# **RAPID COMMUNICATION**

# Preparation of AB-Type Diblock Copolymers Containing Poly-(2,6-dimethyl-1,4-phenylene oxide) and Methyl Methacrylate or Styrene Blocks

# G. HIZAL, N. BICAK, U. TUNCA

Istanbul Technical University, Chemistry Department, Maslak 80626, Istanbul, Turkey

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# INTRODUCTION

High molecular weight poly-(2,6-dimethyl-1,4-phenylene oxide) (PPO) is obtained from 2,6-dimethylphenol (DMP) by oxidative coupling polymerization.<sup>1</sup> The polymerization is accomplished by passing oxygen through a solution of DMP, a catalytic amount of copper(I) salt, and amine in an organic solvent. High molecular weight PPO is a useful material for engineering thermoplastic applications because of its outstanding physical and chemical properties. However, the use of neat poly-PPO is insignificant as a commercial product because of its high melt viscosity. The commercially available products are generally blends of PPO with high-impact polystyrene.<sup>2</sup>

Recently, low molecular weight PPO<sup>3-6</sup> has attracted considerable interest as starting materials for the preparation of block copolymers,<sup>7-13</sup> graft copolymers,<sup>14,15</sup> macromonomers,<sup>14-16</sup> and star-type polymers<sup>17,18</sup> of well-defined architectures. Low molecular weight PPO with a narrow molecular weight distribution can be prepared by the precipitation polymerization of DMP in the solvent/nonsolvent mixture under the action of Cu(I) Cl/amine-catalyst and oxygen<sup>5,6</sup> or by the redistribution of PPO with functional phenols.<sup>17</sup>

Tingerthal et al.<sup>9</sup> carried out the synthesis of an ABA-type triblock copolymer containing PPO (A) and polysulfone (B) blocks. Servens et al.<sup>12</sup> studied the

preparation of a diblock copolymer with PPO and 1,4polyisoprene segments. More recently, VanAert et al.<sup>13</sup> prepared diblock copolymers by the reaction of phenolterminated polystyrene with PPO.

The controlled/"living" radical polymerization such as copper-catalyst-mediated atom transfer radical polymerizations (ATRP) has been utilized for the synthesis of well-defined polymers with narrow molecular weight distributions.<sup>19–21</sup> ATRP involves the activation and deactivation of a propagating chain end as a result of the reversible atom transfer reaction between a metal salt and alkyl halides. A wide variety of monomers such as styrenes, acrylates, and acrylonitrile have been used for ATRP.<sup>22</sup>

To the best of our knowledge, this is the first report on the synthesis and characterization of AB-type block copolymers with well-defined PPO and methyl methacrylate (MMA) blocks. Also, a sample of block copolymer containing PPO and styrene (St) segments was achieved. The PPO oligomers with activated halogen end groups were used as macroinitiators for ATRP.

#### **EXPERIMENTAL**

2-Bromoisobutrylbromide (Aldrich) was used as received. 2,6-Dimethylphenol (Fluka) (DMP) was recrystallized twice from hexane. Cu(I)Cl and (Br) (Aldrich) and diphenylether (DPE) (Fluka) were used as received. N,N,N',N'-Tetramethylethylenediamine (TMED) (Aldrich) and N'',N',N''-pentamethyl-diethylenetriamine (PMDETA) (Aldrich) were distilled at reduced pressure

Correspondence to: U. Tunca (E-mail: tuncau@itu.edu.tr) Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 39, 2426–2429 (2001) © 2001 John Wiley & Sons, Inc.

Polymer Code	Polymer Time (min)	Conversion (%)	${M}_{ m n,theo}$	$M_{ m n,NMR}$	$M_{ m n,GPC}$	$M_{ m w}/M_{ m n}$	$T_{\rm g}(^{ m o}{ m C})$ Onset
PPO-b-MMA1ª	45	48	18,700	19,200	17,500	1.27	117.5
$PPO-b-MMA2^{a}$	90	68	23,700	26,100	21,700	1.24	115
$PPO-b-St^{b}$	240	6	8200	8000	8400	1.38	163

Table I. Synthesis and Characterization of Block Copolymers

<sup>a</sup>  $[MMA]_0 = 4.67$  M;  $[M]_0$ :  $[I]_0$ : [CuCl]: [PMDETA] = 240 : 1 : 1 : 1, in DPE 50% (v/v) at 90 °C. <sup>b</sup>  $[St]_0 = 5.82$  M;  $[M]_0$ :  $[I]_0$ : [CuBr]: [PMDETA] = 240 : 1 : 1 : 1, in DPE 33% (v/v) at 110 °C.

before use. All solvents and monomers were purified by conventional methods.

