Preparation of Linear and Star-Shaped Block Copolymers by ATRP Using Simultaneous Reverse and Normal Initiation Process in Bulk and Miniemulsion

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ABSTRACT: Well-defined linear and star-shaped block copolymers were synthesized using halogenated ATRP macroinitiator via a simultaneous reverse and normal initiation (SR&NI) ATRP process in both bulk and stable aqueous miniemulsion. The miniemulsion was carried out with ~20% solid (based on 100% conversion), 0.58 wt % nonionic surfactant, Brij 98 (based on water), and 3.6 wt % hexadecane (based on monomer). For example, Br-terminated 3-arm poly(methyl acrylate) ($M_n = 9200$ g/mol; $M_w/M_n = 1.08$) was extended with styrene to form star-shaped block copolymer, poly(methyl acrylate)-*b*-polystyrene, with $M_n = 24\,700$ g/mol and $M_w/M_n = 1.41$ in bulk condition (yield = 72%) and $M_n = 22\,100$ g/mol and $M_w/M_n = 1.37$ in miniemulsion (yield = 72%). This newly developed ATRP process requires a significantly reduced amount of highly active ATRP catalyst complex in its oxidatively stable high oxidation state (e.g., $Cu^{II}Br_2$/ligand), while the predominant initiating species was a normal halogen-containing macroinitiator. The compositional analysis of the resulting block copolymer using 2-dimensional chromatography indicated that the final product was essentially composed of block copolymers formed by chain extension of the halogenated macroinitiator via a normal ATRP mechanism. However, the presence of low amounts of linear homopolymers generated by AIBN-initiated species via a reverse ATRP mechanism was also detected.

Introduction

The advent of controlled/living radical polymerization (e.g., stable free radical polymerization,[1] atom transfer radical polymerization,[2−4] reversible addition−fragmentation chain transfer,[5] and degenerative chain transfer polymerization[6]) allows the synthesis of polymers with predictable molecular weights and low polydispersities from a broader spectrum of monomers than was available to ionic polymerization processes. In particular, polymers with a wide range of compositions and architectures have been produced by Cu-mediated atom transfer radical polymerization (ATRP) under mild reaction conditions, in bulk or in organic solvent solutions.[2−4] Recently, attempts are being made to conduct the synthesis of well-defined polymers by ATRP in more environmentally friendly media, such as aqueous dispersed emulsions/miniemulsions.[7−22] It was realized that a miniemulsion approach could enhance the colloidal stability and facilitate a controlled free radical polymerization by eliminating the requirement for mass transfer of the radical activator/deactivator through the aqueous phase during an emulsion polymerization.[12,17] Furthermore, reverse ATRP[23−25] starting with the less air-sensitive Cu^{II} complex was proven to be the better pathway to initiate ATRP in an aqueous miniemulsion. A successful reverse ATRP was demonstrated in a miniemulsion system with a reasonable solid content (≥20%) and low surfactant usage (0.58 wt % nonionic surfactant with respect to water), where polymers with predefined molecular weights and low polydispersities were obtained in stable latexes.[17]

However, these experiments also brought the intrinsic limitations of the reverse ATRP process to our attention. As the thermal radical initiator (e.g., AIBN) is the sole free radical source, reverse ATRP can only readily produce linear homopolymers or linear copolymers. In addition, the concentration of copper complex in the system cannot be independently reduced for a given targeted degree of polymerization, particularly when using highly active catalyst systems, due to the intimate correlation between the initial concentration of deactivator (Cu^{II} complex) and normal radical initiator in the formulation.

A newly developed simultaneous reverse and normal initiation (SR&NI) process[18,19,26] provides a way to produce well-defined (co)polymers with various composition and architectures and reduce the initial concentration of the added Cu^{II} complex without sacrificing control over the polymerization. SR&NI was demonstrated by conducting a fully controlled ATRP starting with a small amount of highly active catalyst in its higher oxidation state (e.g., $Cu^{II}X_2$/ligand) and a dual initiator system consisting of a small amount of free radical initiator and a large amount of alkyl halide, (e.g., $[M]_0/[RX]_0/[CuBr_2\text{-}Me_6TREN]_0/[AIBN]_0 = 200/1/0.1/0.0625$, assuming initiator efficiency of AIBN is ~0.8).[26] As illustrated in Scheme 1, the initiation (step A and B in Scheme 1) begins with deactivation reaction between the small amount of $Cu^{II}X_2$/ligand and radicals ($I^\bullet$ or $I{-}P_1^\bullet$) that are produced from the free radical initiator, I−I. Upon the generation of the activating transition metal complex, $Cu^{I}X$/ligand, the large majority of alkyl halide (R−X), along with a minor concentration of newly formed halogenated chains (I−X or $I{-}P_1{-}X$), can initiate the polymerization concurrently via a normal ATRP process (steps C and D in Scheme 1). Well-defined homopolymers with low polydispersities were synthesized using the SR&NI process in bulk[19,26] and in aqueous miniemulsion.[18,19] Since a highly active transi-

