

Block copolymers by transformation of living ring opening polymerization into an initer process

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Abstract

The transformation of ring opening polymerization into an initer process is reported for the preparation of the block copolymer of ϵ -caprolactone (CL) with styrene (St). In the first step, ring opening polymerization of CL was carried out by using triphenyl methanol (TPM) as the initiator and aluminum alkoxide as the promoter, respectively, to give a triphenylmethyl (trityl)-terminated polymer. UV and $^1\text{H-NMR}$ studies show that the trityl group associated with the active alkoxy group of the initiator is selectively attached to one chain end. In the second step, the trityl-terminated polymer served as a thermal 'initer' for the polymerization of styrene and this makes it possible to prepare a block copolymer. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

A transformation reaction is an elegant way to synthesize block copolymers of monomers that polymerize with different mechanisms. In this concept, a polymer, obtained by a particular polymerization mechanism, is functionalized either by initiation or termination of chemical reactions. The polymer is isolated and purified and finally the functional groups are converted to another kind of species capable of initiating polymerization of the second monomer. A wide range of transformation reactions combining various polymerization modes are available [1,2].

Living polymerization is an essential technique for synthesizing polymers with controlled molecular weight and molecular weight distribution. Moreover, living polymerization methods provide several powerful tools for the synthesis of macromonomers, macroinitiators, functional polymers, block and graft copolymers with

a well defined structure. In this way, the need for special polymers having a desired combination of physical properties can be fulfilled. Controlled polymerization proceeds by anionic or cationic group transfer or radical mechanisms.

In the last few years many efforts have been devoted to the development of living radical polymerization [3]. Inifer or iniferter systems [4], stable radical polymerization [5] and atom transfer radical polymerization [6] were proposed. The iniferter technique was extensively explored during the last decades for the preparation of block copolymers. The concept of iniferter (*initiator-transfer agent-terminator*) was proposed by Otsu et al. [7] for the design of the polymer chain end structure. The mechanism of the polymerization by an initiator ($\text{R-R}'$) may be expressed as follows, by considering ordinary bimolecular termination.



The same group showed that certain azo compounds, such as phenylazotriphenylmethane can act

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