Preparation of ABC Miktoarm Star Terpolymer Containing Poly(ethylene glycol), Polystyrene, and Poly(*tert*-butylacrylate) Arms by Combining Diels–Alder Reaction, Atom Transfer Radical, and Stable Free Radical Polymerization Routes

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ABSTRACT: The ABC type miktoarm star terpolymer was prepared utilizing "core-in" and "core-out" methods via combination of Diels–Alder reaction (DA), stable free radical polymerization (SFRP), and atom transfer radical polymerization (ATRP). First, in DA reaction, poly(ethylene glycol)-maleimide (PEG-maleimide) precursor was reacted with succinic acid anthracen-9-ylmethyl ester 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxy-carbonyl]-propyl ester, **8**, to give DA adduct, **9**, which has appropriate functional groups for SFRP and ATRP. Second, a previously obtained **9** was used as a macroinitiator for SFRP of styrene at 125 °C. As a third step, this PEG-polystyrene (PEG-PSt) precursor with a bromine functionality in the core was employed as a macroinitiator for ATRP of *tert*-butylacrylate (*t*BA) in the presence of Cu(I)Br and pentamethyldiethylenetriamine at 80 °C to give ABC type miktoarm star terpolymer (PEG-PSt-P*t*BA) with controlled molecular weight and low polydispersity ($M_w/M_n < 1.27$). The obtained polymers were characterized by gel permeation chromatography and ^{1}H NMR.
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INTRODUCTION

Miktoarm star polymers have been synthesized on the basis of two general strategies.[1,2] The first involves the use of living anionic polymers to be consecutively reacted with an appropriate multifunctional core (chlorosilane compound) in a consecutive polymer reaction. The second is the reaction of the active chain with divinylbenzene (DVB). In this route, living polymer (derived from anionic polymerization) is added to DVB affording to the formation of a star polymer with active anionic sites on the polymer core. Subsequent anionic polymerization of another monomer results in the miktoarm star polymer.

The ionic polymerizations (anionic or cationic) were the only living systems available until recently. These systems give the polymers with the controlled molecular weight, well-defined chain ends, and low polydispersity. In recent years, the use of the controlled/living radical polymerization (CRP) techniques in the synthesis of complex macromolecules has fast increased because of the variety of applicable monomers

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