A new strategy for the one-step synthesis of block copolymers through simultaneous free radical and ring opening polymerizations using a dual-functional initiator

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Abstract
Block copolymers are fascinating and complex materials that have been used in a range of diverse scientific and technological capacities. We demonstrate that a single one-step approach based on dual simultaneous polymerizations is a viable technique for the synthesis of a wide range of block copolymers by combining two dissimilar polymerization systems and using a dual-functional initiator. The main advantage of this methodology is that a simple, one-step, and simultaneous polymerization occurs in the bulk, which makes this process very attractive from both industrial and academic points of view. We plan to study the reaction kinetics and evaluate how well the ring opening catalyst [in this case, Sn(oct)2] works under reverse ATRP conditions.

Keywords: Atom transfer radical polymerization; Block copolymer; Ring-opening polymerization

1. Introduction
Block copolymers are remarkable self-assembling systems that can assume a wide variety of morphologies, depending on the relative volume fractions of the blocks [1, 2]. Examples of technologically relevant materials prepared from block copolymers include semiconductor nanoparticles [3], robust vehicles [4], polymeric electrolytes [5], mechanically tough nanocomposites [6], and nanoporous polymers [7]. The molecular architecture, however, of a polymer chain also has a pronounced effect on the morphology and interfacial activity; this phenomenon is of concern in the preparation of dendritic micelles capable of microphase separation. Sanchez et al. [8] predicted that larger values of $n \chi$, where $n$ is the degree of polymerization and $\chi$ is the Flory interaction parameter, will be necessary for the phase separation of branched polymers, including graft and star architectures, than for the corresponding diblock polymers. The desire to control polymer properties through the synthesis of block copolymers and complex macromolecular architectures is a continuous theme throughout polymer chemistry [9].

Traditionally, block copolymers are prepared by the sequential polymerization of different monomer units using the same chemistry, such as two anionic procedures [10], or by the coupling of preformed functional polymers [11]. While this approach is successful, it does not address the issue of dissimilar monomer systems that are polymerized by fundamentally different chemistries [e.g. (reverse) atom transfer radical polymerization ((R)ATRP), cationic or anionic ring opening polymerization (ROP), nitroxide mediated polymerization (NMP), and free radical polymerization (FRP)]. To solve this problem, a number of workers have examined the use of a dual-initiator in the two-step process for the synthesis of well-defined diblock copolymers, using combinations such as ‘ATRP–NMP’ [12, 13], ‘ATRP–ROP’ [14–16], ‘NMP-Cationic’ [17], ‘ATRP-Cationic’ [18], ‘RATRP-Cationic’ [19] and ‘NMP–ROP’ [20–25]. Furthermore, only few reports describe the synthesis of block copolymers in a one-step approach.
Sogah et al. [17] (‘Cationic-NMP’), Hedrick et al. [20] (‘NMP–ROP’), and, recently, Heise et al. [15] (‘ATRP–enzymatic ROP’) have proved the feasibility of such syntheses. In these one-step processes, the block copolymer composition was controlled mainly by the initial monomer/monomer feed ratio.

ATRP, which is one of the most successful methods to polymerize various vinyl monomers in controlled fashion, can be realized using two different initiating systems: using either an alkyl halide and transition metal compound in its lower oxidation state (e.g., CuBr complexed by an appropriate ligand) or a conventional radical initiator (such as azobis(isobutynitrile) (AIBN)) with a transition metal compound in its higher oxidation state (e.g., CuBr2 complexed by an appropriate ligand). The latter approach, which has been named ‘reverse ATRP’ (RATRP), has been used successfully for copper-based heterogeneous and homogeneous systems [26,27]. With regard to ring opening polymerization (ROP), stannous octanoate [Sn(oct)2] is the metal compound in its higher oxidation state (e.g., CuBr2 complexed by an appropriate ligand). The dual initiator is able to combine two dissimilar polymerizations of two comonomers by different polymerization chemistries. In such an approach, the initiator remains attached to each type of growing chain. Implementing such a one-step synthesis is, however, not so straightforward: the two mechanisms of polymerization must be compatible and tolerant of one another, as well as of the monomers, the reaction temperature must maintain constant, and the kinetics must be nearly identical. Such a unimolecular dual initiator is able to combine two dissimilar polymerization systems. A fundamental advantage of such a strategy is that novel block copolymers can be prepared in one step without requiring any intermediate functionalization reactions.

2. Experimental part

2.1. Materials

Styrene and ε-caprolactone were distilled from calcium hydride before use. Following purification, all monomers were stored in a freezer. All solvents were distilled prior to use. Amberlite IR-120 (H form) cation exchange resin, N,N,N′,N′′,N″′-pentamethyldiethylenetriamine (PMDETA) (99% Acros), 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (98% WAKO), and 4,4′-dino- 

2.2. General procedure for synthesis of block copolymers

In a typical experiment, a 100-ml round-bottom flask was charged with appropriate amounts of CuBr2, initiator I, and Sn(oct)2; O2 was removed by repeated vacuum/nitrogen cycles. Once filled with N2, deoxygenated styrene, ligand, and ε-caprolactone were added and the solution was stirred for 30 min at room temperature to promote the formation of the Cu complex. All processes were undertaken in a N2-filled dry box. The polymerizations were then performed in an oil bath at an appropriate temperature. The reaction mixture immediately became dark-green and progressively more viscous. After a specific time, the mixture was cooled and diluted five-fold with tetrahydrofuran (THF) and stirred with Amberlite IR-120 (H form) cation-exchange resin (3–5 g) for 30–60 min to remove the catalyst. The mixture was then passed through an alumina column and precipitated into MeOH. The product was dissolved in THF and purified by repeating its precipitation three times from MeOH and ether. The resulting polymers were filtered and dried overnight at 50 °C under vacuum to provide white powders.

