ELSEVIER

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

Chih-Feng Huang, Shiao-Wei Kuo, Hsin-Fang Lee, Feng-Chih Chang*

Institute of Applied Chemistry, National Chiao Tung University, 30050 Hsin Chu, Taiwan, Republic of China

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.
© 2004 Elsevier Ltd. All rights reserved.

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 χ 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.

* Corresponding author. Tel.: +886 357 270 77; fax: +886 357 195 07.
 E-mail addresses: changfc@cc.nctu.edu.tw (F.-C. Chang), kuosw@cc.nctu.edu.tw (F.-C. Chang).

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(isobutyronitrile) (AIBN)] with a transition metal compound in its higher oxidation state (e.g., $CuBr_2$ 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 catalyst used most widely to synthesize designed polymers based on poly(ε-caprolactone) (PCL). Several new initiators have been discovered for polymerization of the ε-caprolactone monomer that enable the creation of macromolecular architectures containing PCL segments [28].

In this paper, we propose a new strategy for the one-step synthesis of block copolymers by using a combination of conventional free radical or reverse ATRP and ring opening polymerizations (Scheme 1(a)). These strategies ('FRP–ROP' and 'RATRP–ROP') involve the use of a symmetric difunctional initiator that initiates simultaneous 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′-dinonyl-2,2′-dipyridyl (dNBipy), were used as received (97% Aldrich).

## 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 $CuBr_2$, initiator **1**, and Sn(oct)$_2$; O_2 was removed by repeated vacuum/nitrogen cycles. Once filled with N_2, 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 N_2-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 10^3 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. ^{1}H NMR spectra were recorded in CDCl$_3$ 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 ^{1}H NMR spectroscopy. The ^{1}H-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

(a)

(b)
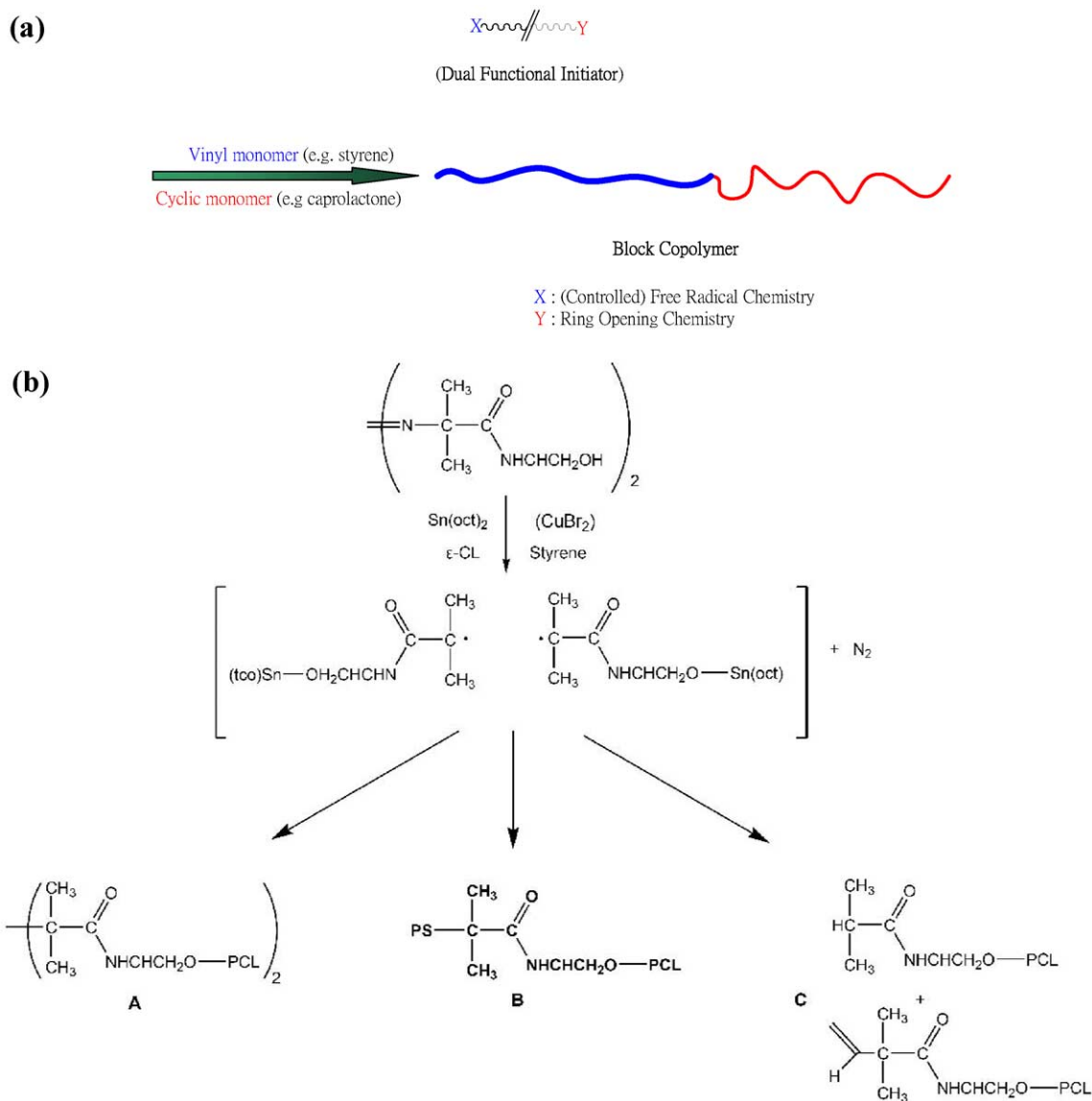
Scheme 1.

