolymers **2** and **3** (150 and 158 °C, respectively) were higher than that of **1** (138 °C). This may be due to the increase of the polymer molecular weight and/or to the increased stiffness of the main chain.

TG traces of **1-3** are shown in Figure 2. The measurement was performed under nitrogen. Polymer **1** began to decompose at 240 °C, whereas the onset temperature of the thermal decomposition of copolymers **2** and **3** was more than 280 °C. Temperatures at 5 weight-% loss ($T_{5\%}$) of **1-3** were 329, 365, and 385 °C, respectively. These data indicate that the multiblock copolymers had higher thermal stability than **1**. Larger $T_{5\%}$ of **3** than that of **2** is probable because of no aliphatic moiety in polyester moiety of **3**.

In conclusion, a PPO derivative having a carboxylic acid at one end and a phenolic hydroxy group at the other was copolymerized with bisphenol-A / isophthalic acid or hydroxybenzoic acids to give PPO - aromatic polyester multiblock copolymers. The resulting copolymer showed relatively high thermal stability. The multiblock copolymer is expected to have unique properties derived from PPO and aromatic polyesters. Further studies on synthesis of multiblock copolymers by using the end-functional PPO are now under way in our laboratory.

Experimental part

Materials

End-functional PPO (**1**) was synthesized by laccase-catalyzed oxidative polymerization of syringic acid (**8**). Other reagents and solvents were commercially available and used as received.

Synthesis of Multiblock Copolymer

0.20 g (0.11 mmol) of **1**, 0.16 g (0.70 mmol) of bisphenol-A, 0.12 g (0.70 mmol) of isophthalic acid, and 0.53 g (2.0 mmol) of triphenylphosphine were dissolved in 4 mL of pyridine. To the solution, 0.47 g (2.0 mmol) of hexachloroethane in 2 mL of pyridine was dropwise at 0 °C. The mixture was kept at 0 °C for 1 h, successively at room temperature for 1 h. The solvent was evaporated under reduced pressure and a large amount of acetone was added to the residue. The insoluble powdery materials were

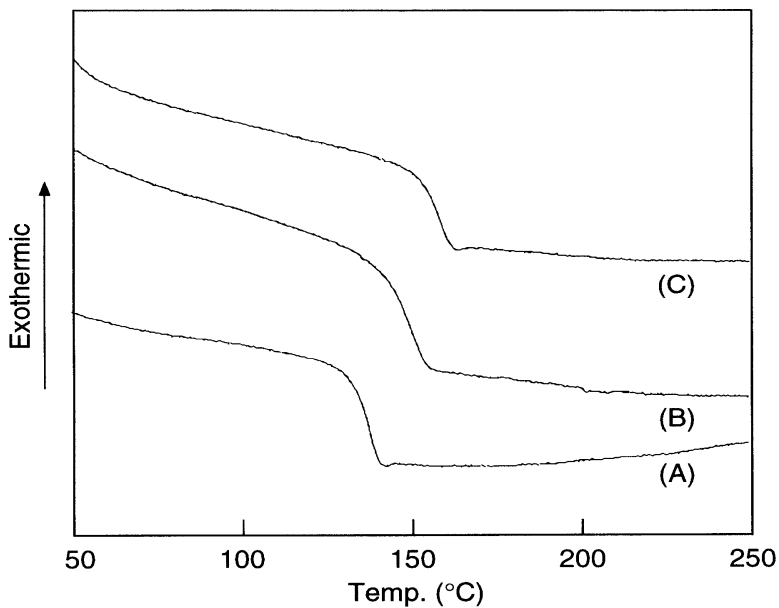


Figure 1. DSC traces of (A) polymer 1, (B) copolymer 2, and (C) copolymer 3.

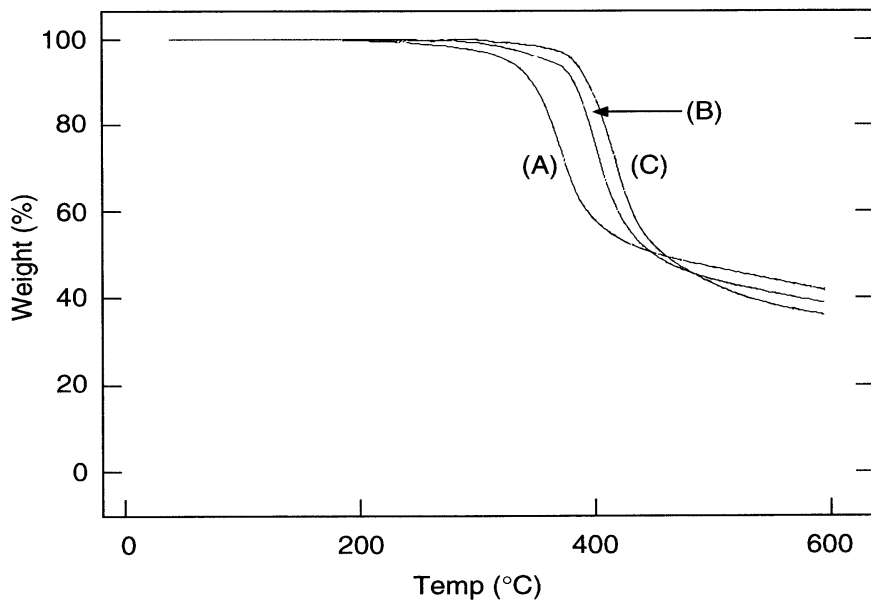


Figure 2. TG traces of (A) polymer 1, (B) copolymer 2, and (C) copolymer 3.

collected by filtration and dried in vacuo to give 0.30 g (yield 67 %) of the polymer.

^1H NMR (CDCl_3 / pyridine- d_5): δ 1.7 (s, CH_3C), 3.7 (s, CH_3OAr), 6.2 (s, Ar of PPO moiety), 7.0-7.4 (m, Ar of polyester moiety).

IR (KBr): 3450 (ν O-H), 2937, 2839 (ν C-H of CH_3), 1743 (ν C=O), 1603, 1493 (ν C=C of Ar), 1201 (ν C(Ar)-O-C(Ar)), 812 cm^{-1} (ν C-H of Ar).

In the combination of **1** (0.11 mmol), *m*- and *p*-hydroxybenzoic acids (each 0.70 mmol) under the similar reaction conditions, the corresponding copolymer was obtained in 53 % yield.

^1H NMR (CDCl_3) δ 3.7 (s, CH_3OAr), 6.2 (s, Ar of PPO moiety), 7.3-8.5 (m, Ar of polyester moiety).

Measurements

Size exclusion chromatographic (SEC) analysis was carried out using a Toso SC8020 apparatus with a refractive index (RI) detector under the following conditions: TSKgel GMH_{HR} -H, GMH_{HR} -N, GMH_{HR} -L, and G2000 H_{HR} columns and DMF containing 0.4 wt% LiCl eluent at a flow rate of 1.0 mL/min. ^1H NMR spectra were recorded on a Bruker DPX-400 spectrometer. IR spectra were recorded on Horiba FT-720 spectrometer. DSC measurement was made at a 10 $^\circ\text{C}/\text{min}$ heating rate under nitrogen using a Seiko SSC/5200 differential scanning calorimeter calibrated with an indium reference standard. TG analysis was performed using a Seiko SSC/5200 apparatus for thermogravimetry / differential thermal analysis at a heating rate of 10 $^\circ\text{C}/\text{min}$ in a gas flow rate of 300 mL/min.

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