One-Step Synthesis of Triarm Block Copolymers via Simultaneous Reversible-Addition Fragmentation Chain Transfer and Ring-Opening Polymerization

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ABSTRACT: One-step synthesis of star copolymers by reversible addition–fragmentation chain transfer (RAFT) and ring-opening polymerization (ROP) by using a novel dual initiator is reported. Triarm block copolymers comprising one polystyrene (or polyacrylamide) arm and two poly(β-butyrolactone) arms were synthesized in one-step by simultaneous RAFT polymerization of styrene (St) (or acrylamide, designated as AAm) and ROP of β-butyrolactone (BL) in the presence of a novel trifunctional initiator, 1,2-propanediol ethyl xanthogenate (RAFT-ROP agent). This dual initiator was obtained through the reaction of 3-chloro-1,2-propanediol with the potassium salt of ethyl xanthogenate. The principal parameters such as monomer concentration, initiator concentration, and poly- merization time that affect the one-step polymerization reaction were evaluated. The characterization of the products was achieved using Fourier-transform infrared spectroscopy (FTIR), ^{1}H-nuclear magnetic resonance (^{1}H-NMR), ^{13}C-nuclear magnetic resonance (^{13}C-NMR), Gas chromatography–mass spectrometry (GC–MS), gel-perme-ation chromatography (GPC), thermogravimetric analysis (TGA), and fractional precipitation (γ) techniques. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1638–1645, 2010

Key words: reversible-addition fragmentation chain transfer; ring-opening polymerization; one-step poly- merization; triarm block copolymer; fractional preci- pitation

INTRODUCTION

Polymers of a well-defined structure and molecular weight can be prepared by controlled radical-poly-merization methods, such as nitroxide-mediated polymerization,[1,2] atom-transfer radical polymeriza-tion,[3–9] and RAFT polymerization.[10–19] Reversible chain transfer involves homolytic substitution or addition fragmentation, or other transfer mecha-nisms. RAFT polymerization represents the most recently developed controlled radical-polymerization method and is a powerful technique for the macro-molecular synthesis of a broad range of well-defined polymers. The versatility of the method is proved by its compatibility with a very wide range of mono-mers and reaction conditions.[10–19]

Block copolymers are one of the most important polymeric materials used in technological applica-tions and theoretical research because of their excep-tional properties based on the microphase separa-tion.[20–44] A variety of synthetic methods for the preparation of block copolymers with various struc-tures, such as linear diblock (AB), triblock (ABA or ABC), pentablock (ABABA), multiblock (also referred as segmented), comb, and star-block copoly-mers, have been proposed.[45–62]

A star-block copolymer is of higher viscosity than the linear copolymer having the same molecular weight and hence is widely used as a resistant mate-rial. There are several excellent articles published on this subject.[48–62]

In recent years, the one-step process has been suc-cessfully used for the synthesis of block copolymers using different techniques, which thus has several advantages over other popular methods. Because of the applicability of at least two transformation steps simultaneously, side reactions that lead to homopol-ymer formation are minimized.[63–77] Barner-Kowollik and coworkers[63] carried out the synthesis of poly(2-hydroxyethyl methacrylate-g-ε-caprolactone) graft copolymers through the one-step combination of ROP and RAFT polymerization in the presence of cyanoisopropyl dithiobenzoate and tin(II)2-ethylhex-anoate using toluene as the solvent. Furthermore, various copolymers containing St,[64–73] chloromethyl

styrene,[72] butadiene,[66] N-isopropylacrylamide,[74,75] lactide,[68,73,74,76] ε-caprolactone,[69,70,75] 10-methylene-9,10-dihydroanthryl-9-spirophenylcyclopropane,[67] ethylene oxide,[68,69] hydroxyethyl methacrylate,[69,70] methyl acrylate,[76] hydroxyethyl acrylate,[76] 1,3-dioxepane,[71,77] tetrahydrofuran (THF),[72] 1,5-cyclooctadiene,[66] and methyl methacrylate[77] monomers were synthesized by a combination of the ROP and RAFT methods.