<sup>1</sup>H NMR spectra were measured at 250 MHz on a Bruker AC 250. The number-average molecular weights of PPO were determined using <sup>1</sup>H NMR spectra by comparing the aromatic protons of the end groups with those of the repeating unit.

Gel permeation chromatographic (GPC) analysis was performed with a setup consisting of the Agilent pump and refractive-index detector (Model 1100) and three Waters Styragel columns (HR 4, HR 3, and HR 2). Tetrahydrofuran (THF) was the eluent at a flow rate of 0.3 mL/min. The molecular weight of the polymers was calculated with the aid of polystyrene standards.

The thermal transitions [glass-transition temperature  $(T_{\sigma})$ ] were obtained on a PerkinElmer DSC 6 instrument at a heating rate of 10 °C/min in nitrogen atmosphere.  $T_{\rm g}$  values were determined from the second heating scan as onset temperatures.

# Synthesis of PPO Macroinitiator Containing Bromoester **Functional End Group**

A sample of PPO with a phenolic OH functional end group was prepared by the precipitation polymerization of DMP similar to the literature procedure.<sup>6</sup> About 0.2 g (1.6 mmol) of DMP and 0.77 mL (5.1 mmol) of TMED were dissolved in 41.6 mL of methanol. The reaction mixture was heated to 35 °C, bubbling the air through. The addition of 0.04 g (0.4 mmol) of CuCl started the reaction. Then, 4.8 g (39 mmol) of DMP dissolved in 25 mL of methanol were added dropwise to the reaction mixture in 1 h. After 5 h, the precipitated PPO was filtered, washed with methanol several times, and dried to yield 4 g of polymer. The polymer was purified two times by precipitation into methanol from chloroform:  $M_{\rm n,GPC} = 6900, M_{\rm w}/M_{\rm n} = 1.81,$  and  $M_{\rm n,NMR}$ = 6500;  $T_{\rm g}$  = 183 °C (DSC).

The synthesis of PPO macroinitiator containing a bromoester functional end group was carried out as follows: About 2.5 g of PPO ( $M_{n,NMR} = 6500$ ) were dissolved in 30 mL of dry 1,2-dimethoxyethane and cooled to 0 °C under nitrogen. To the stirred reaction mixture was added 0.9 mL of 2-bromoisobutrylbromide.

Next, 1 mL of triethylamine dissolved in 10 mL of 1,2-dimethoxyethane was added slowly in 1 h, and the reaction mixture was stirred at room temperature overnight. The solution was precipitated into 350 mL of distilled water, filtered, washed with water, and dried. The crude product was dissolved in toluene and precipitated in methanol to give a white powder in 96% yield:  $M_{
m n,GPC} = 6600, M_{
m w}/M_{
m n} = 1.46,$  and  $M_{
m n,NMR} = 6700; T_{
m g}$  $= 188 \ ^{\circ}C \ (DSC).$ 

# A Typical Procedure for the Syntheses of PPO-*b*-methyl methacrylate and PPO-b-styrene Using PPO Macroinitiator

ATRP was carried out in a dried flask equipped with a nitrogen inlet and magnetic stirring bar. A given amount of monomer, CuCl or CuBr, PMDETA, DPE, and macroinitiator were added to the flask under slightly positive nitrogen pressure. The flask content was then subjected to freeze-vacuum-thaw cycles three times to remove dissolved gases. Then, the flask was immersed in an oil bath and heated for a given time. The polymer was isolated by dissolving in THF and passing through an alumina column, concentrated, and then isolated by precipitation into methanol. All polymers were vacuum-dried at 50 °C overnight. The results are summarized in Table I.

