Facile Synthesis of AB_2-Type Miktoarm Star Polymers through the Combination of Atom Transfer Radical Polymerization and Ring-Opening Polymerization

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ABSTRACT: A novel miktofunctional initiator (**1**), 2-hydroxyethyl 3-[(2-bromopropanoyl)oxy]-2-{[(2-bromopropanoyl)oxy]methyl}-2-methyl-propanoate, possessing one initiating site for ring-opening polymerization (ROP) and two initiating sites for atom transfer radical polymerization (ATRP), was synthesized in a three-step reaction sequence. This initiator was first used in the ROP of ϵ-caprolactone, and this led to a corresponding polymer with secondary bromide end groups. The obtained poly(ϵ-caprolactone) (PCL) was then used as a macroinitiator for the ATRP of *tert*-butyl acrylate or methyl methacrylate, and this resulted in AB_2-type PCL–[poly(*tert*-butyl acrylate)]$_2$ or PCL–[poly(methyl methacrylate)]$_2$ miktoarm star polymers with controlled molecular weights and low polydispersities (weight-average molecular weight/number-average molecular weight < 1.23) via the ROP–ATRP sequence. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 2313–2320, 2004
Keywords: atom transfer radical polymerization (ATRP); ring-opening polymerization (ROP); miktoarm star polymers

INTRODUCTION

The combination of various controlled free-radical and conventional living polymerization techniques to produce novel polymer architectures is quite important because of the synthetic limitations of the various techniques. This approach enables researchers to combine very different types of monomers into one polymeric structure by a one-pot or sequential two-step method. Atom transfer radical polymerization (ATRP),[1–4] which is the most versatile method of the controlled free-radical polymerization systems, uses a wide variety of monomers, catalysts, solvents, and reaction temperatures. It has been used for the synthesis of polymers with well-defined compositions (e.g., block, gradient, or alternating), topologies (e.g., star, comb, or branched), and chain functionalities.[5–8] The living ring-opening polymerization (ROP) of lactones and lactides has recently received much attention for the preparation of polymers with complex structures.[9] Through the combination of ATRP and ROP, block,[10,11] graft,[12] dendrimer-like star,[13] and hyperbranched[14] polymers have been successfully prepared. To the best of our knowledge, however, there have been few studies concerning the synthesis of miktoarm star polymers with consecutive ATRP and ROP processes. Recently, Hedrick et al.[15] synthesized a miktofunctional initiator with initiating sites for both ATRP and ROP and used it to prepare miktoarm star polymers (A_3B_3-type) containing alternating poly(ϵ-caprolactone) (PCL) and poly(methyl methacrylate) (PMMA) arms.

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