This work is an extension of the recent studies carried out by the authors of this article involving the one-step synthesis of star-block copolymers through simultaneous free-radical polymerization and ROP processes.[78–80] In this study, the synthesis of a novel trifunctional initiator (RAFT-ROP agent)—1,2-propanediol ethyl xanthogenate—obtained by the reaction of 3-chloro-1,2-propanediol with the potassium salt of ethyl xanthogenate, is reported. Poly(AAm-b-BL) and poly(styrene-b-BL) triarm block copolymers were synthesized using this novel RAFT-ROP agent by the simultaneous ROP and RAFT polymerization of the reactants in one-step. Star copolymers synthesized could be used to prepare with the desired segment ratio by changing the polymerization conditions. The amphiphilic poly(AAm-b-BL) block copolymers are soluble in water and can be used for many area such as medical applications. The dual initiator used for the one-step synthesis of these types of amphiphilic copolymers can be crucial for the synthesis of amphiphilic copolymers based on biodegradable polyesters.

EXPERIMENTAL

Materials

The potassium salt of ethyl xanthogenate, dibutyltin dilaurate (DBTDL), THF, and methanol were supplied by Merck and used as received. N,N-Dimethylformamide (DMF) was received from Fluka. 3-Chloro-1,2-propanediol, 2,2′-azobisisobutyronitrile (AIBN), and diethyl ether were received from Aldrich and used as received. β-Butyrolactone was supplied by Aldrich and dried with anhydrous CaSO$_4$, then fractionally distilled. Acrylamide was received from Merck and crystallized from chloroform, dried in vacuum and kept in the dark under vacuum, and then recrystallized from chloroform. The crystals were collected with suction in a cooled funnel and washed with 300 mL of cold methanol. St was supplied by Aldrich, which was purified as follows: it was washed with a 10 wt % aqueous NaOH solution, dried over anhydrous CaCl$_2$ overnight, and distilled over CaH$_2$ under reduced pressure before use. All other chemicals were reagent grade and used as received.
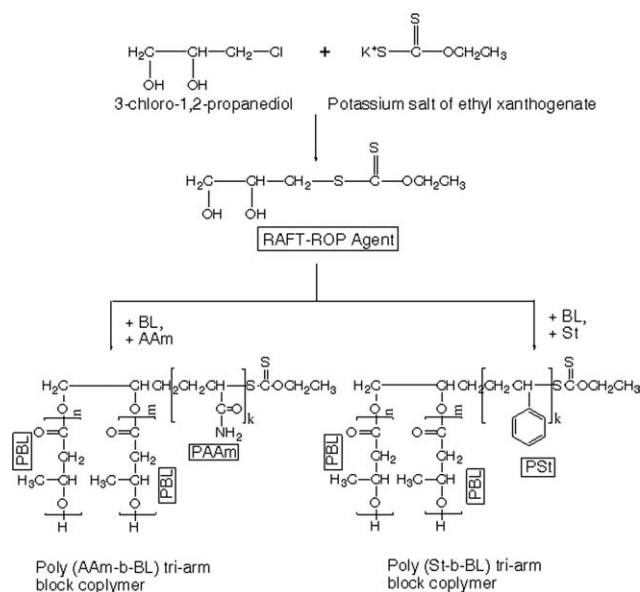
Scheme 1 Reaction pathways in the synthesis of the novel dual initiator and the triarm block copolymers, poly (AAm-b-BL) and poly(St-b-BL).

Synthesis of the trifunctional initiator (RAFT-ROP agent)