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 CuBr$_2$/ligand (conventional free radical polymerization). In the absence of CuBr$_2$/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 CuBr$_2$/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 CuBr$_2$/ligand acts as a deactivator.
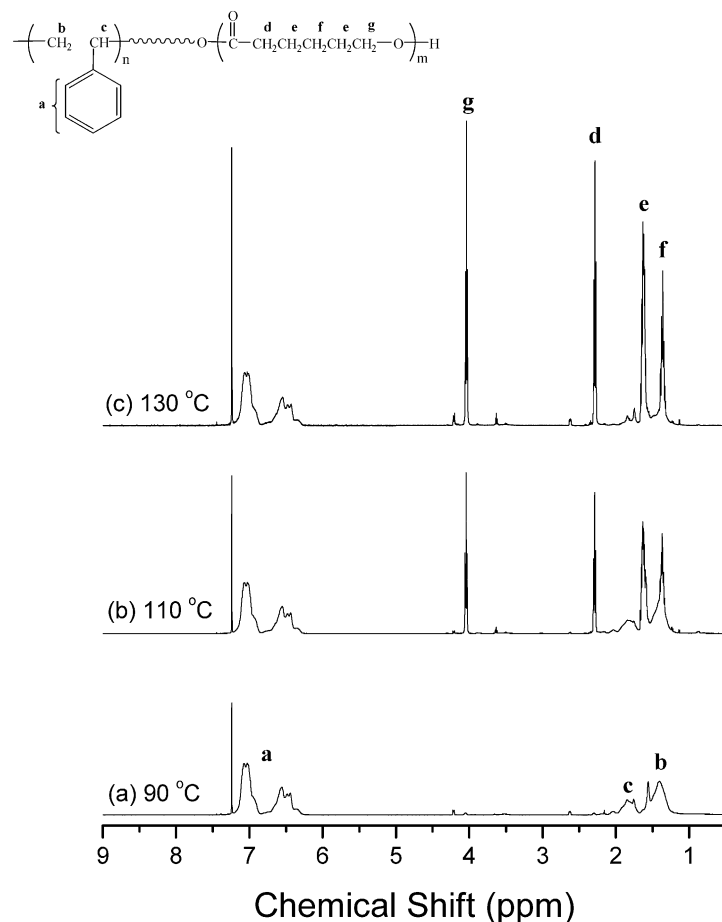
Fig. 1. ^{1}H NMR spectra (CDCl$_3$) of PS-*b*-PCL block copolymers formed at (a) 90 °C; (b) 110 °C and (c) 130 °C.

