

Preparation of Block Copolymers Via Diels Alder Reaction of Maleimide- and Anthracene-End Functionalized Polymers

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ABSTRACT: A number of diblock copolymers were successfully prepared by Diels–Alder reaction, between maleimide- and anthracene-end functionalized poly (methyl methacrylate) (PMMA), polystyrene (PS), poly(*tert*-butyl acrylate) (*Pt*BA), and poly(ethylene glycol) (PEG) in toluene, at 110 °C. For this purpose, 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0_{2,6}]dec-8-en-4-yl)-ethyl ester, **2**, 9-anthrylmethyl 2-bromo-2-methyl propanoate, **3**, and 2-bromo-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0_{2,6}]dec-8-en-4-yl)-ethyl ester, **4**, were used as initiators in atom transfer radical polymerization, in the presence of Cu(I) salt and pentamethyldiethylenetriamine (PMDETA), at various temperatures. On the other hand, PEG with maleimide- or anthracene-end functionality was achieved by esterification between monohydroxy PEG and succinic acid monoanthracen-9-ylmethyl ester, **1**, or 4-maleimido-benzoyl chloride. Thus-obtained PMMA-*b*-PS, PEG-*b*-PS, *Pt*BA-*b*-PS, and PMMA-*b*-PEG block copolymers were characterized by ¹H NMR, UV, and GPC. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 1667–1675, 2006

Keywords: anthracene; atom transfer radical polymerization; diblock copolymer; Diels–Alder reaction; maleimide

INTRODUCTION

In recent years, the use of the controlled/living radical polymerization (CRP) techniques for the synthesis of well-defined, narrow polydispersity polymers has fast increased because of the variety of applicable monomers and more tolerant experimental conditions than the required living ionic polymerization routes. The reversible addition fragmentation chain transfer polymerization,¹ the nitroxide-mediated free radical polymerization² (NMP), and the metal-mediated CRP, often called as atom transfer radical polymerization^{3–5} (ATRP), are versatile methods for the CRPs. However, the latter two cases turned out to

be more extensive. One of the advantages of CRP methods when compared with conventional free radical polymerization is the control of molecular weight (MW) and chain-end functionality. A wide range of functionality may be introduced into a polymer chain using a heterofunctional initiator if one of the functional groups remains intact during the polymerization. This has provided the synthesis of well-defined block copolymers by a sequential two-step or one-pot polymerization method, without any chemical transformation or protection of initiating sites. In this point of view, using this strategy, a number of block copolymers have been prepared by combination of different polymerization mechanisms, such as ATRP-NMP,^{6,7} ATRP-living ring opening polymerization (ROP),^{8–11} NMP-ROP,^{8,9,12,13} and ATRP-living cationic polymerization.¹⁴

On the other hand, there have been alternative routes for the preparation of block copolymers.

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