A fixed quantity (6.0 g or 50 mmol) of 3-chloro-1,2-propanediol was reacted with 16.0 g (100 mmol) of the potassium salt of ethyl xanthogenate in THF at 40°C for 120 h ([Cl]/[K] = 1/2, mol/mol). The solution was filtered to remove the unreacted xanthate, and the solvent was removed by a rotary evaporator. The RAFT-ROP agent was precipitated in cold diethyl ether and dried under vacuum at room temperature for 4 days. The yield of the products was greater than 60 wt %. The first line in Scheme 1 contains the basic outline for the synthesis of the novel dual initiator. In the ^{1}H-NMR spectrum of the RAFT-ROP agent and its halide precursor [Fig. 1(a,b)], the signal of —CH$_2$—Cl (3.6 ppm) is nearly diminished, and new signals appear at 3.3 and 3.7 ppm for —CH$_2$—S—; 4.7 ppm for —OCH$_2$—CH$_3$; and 1.1 ppm for —OCH$_2$—CH$_3$. In the ^{13}C-NMR spectrum of the RAFT-ROP agent [Fig. 1(c)], the signal of —OCH$_2$—CH$_3$ appears at 19 ppm, that of —CH$_2$—S— appears at 47 ppm, that of —OCH$_2$—CH$_3$ appears at 72 ppm, and the signal of —C═S appears at 230 ppm. The FTIR spectrum of the dual initiator in Figure 2 also indicates the characteristic signals of —C═S at 1780 cm^{-1} and at 3369 cm^{-1} for the —OH groups. The GC–MS/MS gave [M+1]$^+$ at m/z 198(1), [M-29]$^+$ at m/z 168(14), [M-31]$^+$ at m/z 166(100), [M-89]$^+$ at m/z 108(5), [M-107]$^+$ at m/z 90(17), and [M-121]$^+$ at m/z 76(5) (Fig. 3).
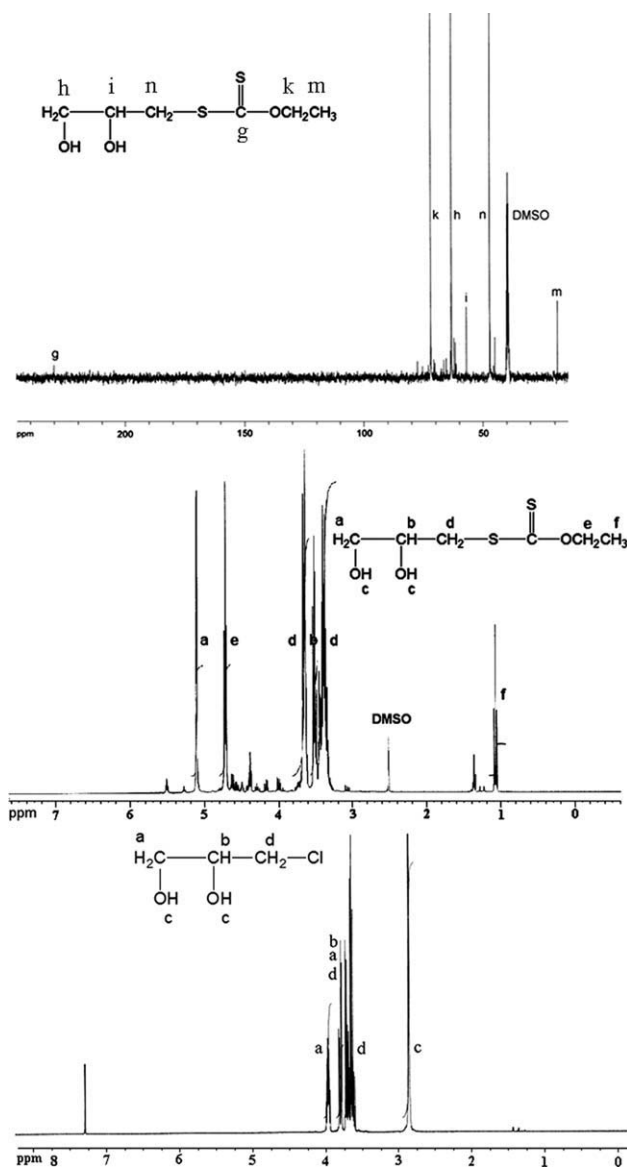
Figure 1 ^{1}H-NMR spectra of 3-chloro-1,2-propanediol (a), and the novel RAFT-ROP agent (b), ^{13}C-NMR spectra of the novel RAFT-ROP agent (c).

One-step polymerization

A total of 0.76, 1.0, 1.25, 1.50, 1.76, and 2.02 g of St; 1.5 g of BL; 0.4×10^{-2}, 0.6×10^{-2}, 0.8×10^{-2}, 1.0×10^{-2}, 1.2×10^{-2}, and 1.6×10^{-2} g of AIBN; 6.32×10^{-4} g of DBDTL; 0.05, 0.08, 0.1, 0.15, and 0.21 g of the RAFT-ROP agent, 3 mL of DMF (as solvent) were charged separately into a Pyrex tube, and subsequently argon was purged into the tube through a needle. The tube was tightly capped with a rubber septum and was dropped into an oil bath thermostated at 90°C for 0.5, 1.0, 1.5, 3.0, 5.0, 6.0, and 10 h. After the polymerization, the reaction mixture was poured into an excess of methanol to separate the poly(St-b-BL) triarm block copolymer. The polymers were dried at 40°C under vacuum for 3 days. The
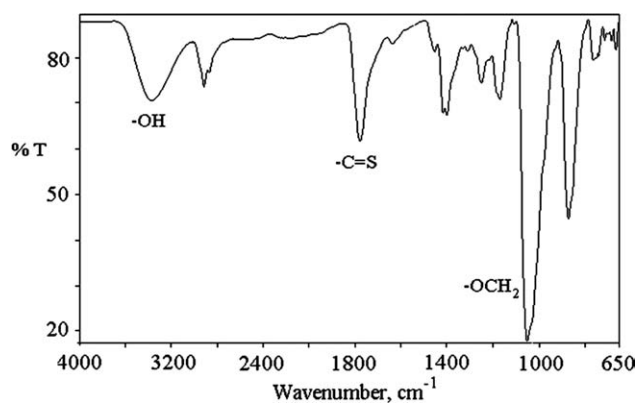
Figure 2 FTIR spectrum of the RAFT-ROP agent.

