

# Synthesis of $A_3B_3$ -type polystyrene–poly(methyl methacrylate) miktoarm star polymers *via* combination of stable free radical and atom transfer radical polymerization routes

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**Abstract**—An  $A_3B_3$ -type miktoarm star polymer was prepared utilizing a “core-out” method *via* combination of stable free radical polymerization (SFRP) and atom transfer radical polymerization (ATRP). First, SFRP of styrene was carried out by using a miktofunctional initiator, benzene-1,3,5-tricarboxylic acid tris{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethoxy-carbonyl]propyl} ester, at 125 °C. Second, previously obtained polystyrene ( $A_3$ -type PSt) precursor with three bromine functionalities in the core was used as a macroinitiator for ATRP of methyl methacrylate (MMA) in the presence of Cu(I)Cl and pentamethyldiethylenetriamine at 90 °C in order to give an  $A_3B_3$ -type miktoarm star polymer,  $(PSt)_3$ -(PMMA) $_3$ , with controlled molecular weight and moderate polydispersity ( $M_w/M_n < 1.41$ ). The obtained polymers were characterized by gel-permeation chromatography and  $^1H$ -NMR.

**Keywords:** Miktoarm star polymer; atom transfer radical polymerization (ATRP); stable free radical polymerization (SFRP).

## 1. INTRODUCTION

To date, 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.

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