

Photoresponsive Poly(methyl methacrylate)₂–(Polystyrene)₂ Miktoarm Star Copolymer Containing an Azobenzene Moiety at the Core

TUBA ERDOGAN, EDA GUNGOR, HAKAN DURMAZ, GURKAN HIZAL, UMIT TUNCA

Department of Chemistry, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

Received 18 October 2005; accepted 22 November 2005

DOI: 10.1002/pola.21253

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We prepared a novel miktoarm star copolymer with an azobenzene unit at the core via combination of atom transfer radical polymerization (ATRP) and nitroxide-mediated free radical polymerization (NMP) routes. For this purpose, first, miktofunctional initiator, **3**, with tertiary bromide (for ATRP) and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (for NMP) functionalities and an azobenzene moiety at the core was synthesized. The initiator **3** thus obtained was used in the subsequent living radical polymerization routes such as ATRP of MMA and NMP of St, respectively, to give A₂B₂ type miktoarm star copolymer, (PMMA)₂-(PSt)₂ with an azobenzene unit at the core with controlled molecular weight and low polydispersity ($M_w/M_n < 1.15$). The photoresponsive properties of **3** and (PMMA)₂-(PSt)₂ miktoarm star copolymer were investigated. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 1396–1403, 2006

Keywords: atom transfer radical polymerization; azobenzene; cis- and trans-isomerization; miktoarm star polymer; nitroxide-mediated free radical polymerization

INTRODUCTION

Miktoarmstar polymers have been synthesized on the basis of the 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 provide 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 increased fast because of the variety of applicable monomers and more tolerant experimental conditions than that the living ionic polymerization routes require. The reversible addition fragmentation chain transfer (RAFT)³ polymerization, the nitroxide-mediated free radical polymerization (NMP),⁴ and the metal mediated controlled/living radical polymerization often called as atom transfer radical polymerization (ATRP)^{5–7} are versatile methods for the CRPs. However, the latter two cases turned out to be more extensive.

In addition, living ring opening polymerization (ROP) technique has found wide applications in the polymerization of lactones and lactides.⁸

Correspondence to: G. Hizal or U. Tunca (E-mail: hizal@itu.edu.tr or tunca@itu.edu.tr)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 44, 1396–1403 (2006)
© 2006 Wiley Periodicals, Inc.