yield of the polymer was determined gravimetrically. The same synthesis procedure was carried out with AAm to obtain poly(AAm-b-BL) triarm block copolymer. The results of the polymerization of St and AAm are shown in Tables I–III. The conversion of the copolymers was between 3.44% and 51.01%. Typical ^{1}H-NMR spectra of the star copolymers are shown in Figure 4. The signals at 6.6 and 7.0 ppm corresponding to the aromatic protons of poly(St-b-BL) (signal g) completely disappears in the ^{1}H-NMR spectra of the poly(AAm-b-BL), and a new signal appears at 6.2 ppm for the —NH$_2$ group (signal o).

Fractional precipitations of the polymers

Fractional precipitations of the polymers were carried out according to the procedure cited in literature.[37,38] Vacuum-dried polymer sample (~0.5 g) was dissolved in 10 mL of THF. Petroleum ether was added dropwise as a nonsolvent to the solution
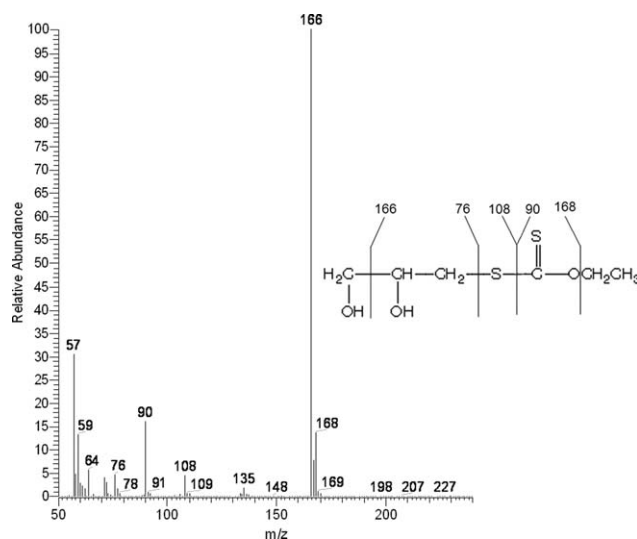

Figure 3 MS chromatogram of the novel RAFT-ROP agent.

TABLE I
The Effect of the Polymerization Time on One-Step Copolymerization

Code	RAFT-ROP agent (g)	BL (g)	St (g)	AAm (g)	Time (h)	Yield (g)	Conv. (%)	γ^a	$M_{n,\text{GPC}}$	M_w/M_n	PBL segment (mol %)
MG-1	0.11	1.52	1.01	–	0.50	0.11	6.79	1.66	2927	3.10	2
MG-2	0.10	1.55	1.02	–	1.00	0.16	5.99	1.50	7615	2.19	–
MG-3	0.10	1.51	1.04	–	1.50	0.22	13.33	1.50	6311	2.25	4
MG-4	0.11	1.51	1.01	–	3.00	0.27	16.56	1.66	7269	2.27	–
MG-5	0.10	1.55	1.04	–	5.00	0.33	19.53	1.66	10,031	2.32	9
MG-7	0.10	1.54	1.03	–	6.00	0.36	21.56	1.60	8787	2.91	13
MG-6	0.10	1.58	1.01	–	8.50	0.38	22.49	1.80	8923	2.32	40
ME-4	0.20	1.01	–	1.01	0.50	0.82	36.94	–	–	–	–
ME-2	0.21	1.02	–	1.00	1.50	0.89	39.91	–	–	–	11
ME-7	0.21	1.04	–	1.01	2.50	0.93	41.15	–	–	–	6
ME-8	0.21	1.01	–	1.01	5.17	0.93	41.70	–	–	–	4

AIBN = 1.59×10^{-2} g for ME series, 0.80×10^{-2} g for MG series; DBTDL = 6.32×10^{-4} g (1.00×10^{-6} mol); polym. temp. = 110°C for ME series, 90°C for MG series.
[a] Nonsolvent (petroleum ether, mL)/solvent (THF, mL); DMF = 3 mL.

with stirring until completion of the first precipitation. After decantation, the upper layer of solvent was treated by adding the nonsolvent for the second fractionation. The same procedure was repeated until no more precipitation was observed. The gamma (γ) values were calculated as the ratios of the total volume of petroleum ether used for each fraction to the volume of THF used for the same. The polymer fractions were subsequently dried under vacuum.

