

Synthesis of Poly(methyl methacrylate)-*b*-Polystyrene Containing a Crown Ether Unit at the Junction Point via Combination of Atom Transfer Radical Polymerization and Nitroxide Mediated Radical Polymerization Routes

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ABSTRACT: Poly(methyl methacrylate)-*b*-polystyrene (PMMA-*b*-PS) containing a benzo-15-crown-5 unit at the junction point was prepared by combining atom transfer radical polymerization and nitroxide-mediated radical polymerization. For this purpose, 6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecene-2-carboxylic acid 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl ester (**3**) was synthesized and used as an initiator in atom transfer radical polymerization of methyl methacrylate in the presence of CuCl and pentamethyldiethylenetriamine at 60°C. A linear behavior was observed in both plots of $\ln([M]_0/[M])$ versus time and $M_{n, GPC}$ versus conversion indicating that the polymerization proceeded in a controlled/living manner. Thus obtained PMMA precursor was used as a macroinitiator in nitroxide-mediated radical polymerization of styrene (St) at 125°C to give well-defined PMMA-*b*-PS with crown ether per chain. Kinetic data were also obtained for copolymerization. Moreover, potassium picrate (K^+ picrate) complexation of **3** and PMMA-*b*-PS copolymer was studied. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 3242–3249, 2006

Keywords: atom transfer radical polymerization; crown ether; diblock copolymer; nitroxide-mediated free-radical polymerization

INTRODUCTION

Recently, the controlled/living radical polymerizations have been used for the synthesis of well-defined, narrow polydispersity polymers.^{1–5} Among them, metal catalyzed free-radical polymerization, often called atom transfer radical polymerization (ATRP) and nitroxide-mediated free-radical polymerization (NMP) are more versatile methods for the controlled/living radical polymerization of various types of monomers.

One of the advantages of controlled/living radical polymerizations when compared with conventional free-radical polymerization is the control of the molecular weight, narrow molecular weight distribution, and chain end functionality.

Pedersen's⁶ pioneering invention on macrocyclic polyethers (crown ethers) led to supramolecular chemistry. The crown ethers and the related compounds have attracted more interest because of their potential for a large number of applications. The reason for their current development is based on their powerful and selective complexation properties. The syntheses and properties of crown ethers and their large number of derivatives have been studied extensively.^{7,8}

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