RAPID COMMUNICATION

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

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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.[1] 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.[2]

Recently, low molecular weight PPO[3–6] has attracted considerable interest as starting materials for the preparation of block copolymers,[7–13] graft copolymers,[14,15] macromonomers,[14–16] and star-type polymers[17,18] 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[5,6] or by the redistribution of PPO with functional phenols.[17]

Tingerthal et al.[9] carried out the synthesis of an ABA-type triblock copolymer containing PPO (A) and polysulfone (B) blocks. Servens et al.[12] studied the preparation of a diblock copolymer with PPO and 1,4-polyisoprene segments. More recently, VanAert et al.[13] prepared diblock copolymers by the reaction of phenol-terminated 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.[19–21] 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.[22]

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

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