Instrumentation

The molecular weights and molecular-weight distributions were measured with an Agilent 1100 HPLC System. A calibration curve was generated with four polystyrene green standards: 162, 2960, 50,400, and 696,500 Da, of low polydispersity. FTIR—attenuated total reflectance (FTIR-ATR) spectra were recorded using a Nicolet-520 model FTIR spectrometer. ^{1}H-NMR spectra of the samples in DMSO (RAFT-ROP agent), CDCl$_3$ (for PSt-b-PBL, and 3-chloro-1,2-pro-

panediol), and D$_2$O (for PAAm-b-PBL) as the solvent, with tetra methylsilane as the internal standard, were recorded using a Bruker DPX-400, 400 MHz high performance digital FT-NMR spectrometer. TGA of the obtained polymers was carried out under nitrogen using a Seiko II Exstar 6000 TG/differential thermal analyzer to determine thermal degradation. A dried sample was heated from 30 to 650°C at a rate of 20°C min^{-1}. The mass spectral analyses were carried out on a Thermo-Finnigan MAT 4500 GC–MS/MS instrument operating in the electron impact (EI) ionization.

RESULTS AND DISCUSSION

Synthesis of the RAFT-ROP agent

The novel dual initiator, the RAFT-ROP agent with an ethyl xanthogenate and two hydroxyl groups, was synthesized by the reaction of 3-chloro-1,2-propanediol with the potassium salt of ethyl xanthogenate.

TABLE II
The Effect of the Amount RAFT-ROP Agent on One-Step Copolymerization

Code	RAFT-ROP agent (g)	BL (g)	St (g)	AAm (g)	AIBN (g)	Yield (g)	Conv. (%)	γ^a	$M_{n,\text{GPC}}$	M_w/M_n	PBL segment (mol %)
MI-1	0.05	1.57	1.00	–	0.004	0.09	3.44	1.50	8265	2.21	8
MI-2	0.08	1.53	1.00	–	0.006	0.11	4.42	2.13	6095	2.32	8
MI-3	0.13	1.54	1.02	–	0.010	0.18	6.69	1.80	3496	3.03	10
MI-4	0.15	1.53	1.07	–	0.012	0.20	7.27	1.83	3473	3.37	9
MI-5	0.21	1.50	1.03	–	0.016	0.21	7.66	2.00	4993	2.02	7
MB-1	0.10	1.01	–	1.00	0.008	0.77	36.49	–	–	–	13
MB-3	0.30	1.07	–	1.01	0.024	0.81	34.03	–	–	–	18
MB-4	0.40	1.02	–	1.01	0.032	0.81	33.33	–	–	–	11
MB-5	0.60	1.01	–	1.01	0.040	0.86	32.82	–	–	–	12

Polym. time = 1 h; DBTDL = 6.32×10^{-4} g (1.00×10^{-6} mol); polym. temp. = 80°C for MB series, 90°C for MI series.
[a] Nonsolvent (petroleum ether, mL)/solvent (THF, mL); DMF = 3 mL.

TABLE III
The Effect of the Amount of the Monomer on One-Step Copolymerization

Code	RAFT-ROP agent (g)	BL (g)	St (g)	AAm (g)	Yield (g)	Conv. (%)	γ^a	$M_{n,GPC}$	M_w/M_n	PBL segment (mol %)
MH-2	0.10	1.50	0.76	–	0.10	4.24	1.86	2882	3.17	12
MH-3	0.11	1.51	1.25	–	0.24	8.36	1.66	8415	2.24	–
MH-4	0.10	1.50	1.50	–	0.26	8.39	1.70	9889	2.20	15
MH-5	0.10	1.53	1.76	–	0.29	8.55	1.46	12,711	2.04	8
MH-6	0.10	1.51	2.02	–	0.35	9.64	1.80	14,570	1.99	8
MA-1	0.20	1.02	–	0.50	0.48	27.91	–	–	–	23
MA-2	0.21	1.13	–	0.75	0.69	33.01	–	–	–	30
MA-3	0.21	1.01	–	1.00	0.87	39.19	–	–	–	31
MA-4	0.21	1.01	–	1.25	1.26	51.01	–	–	–	19
MA-5	0.21	1.02	–	1.50	1.29	47.25	–	–	–	15

Polym. time: 1 h; AIBN = 1.59×10^{-2} g for MA series, 0.80×10^{-2} g for MH series; DBTDL = 6.32×10^{-4} g (1.00×10^{-6} mol); polym. temp. = 80°C for ME series, 90°C for MG series.
^{a} Nonsolvent (petroleum ether, mL)/solvent (THF, mL); DMF = 3 mL.