2.3. Measurements

Molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC) using a Waters 510 HPLC—equipped with a 410 Differential Refractometer, a UV detector, and three Ultrastyragel columns (100, 500, and 103 Å) connected in series in order of increasing pore size—using THF as an eluent at a flow rate of 0.4 ml/min. The molecular weight calibration curve was obtained using polystyrene standards. 1H NMR spectra were recorded in CDCl3 on a Bruker AM 500 (500 MHz) spectrometer and using the solvent signal as an internal standard.

3. Results and discussion

The dual-functionalized initiator possesses a primary hydroxyl functionality, which is the initiation center for the living ROP of cyclic lactones or lactides, and an azo group, which initiates the radical polymerization of vinyl monomers upon its thermal decomposition. A monomer mixture of styrene (S) and ε-caprolactone (CL) that is initiated by the dual initiator in the presence of Sn(oct)2 as the ROP catalyst produces the diblock copolymer PS-b-PCL. We characterized the structure of the synthesized block copolymers using 1H NMR spectroscopy. The 1H-NMR spectra (Fig. 1) clearly indicates the existence of PS and PCL block units. Fig. 2 presents the content of PCL in these block copolymers based on these analyses. We observe that
ring opening of CL occurs only at temperatures above 90°C. Between temperatures of 110 and 150 °C, in which the two dissimilar reaction chemistries occur, the mole fraction of PCL is quite similar to that of the PS segments. Therefore, the use of this unique dual-functional initiator is a simple and effective method for synthesizing PS-b-PCL block copolymers. Table 1 summarizes the characteristics of the resulting block copolymers. This finding indicates that the rate of CL ring opening polymerization is higher than that of free radical polymerization.

During the ROP and free radical polymerizations, the radicals formed by the thermal dissociation of the azo group may be involved in three reactions: (A) in-cage termination by coupling, (B) escape from the cage followed by cross-propagation and formation of the block copolymer with styrene, and (C) in-cage termination by disproportionation (Scheme 1(b)). After completing the polymerization, the product was dissolved in tetrahydrofuran and precipitated into ether or methanol, repeatedly, to give the purified block copolymer. Fig. 3(a) presents typical SEC profile obtained from the product after precipitation. The block copolymers slightly display a high molecular weight shoulder, which might be due to in-cage termination by radical–radical coupling. We compared the results of polymerizations conducted in the presence and absence of CuBr2/ligand (conventional free radical polymerization). In the absence of CuBr2/ligand (RATRP), we obtained a PS-b-PCL block copolymer having $M_n = 26,000$ and $M_w/M_n = 1.65$ in 51% yield after 8 h at 110 °C [Fig. 3(a)]. Under the same polymerization conditions, but with CuBr2/ligand present, we observed [Fig. 3(b)] a slower polymerization rate ($M_n = 16,000$) and a narrower molecular distribution ($M_w/M_n = 1.25$), which is consistent with the notion that CuBr2/ligand acts as a deactivator.
To further characterize these synthesized copolymers, we cleaved off the ester groups of the PCL block through basic hydrolysis so that we could determine the size of the PS block in the block copolymer. We performed this hydrolysis under the same basic conditions described in the literature [29], and we monitored the linear PS formed by analyzing $^1$H NMR spectra and SEC traces. Fig. 3(c) presents typical SEC traces. The PS block fraction obtained after total hydrolysis of the PCL block is consistent with the data presented in Figs. 3(a) and 1(b), with a significant decrease in molecular weight, from 26,000 to 12,000, determined by $^1$H NMR spectra.

![Chemical Shift (ppm)](image)

Fig. 1. $^1$H NMR spectra (CDCl$_3$) of PS-$b$-PCL block copolymers formed at (a) 90°C; (b) 110°C and (c) 130°C.

![Graph](image)

Fig. 2. Relationship between the reaction temperature and the molar fraction of PCL.

![Graph](image)

Fig. 3. Comparison of the SEC traces of (a, b) the PS-$b$-PCL block copolymers and (c, d) the homopolymers obtained after hydrolysis of the PS-$b$-PCL block copolymers.
SEC using polystyrene standards [Fig. 3(A)]. We observed similar results for the polymerization undertaken in the presence of CuBr2/ligand [Fig. 3(B)]. The molecular weight of the cleaved block copolymer is close to the target value. The polydispersity of the product from the one-step polymerization in the presence of CuBr2/ligand (i.e., reverse ATRP) is narrower than that obtained from the corresponding conventional free radical system, as is expected.

4. Conclusions

We have demonstrated that a one-step approach, based on dual, simultaneous polymerizations, is a viable technique for the synthesis of a wide range of block copolymers by combining two dissimilar polymerization systems using a dual-functional initiator. The main advantage of this methodology is that this simple, one-step, and simultaneous polymerization occurs in the bulk, which makes it very attractive from both industrial and academic points of view. Therefore, in future we will examine the reaction kinetics in more detail and evaluate how well the ring opening catalyst [in this case, Sn(oct)2] functions under reverse ATRP conditions. In addition, we will concentrate on developing procedures for reducing the polydispersity of the block copolymers and try to extend this method to other monomer combinations.

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