Synthesis and Characterization of Well-Defined ABC-Type Triblock Copolymers via Atom Transfer Radical Polymerization and Stable Free-Radical Polymerization

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ABSTRACT: An asymmetric difunctional initiator 2-phenyl-2-[(2,2,6,6 tetramethylpiperidino)oxy] ethyl 2-bromo propanoate (**1**) was used for the synthesis of ABC-type methyl methacrylate (MMA)-*tert*-butylacrylate (*t*BA)-styrene (St) triblock copolymers via a combination of atom transfer radical polymerization (ATRP) and stable free-radical polymerization (SFRP). The ATRP-ATRP-SFRP or SFRP-ATRP-ATRP route led to ABC-type triblock copolymers with controlled molecular weight and moderate polydispersity ($M_w/M_n < 1.35$). The block copolymers were characterized by gel permeation chromatography and ^{1}H NMR. The retaining chain-end functionality and the applying halide exchange afforded high blocking efficiency as well as maintained control over entire routes. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 2025–2032, 2002
Keywords: atom transfer radical polymerization (ATRP); stable free-radical polymerization (SFRP); triblock copolymer

INTRODUCTION

Recently, the controlled/"living" radical polymerizations have been used for the synthesis of well-defined, narrow polydispersity polymers. Among them, copper catalyst-mediated atom transfer radical polymerization (ATRP) and stable free-radical polymerization (SFRP) are versatile methods for the controlled radical polymerization of vinylic-type monomers.[1–10] One of the advantages of controlled radical polymerizations when compared with traditional free-radical polymerization is the control of the molecular weight and chain-end functionality.[11] A wide range of functionality may be introduced into a polymer chain end with an asymmetric difunctional initiator if one of the functional groups remains intact during the polymerization. It has provided the synthesis of well-defined block copolymers by a sequential two-step or one-pot method without any transformation or protection of initiating sites. In this circumstance, a number of articles have reported by using ATRP living ring-opening polymerization (ROP),[12,13] SFRP-ROP,[14–16] and SFRP-ATRP[17] in which the strategy used in those experiments, however, is different from those presented here. Moreover, the syntheses of ABC- or ABA-type block copolymers have been reported using controlled/'living' polymerization techniques, for example, ATRP or reverse addition–fragmentation chain-transfer polymerization.[18–24]

A key issue for the synthesis of well-defined block copolymers in ATRP is the nature and quantity of the chain-end functionality of the first block that controls both the initiation and the blocking efficiency during the polymerization of a second monomer. In addition, the producing fully functionalized chains require the suppression of termination and transfer reactions and can be achieved by adjusting the ratio of (k_{deact}/k_{act}) in ATRP. In this respect, it was shown that the amine ligand plays a cru-

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