

Synthesis of Miktoarm Star and Miktoarm Star Block Copolymers via a Combination of Atom Transfer Radical Polymerization and Stable Free-Radical Polymerization

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ABSTRACT: A trifunctional initiator, 2-phenyl-2-[(2,2,6,6-tetramethyl)-1-piperidinyloxy] ethyl 2,2-bis[methyl(2-bromopropionato)] propionate, was synthesized and used for the synthesis of miktoarm star AB_2 and miktoarm star block AB_2C_2 copolymers via a combination of stable free-radical polymerization (SFRP) and atom transfer radical polymerization (ATRP) in a two-step or three-step reaction sequence, respectively. In the first step, a polystyrene (PSt) macroinitiator with dual ω -bromo functionality was obtained by SFRP of styrene (St) in bulk at 125 °C. Next, this PSt precursor was used as a macroinitiator for ATRP of *tert*-butyl acrylate (*t*BA) in the presence of Cu(I)Br and pentamethyldiethylenetriamine at 80 °C, affording miktoarm star (PSt)(*t*BA)₂ [where *t*BA is poly(*tert*-butyl acrylate)]. In the third step, the obtained St(*t*BA)₂ macroinitiator with two terminal bromine groups was further polymerized with methyl methacrylate by ATRP, and this resulted in (PSt)(*t*BA)₂(PMMA)₂-type miktoarm star block copolymer [where PMMA is poly(methyl methacrylate)] with a controlled molecular weight and a moderate polydispersity (weight-average molecular weight/number-average molecular weight < 1.38). All polymers were characterized by gel permeation chromatography and ¹H NMR. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 2542–2548, 2003

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INTRODUCTION

Miktoarm star polymers have been synthesized with two general strategies.^{1,2} The first involves living anionic polymers being consecutively reacted with an appropriate multifunctional core (a chlorosilane compound) in a consecutive polymer reaction. The second is the reaction of the active chain with divinylbenzene (DVB). In this route, the living polymer (derived from anionic polymerization) is added to DVB, and this affords the formation of a star polymer with active anionic

sites in the polymer core. The subsequent anionic polymerization of another monomer results in a miktoarm star polymer.

However, in recent years, there has been very fast growth in the use of controlled/living radical polymerizations, which offer some advantages over anionic polymerizations because they do not demand rigorous experimental conditions and are applicable to a wide range of monomers. Stable free-radical polymerization (SFRP),³ based on the use of stable nitroxide free radicals, and M_t^n /ligand-catalyst-mediated atom transfer radical polymerization (ATRP)^{4–7} are versatile methods for controlled radical polymerizations. Therefore, controlled/living radical polymerizations have been used for the synthesis of polymers with well-

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