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
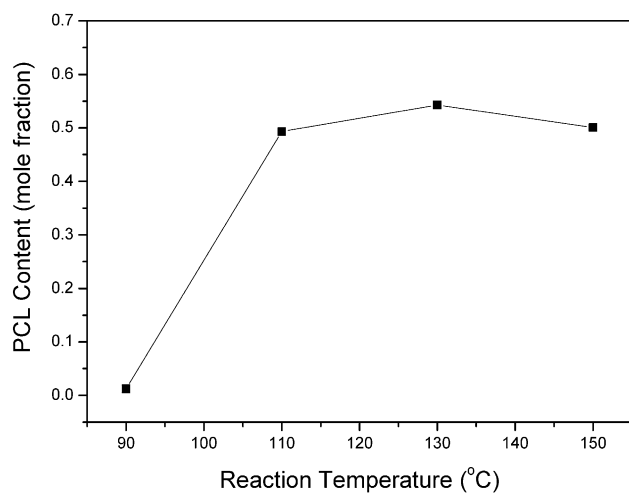
^{1}H NMR spectra and SEC traces. Fig. 3(c) presents typical SEC traces. The PS block fraction obtained after total hydrolysis of the PCL block is consistent with the data presented in Figs. 3(a) and 1(b), with a significant decrease in molecular weight, from 26,000 to 12,000, determined by

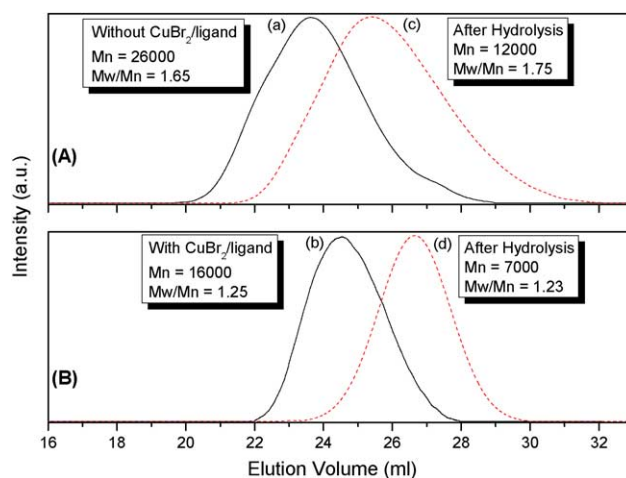Fig. 2. Relationship between the reaction temperature and the molar fraction of PCL.

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.

Table 1
Block copolymerizations of styrene and ε-caprolactone in the bulk and their characterization

Polymer	T (°C)	t (h)	$f_{CL}{}^a$ (%)	$F_{CL}{}^b$ (%)	Yield (%)	$M_{n(SEC)}$	$M_w/M_{n(SEC)}$
2a[c]	90	8	37.5	1.2	40	30,500	1.81
2b	110	8	37.5	49.3	51	26,000	1.65
2c	130	8	37.5	54.0	53	24,000	1.63
2d	150	8	37.5	50.1	52	25,000	1.66
3a[d]	110	4	37.5	39.6	30	11,500	1.28
3b	110	8	37.5	55.4	41	16,000	1.25

[a] Molar ratio of CL in feed $= [CL]_0 ([CL]_0 + [S]_0)^{-1}$.

[b] Molar ratio of CL in the block copolymer as determined by ^{1}H-NMR spectroscopy.

[c] Conditions for **2a–2d**: $[S]_0 = 8.7$ M (bulk); $[S]_0/[I]_0 = 200$; $[CL]_0 = 9$ M (bulk); $[CL]_0/[I]_0 = 120$; $[CL]_0/[Sn(oct)_2]_0 = 1000$; $[CuBr_2]_0 = 0$.

