

# Novel Miktofunctional Initiator for the Preparation of an ABC-Type Miktoarm Star Polymer via a Combination of Controlled Polymerization Techniques

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**ABSTRACT:** An ABC-type miktoarm star polymer was prepared with a core-out method via a combination of ring-opening polymerization (ROP), stable free-radical polymerization (SFRP), and atom transfer radical polymerization (ATRP). First, ROP of  $\epsilon$ -caprolactone was carried out with a miktofunctional initiator, 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yl oxy)-ethyl ester, at 110 °C. Second, previously obtained poly( $\epsilon$ -caprolactone) (PCL) was used as a macroinitiator for SFRP of styrene at 125 °C. As a third step, this PCL–polystyrene (PSt) precursor with a bromine functionality in the core was used as a macroinitiator for ATRP of *tert*-butyl acrylate in the presence of Cu(I)Br and pentamethyldiethylenetriamine at 100 °C. This produced an ABC-type miktoarm star polymer [PCL–PSt–poly(*tert*-butyl acrylate)] with a controlled molecular weight and a moderate polydispersity (weight-average molecular weight/number-average molecular weight < 1.37). The obtained polymers were characterized with gel permeation chromatography and <sup>1</sup>H NMR. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 4228–4236, 2004

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## INTRODUCTION

Miktoarm star polymers are synthesized with two general strategies.<sup>1,2</sup> The first involves living anionic polymers being 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, a living polymer (derived from anionic polymerization) is added to DVB, and this leads to the formation of a star polymer with active anionic sites on the polymer core. The subse-

quent anionic polymerization of another monomer results in a miktoarm star polymer.

Ionic polymerizations (anionic or cationic) were the only living systems available until recently. These systems produce polymers with controlled molecular weights, well-defined chain ends, and low polydispersity. However, in recent years there has been rapid growth in the area of growing controlled/living radical polymerizations, which have some advantages over anionic polymerization, in that they do not require rigorous experimental conditions and are applicable to a wide range of monomers. Stable free-radical polymerization<sup>3</sup> (SFRP), based on the use of stable nitroxide free radicals, and  $M_n^+$ /ligand catalyst-mediated atom transfer radical polymerization (ATRP)<sup>4–6</sup> are versatile methods for controlled radical polymerizations. Although there has been remarkable progress in all controlled/living

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