One-step synthesis of triarm block copolymer

The one-step polymerization of a vinyl monomer and a lactone initiated by the RAFT-ROP initiator is shown in Scheme 1. This process creates three new active sites—two sites on an equal number of hydroxyl groups for the ROP reaction and one on the thiocarbonate group for RAFT polymerization. During this one-pot synthesis, RAFT polymerization of the vinyl monomer is carried out simultaneously as the ROP of BL proceeds, to yield the triarm star copolymer. Two different types of star copolymers, poly(St-b-BL) and poly(AAm-b-BL), are obtained by this method.
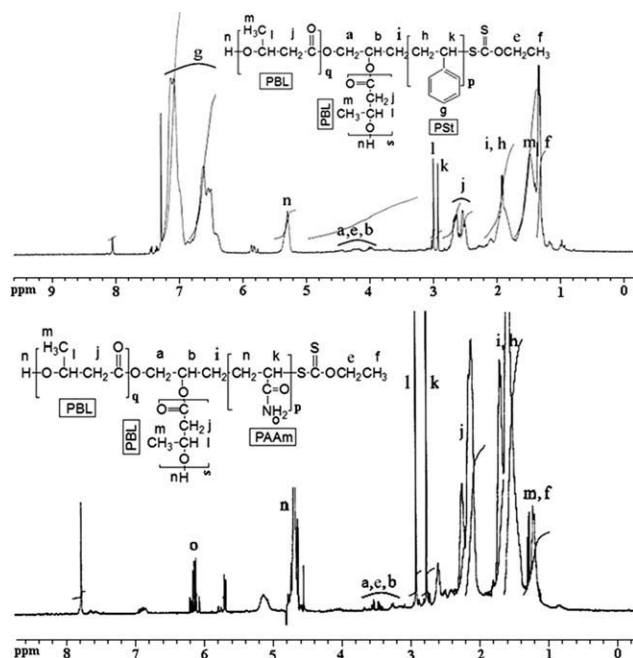

Figure 4 ^{1}H-NMR spectra of the star copolymers: (a) poly(St-b-BL) (in CDCl$_3$), MG-7 in Table I, and (b) poly(AAm-b-BL) (in D$_2$O), MB-3 in Table II.

PBL is also known as poly(3-hydroxy butyrate) (PHB) and is synthesized naturally by bacteria as an energy-reserve material.[81–84] Amphiphilic copolymers of PBL are very attractive for medical applications in drug-delivery systems and tissue engineering.[85] The effects of polymerization time, initiator concentration, and monomer concentration on the copolymerization in the presence of the RAFT-ROP agent by the application of simultaneous RAFT and ROP processes have been studied. The effect of the polymerization time on the one-step block copolymerization is presented in Table I. The plot of M_n versus polymerization time is shown in Figure 5. For polymerizations of longer durations, polymers of higher molecular weights are obtained in the beginning; however, after almost 6 h of polymerization, the plot reaches a plateau; thus, the value of M_n does not change after this point. However, the value of M_w decreases after 6 h of polymerization. Longer polymerization times cause higher polymer yields; these results being in good agreement with those stated by Heidenreich and Puskas[86] for the RAFT polymerization of St. Higher amounts of the RAFT-
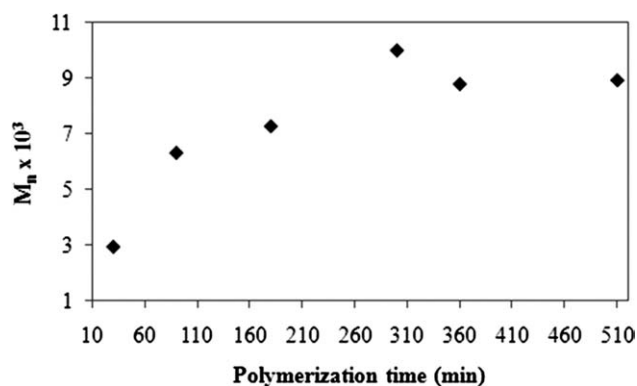

Figure 5 The plot of M_n versus polymerization time of poly(St-b-BL) triarm block copolymers.

