

Heteroarm H-Shaped Terpolymers through the Combination of the Diels–Alder Reaction and Controlled/Living Radical Polymerization Techniques

HAKAN DURMAZ, FIGEN KARATAS, UMIT TUNCA, GURKAN HIZAL

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

Received 22 February 2006; accepted 12 April 2006

DOI: 10.1002/pola.21499

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

ABSTRACT: Heteroarm H-shaped terpolymers (PS)(PtBA)–PEO–(PtBA)(PS) and (PS)(PtBA)–PPO–(PtBA)(PS) [where PS is polystyrene, PtBA is poly(*tert*-butyl acrylate), PEO is poly(ethylene oxide), and PPO is poly(propylene oxide)], containing PEO or PPO as a backbone and PS and PtBA as side arms, were prepared via the combination of the Diels–Alder reaction and atom transfer radical and nitroxide-mediated radical polymerization routes. Commercially available PEO or PPO containing bismaleimide end groups was reacted with a compound having an anthracene functionality, succinic acid anthracen-9-yl methyl ester 3-(2-bromo-2-methylpropionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethoxycarbonyl]propyl ester, with a Diels–Alder reaction strategy. The obtained macroinitiator with tertiary bromide and 2,2,6,6-tetramethylpiperidin-1-oxy functional end groups was used subsequently in the atom transfer radical polymerization of *tert*-butyl acrylate and in the nitroxide-mediated free-radical polymerization of styrene to produce heteroarm H-shaped terpolymers with moderately low molecular weight distributions (<1.31). The polymers were characterized with ¹H NMR, ultraviolet, gel permeation chromatography, and differential scanning calorimetry. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 3947–3957, 2006

Keywords: anthracene; atom transfer radical polymerization (ATRP); Diels–Alder reaction; H-shaped polymers; maleimide; nitroxide-mediated radical polymerization; poly(ethylene oxide); poly(propylene oxide); polystyrene; poly(*tert*-butyl acrylate)

INTRODUCTION

H-shaped polymers, complex macromolecular structures in which two side arms are attached to each end of a polymer chain, have been generally synthesized through an anionic polymerization route with chlorosilane or aromatic diolefins as coupling agents.^{1–5} Thus, H-shaped polymers with a polystyrene (PS) backbone and side arms,¹ a polyisoprene (PI) backbone and side arms,³ a PI backbone and

PS side arms,^{2,4} and a polybutadiene backbone and side arms⁵ have been prepared with the anionic polymerization technique.

Ionic polymerizations (anionic or cationic) were the only living systems available until recently. These systems provide polymers with controlled molecular weights, well-defined chain ends, and low polydispersity. In recent years, the use of controlled/living radical polymerization techniques in the synthesis of complex macromolecules has quickly increased because of the variety of applicable monomers and because the techniques are more tolerant of experimental conditions than living ionic polymerization routes. Reversible addi-

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

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 44, 3947–3957 (2006)
© 2006 Wiley Periodicals, Inc.