# **RESULTS AND DISCUSSION**

PPO macroinitiator was prepared by treating PPO with 2-bromoisobutrylbromide in the presence of triethylamine as an acid acceptor (Scheme 1). The molecular weights of PPO and the PPO macroinitiator determined by GPC were consistent with those determined by <sup>1</sup>H NMR analyses. In the <sup>1</sup>H NMR spectrum of the PPO macroinitiator, a peak assignable to CH<sub>3</sub> protons of 2-bromoisobutryl group might be overlapped with the large peaks assigned to CH<sub>3</sub> protons of PPO at 2.09-1.90 ppm. On the other hand, two aromatic protons, meta to bromoester group, shifted from 6.36 to 6.42 ppm. This increment indicated that esterification



changed the chemical environment of the two aromatic end protons.

The ATRP of MMA and St initiated by the PPO macroinitiator has been carried out in DPE solution. The corresponding block copolymers were obtained according to the reaction given in Scheme 1, and the results are summarized in Table I. In the case of MMA polymerization, the halide-exchange technique<sup>23</sup> was applied to improve the initiation efficiency. Figure 1 shows the GPC chromatograms of precursor polymer and block copolymers. As is clearly seen, the peak corresponds to the PPO-*b*-MMA block copolymer shifted to the lower retention time. This suggests that the PPO



**Figure 1.** GPC traces of PPO macroinitiator and block copolymers: PPO macroinitiator (a), PPO-*b*-St (b), and PPO-*b*-MMA1 (c).



**Figure 2.** <sup>1</sup>H NMR spectra of block copolymers (CDCl<sub>a</sub>): PPO-*b*-MMA1 (a) and PPO-*b*-St (b).

macroinitiator is fully functionalized in our experimental condition. The observed decreases in the polydispersity of the PPO-*b*-MMA block copolymer can be attributed to the well-defined side blocks prepared by ATRP. In the case of the ATRP of St in DPE solution, however, slow polymerization was observed so that conversion only reached up to 6% in 4 h. This finding is in agreement with the experimental data obtained by Matyjaszewski et al.<sup>24</sup> These researchers also showed that under the dilute polymerization conditions in which the polymerization rate is slow a termination reaction was observed for the ATRP of St. This effect was more pronounced for the bromine-containing initiator. The process was promoted by polar solvents. In this respect, utility of this process for the ATRP of St is limited.

The block copolymer structures were also elucidated by means of <sup>1</sup>H NMR measurements. The <sup>1</sup>H NMR spectrum of the PPO-*b*-MMA1 block copolymer displays signals at 3.6 ppm [—OCH<sub>3</sub> of poly(methyl methacrylate) (PMMA)] and centers at 6.47 ppm (ArH of PPO) [Fig. 2(a)]. On the basis of a comparison of the aromatic protons to —OCH<sub>3</sub> protons of PMMA, the molecular weight of the block copolymer was calculated. A similar calculation was performed for the PPO*b*-St block copolymer using the integration ratio of signals around 7.0 ppm (ArH of St) to 6.47 ppm (ArH of PPO) [Fig. 2(b)]. The molecular weights of the block copolymers obtained in this way are in agreement with the theoretical molecular weights calculated from  $M_{\rm n,theo} = ([{\rm M}]_0/[{\rm I}]_0 \times {\rm conv.} \times {\rm MW}_{\rm monomer}) + 6700$ , where 6700 is the molecular weight of the PPO macroinitiator (Table I). The low  $M_{\rm n,gpc}$  values of the PPO-*b*-MMA block copolymers could be result of the differences between the hydrodynamic volume of the block copolymers and polystyrene standards.

DSC analysis of the diblock copolymers displayed a single  $T_{\rm g}$  for each case indicating a homogeneous system (Table I). Incorporation of the MMA segment to PPO lowered the  $T_{\rm g}$  of 188 to 115 °C between those of the homopolymers. On the other hand, the PPO (A)-St (B) diblock copolymer also showed a single  $T_{\rm g}$  of 163 °C. The blends prepared from PPO and polystyrene form a miscible system for all compositions.

The synthesis of well-defined block copolymers containing PPO and MMA has been carried out using the halogenated PPO macroinitiator for ATRP, and the utility of this process was shown for St. By means of this strategy, synthesis of star block copolymers containing PPO and MMA blocks will be in progress.

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