ROP agent cause a higher polymer yield (Table II). Increased amounts of initiator in the reaction mixture lead to the formation of a higher number of active centers. Consequently, increased numbers of growing macroradicals are formed in the system. Hence, it may be expected that they have shorter PSt (or PAAm) and PBL segments, which is confirmed by a decrease in the molecular weights of the triblock copolymers, as shown in Table II. Increasing the amount of monomers also causes an increase in both the yield and the molecular weights of the block copolymers as expected (Table III). Because the poly (St-*b*-BL) block copolymers are soluble in common solvents, amphiphilic poly(AAm-*b*-BL) block copolymers are also soluble in water. The ^{1}H-NMR of poly(AAm-*b*-BL) block copolymers was recorded using D_2O solvent. The M_w/M_n values of the poly(St-*b*-BL) block copolymers are between 1.99 and 3.37 (Table I–III). Because of the branched structure, more than one propagating center initiates the polymerization, and the M_w/M_n values of the block copolymers are relatively higher than expected.

All GPC chromatograms were unimodal, which can be attributed to the fact that any the homopolymer was formed. For example, Figure 6 shows the unimodal GPC curves of poly(St-*b*-BL) copolymers (MH series in Table III). The GPC profiles of poly(St-*b*-BL) [MH series] with time are shown in Figure 7. The polymer composition of the star copolymers was calculated using the integral ratios of the signals corresponding to the —CH_2 groups of PBL (δ = 2.5–2.7 ppm), the phenyl protons of PSt (δ = 6.4–7.2 ppm), and —NH_2 groups of PAAm (δ = 6.2 ppm). Varying amounts of the initiator resulted in star copolymers with nearly the same PBL content (7–18 mol % of PBL, Table II). Similarly, variation of monomer feed in the one-pot reaction yielded the star copolymers with 8–31 mol % of PBL (Table III). Interestingly, the PBL content increased as the polymerization time increased for poly(St-*b*-BL) star copolymers (>8.5 h, ~40 mol % of PBL in Table I), but the PBL content decreased as the polymerization
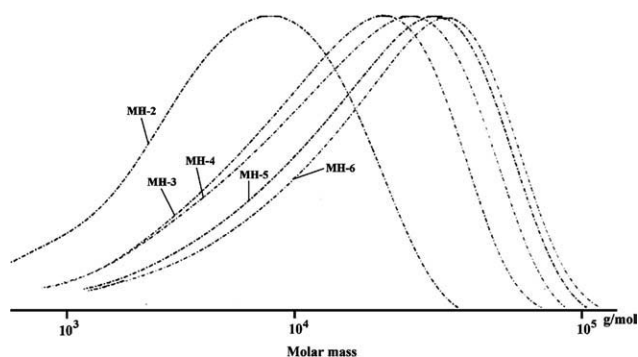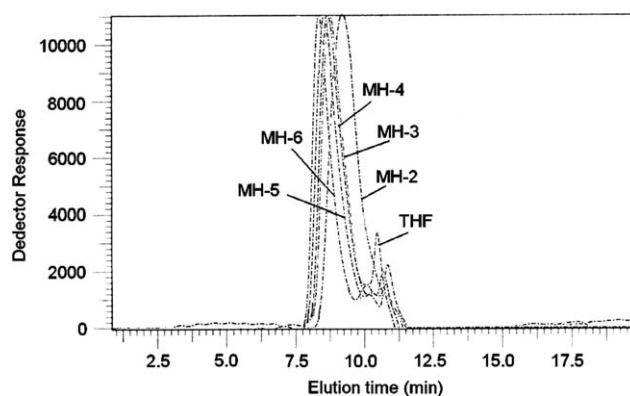

Figure 7 GPC profiles of poly(St-*b*-BL) copolymers [MH series in Table III] with time.

time increased for poly(AAm-*b*-BL) star copolymers (>5.17 h, ~4 mol % of PBL in Table I) These results indicate that the one-pot reaction can be used to prepare star copolymers containing the desired segment ratio by changing the polymerization conditions.