[d] Conditions for **3a–3b**: $[S]_0 = 8.7$ M (bulk); $[S]_0/[I]_0 = 200$; $[CL]_0 = 9$ M (bulk); $[CL]_0/[I]_0 = 120$; $[CL]_0/[Sn(oct)_2]_0 = 1000$; $[I]/[CuBr_2]/[PMDETA] = 1/1/1$.

SEC using polystyrene standards [Fig. 3(A)]. We observed similar results for the polymerization undertaken in the presence of CuBr$_2$/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 CuBr$_2$/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.

Acknowledgements

References

[1] Thomas EL, Anderson DM, Henkee CS, Hoffman D. Nature 1988; 334:598.

[2] Bates FS. Science 1991;251:898.

[3] Chan YNC, Schrock RR, Cohen RE. Chem Mater 1992;4:24.

[4] Discher BM, Bermudez H, Hammer DA, Discher DE, Won YY, Bates FS. J Phys Chem B 2002;106:2848.

[5] Matsumi N, Sugai K, Ohno H. Macromolecules 2002;35:5731.

[6] Lipic PM, Bates FS, Hillmyer MA. J Am Chem Soc 1998;120:8963.

[7] Buchmeiser MR. Angew Chem, Int Ed 2001;40:3795.

[8] Olvera de la Cruz M, Sanchez IC. Macromolecules 1986;19:2501.

[9] Frechet JMJ. Science 1994;263:1710.

[10] Quirk RP, Kinning DJ, Fetters LJ. In: Aggarwal SL, editor. Comprehensive polymer science, 7. London: Pergamon Press; 1989. p. 1.

[11] Fradet A. In: Aggarwal SL, Russo S, editors. Comprehensive polymer science, 2nd supp. London: Pergamon Press; 1996. p. 133.

[12] Tunca U, Karliga B, Ertekin S, Ugur AL, Sirkecioglu O, Hizal G. Polymer 2001;42:8489.

[13] Tunca U, Erdogan T, Hizal G. J Polym Sci, Part A: Polym Chem 2002;40:2025.

[14] Liu T, Baker GL. Polymer Prepr 2002;43:245.

[15] Palmans ARA, Heise A. Polym Mater Sci Eng 2001;86:60.

[16] Meyer U, Palmans ARA, Heise A. Macromolecules 2002;35:2873.

[17] Puts DR, Sogah DY. Macromolecules 1997;30:7050.

[18] Bernaerts KV, Schacht EH, Goethals EJ, du Prez FE. J Polym Sci, Part A: Polym Chem 2003;41:3206.

[19] Cianga I, Hepuzer Y, Serhatli E, Yagci Y. J Polym Sci, Part A: Polym Chem 2002;40:2199.

[20] Mecerreyes D, Moineau G, Dubois Ph, Jerome R, Hedrick JL, Hawker CJ, Malmstrom EE, Trollas M. Angew Chem, Int Ed 1998; 37:1274.

[21] Hua FJ, Yang YL. Polymer 2001;42:1361.

[22] Weiner MW, Scherman OA, Sogah DY. Macromolecules 1998;31: 8425.

[23] Hawker CJ, Hedrick JL, Malmstrom EE, Trollas M, Mecerreyes D, Moineau G, Dubois P, Jerome R. Macromolecules 1998;31:213.

[24] Morgan AM, Pollack SK, Beshah K. Macromolecules 2002;35:4238.

[25] Osagawam Y, Yoshida E. Macromolecules 1998;31:1146.

[26] Xia J, Matyjaszewski K. Macromolecules 1997;30:7697.

[27] Patten TE, Matyjaszewski K. Adv Mater 1998;10:901.

[28] Zhong Z, Dijkstra PJ, Birg C, Westerhausen M, Feijen J. Macromolecules 2001;34:3863.

[29] Angot S, Taton D, Gnanou Y. Macromolecules 2000;33:5418.