Thermal analysis

Thermal analysis of the samples was carried out using TGA and analysis of the curves obtained (Fig. 8). The TGA showed the individual decomposition temperatures (T_d) of the PBL and PSt blocks (255°C and 420°C, respectively). The weight ratio of the polymer composition could also be predicted from this curve as 20 wt % of PBL. In case of the poly(AAm-*b*-BL) block copolymer, two main individual T_ds—250°C for the PBL and 343°C for the PAAm segments—were observed. Similarly, the PBL
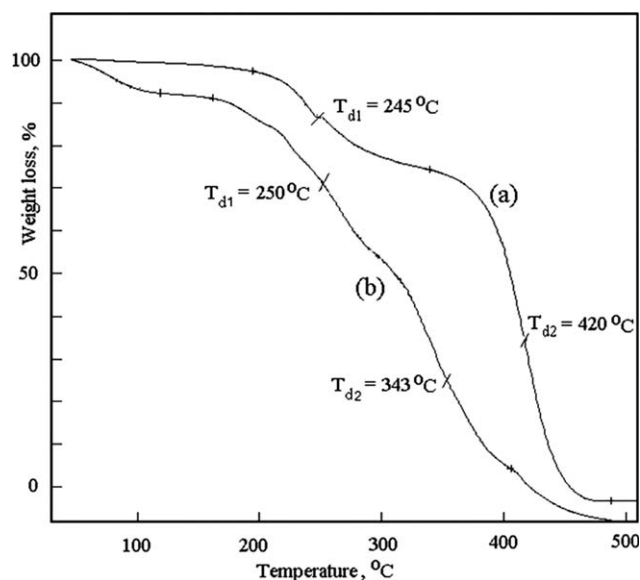

Figure 6 GPC chromatograms of MH series in Table III.

Figure 8 TGA curves of (a) poly(St-*b*-BL) (MG-7 in Table I) and (b) poly(AAm-*b*-BL) (MB-3 in Table II).
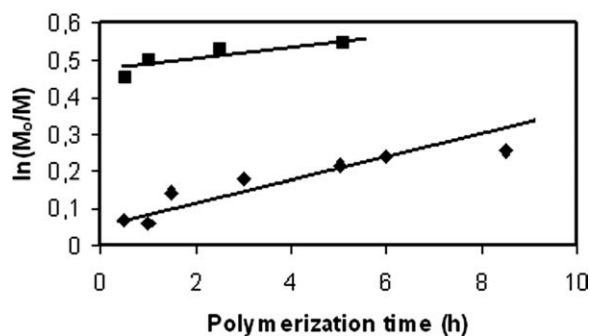
Figure 9 Time dependence of ln (M_0/M) for the one-step polymerization. ◆: for St, ■: for AAm.

content of this star copolymer could be calculated as 30 wt %. The first decomposition observed at 70°C may have been caused by the solvent traces.

Fractional precipitation

Fractional precipitation experiments also provided the evidence for formation of block copolymers. The gamma values (γ) of poly(St-b-BL) block copolymers were between 1.46 and 2.13, as shown in Tables I–III, when the solvent was THF and the nonsolvent was petroleum ether. In this solvent–nonsolvent system, the γ-values were found to be 2.5–3.2 for homo-PSt and 1.33 for homo-PBL. The γ values of the block copolymers were ranged between those of homo-PSt and homo-PBL. It can also be concluded that homopolymer formation was not present because no polymer precipitation was observed at the γ values of the related homopolymers.

Kinetic studies of the one-step polymerization

Figure 9 shows a linear relationship between ln (M_0/M) and polymerization time. The plot of ln (M_0/M) versus reaction time is linear, as expected from a living system, corresponding to first-order kinetics. In living polymerization, it is well known that k is given in the following equation.

$$\ln \frac{[M_0]}{[M]} = kt \tag{1}$$

(M_0) and (M) are the total concentrations of the monomer in the beginning and after a polymerization time (t), respectively; k, is overall rate constant. By using the linear parts of the plots in Figure 9, k was calculated as 1.21×10^{-5} s^{-1} for St and 2.95×10^{-5} s^{-1} for AAm. It can be explained polymerization rate of AAm with the RAFT-ROP agent rather than that of St.

CONCLUSION

A novel dual initiator, a RAFT-ROP agent, was synthesized. A set of one-pot synthesis and RAFT and ROP polymerization conditions of two different star copolymers, poly(St-b-BL) and poly(AAm-b-BL), were evaluated. PBL, also known as PHB, is synthesized naturally by bacteria as an energy-reserve material. Amphiphilic copolymers of PBL are very important for medical applications in drug-delivery systems and tissue engineering. The dual initiator used for the one-step synthesis of these types of amphiphilic copolymers can be crucial for the synthesis of amphiphilic copolymers based on biodegradable polyesters.

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