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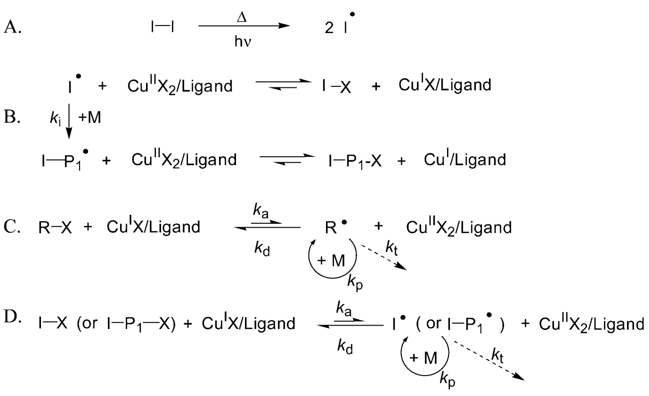
Scheme 1. Proposed Mechanism for SR&NI in ATRP Process



tion metal complex was employed, the catalyst usage was significantly reduced to 5−10 times lower than in a typical reverse ATRP process.

The versatility of ATRP allows the synthesis of (co)polymers with a broad range of composition and architecture.[3,27−31] The same diversity of (co)polymers that have been explored in bulk or solution is also expected to be attainable in aqueous emulsion/miniemulsion, which would be a preferred polymerization process due to the environmental concerns and availability of commercial processing equipment. The synthesis of a waterborne block copolymer, poly(*n*-butyl acrylate)-*b*-polystyrene, via a normal ATRP process in emulsion was previously reported.[11] While the polymerization was controlled and the formation of the block copolymer was attainable through the use of 1 equiv of air-sensitive transition metal compound, (Cu^{I}Br/4,4′-di(alkyl)-4,4′-bipyridine, dAbpy, or Cu^{I}Br/*N*,*N*-bis(2-pyridylmethyl)octadecylamine, BPMODA), colloidal instability was observed even in the presence of a large amount of surfactant. In this paper, we expand our earlier study on the application of the SR&NI process in miniemulsion[19] and report the first examples of the synthesis of linear and star-shaped block copolymers, using mono-, bi-, or multifunctional halogenated macroinitiators. Similar star polymers were earlier formed by homogeneous ATRP.[32−43] The controlled polymerizations with low levels of active transition metal catalyst are conducted under both bulk and stable miniemulsion conditions. The composition of the resulting block copolymers were analyzed using 2-dimensional chromatography.[44−48]

Experimental Section

Materials. Styrene (St, Aldrich), methyl acrylate (MA, Aldrich), and *n*-butyl acrylate (BA, Aldrich) were each purified by passing through a column filled with basic aluminum oxide (Aldrich) to remove inhibitor. The monomers were stored at −5 °C for later use. 1,1,1-Tris(4-(2-bromoisobutyryloxy)phenyl)ethane (TBiBPE),[49] bis(2-pyridylmethyl)octadecylamine (BPMODA),[50] and 4,4′4″-tris(5-nonyl)-2,2′:6′,2″-terpyridine (tNtpy)[51] were synthesized according to previously published procedures. Methyl 2-bromopropionate (MBP, Acros), (1-bromoethyl)benzene (1-PEBr, Aldrich), dimethyl 2,6-dibromoheptanedioate (DMDBHD, Aldrich), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich), CuBr (Aldrich), CuBr$_2$ (Aldrich), polyoxyethylene(20) oleyl ether (Brij 98, Aldrich), hexadecane (HD, Aldrich), 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich), tetrahydrofuran (THF, Fisher Scientific), methanol (Fisher Scientific), chloroform (HPLC grade, Fisher Scientific), and anisole (Aldrich) were used as received.

Synthesis of Macroinitiators. All operations were carried out under a nitrogen atmosphere. A Schlenk flask was charged with CuBr and degassed by three vacuum/nitrogen cycles. Predegassed PMDETA, monomer, and anisole (as internal GC standard) were added to the flask. The solution was magnetically stirred for 10 min to form the Cu^{I}−PMDETA complex, and then the flask was immersed in an oil bath at the desired temperature. The polymerization was initiated by the injection of pre-deoxygenated alkyl halide. Samples were withdrawn periodically to monitor monomer conversion by GC. The reaction was stopped at around 50% conversion. The reaction mixture was diluted with THF and filtered through a neutral alumina column to remove the copper catalyst. To isolate poly(*n*-butyl acrylate) (PBA) and poly(methyl acrylate) (PMA) macroinitiators, the solvent was removed and the polymer was dried under vacuum to a constant mass. In the case of polystyrene (PS) macroinitiator, the polymer was obtained by precipitation in methanol and drying under vacuum. Table 1 lists the results of the synthesis of macroinitiators that were used in the following block copolymerization reactions.

Block Copolymerization in Bulk. In a typical polymerization, the macroinitiator, CuBr$_2$, and ligand were added to a Schlenk flask and degassed by subjecting the mixture to three nitrogen/vacuum cycles. Pre-deoxygenated monomer was added to the flask using previously purged syringes, and the solution was stirred for 10−20 min at 60 °C to ensure the formation of a homogeneous solution of the Cu^{II} complex. The flask was then immersed in an oil bath thermostated at the desired temperature. The polymerization was initiated by the injection of pre-deoxygenated solution of AIBN in anisole using a purged syringe. Samples were withdrawn periodically to monitor the monomer conversion and molecular weight.

Block Copolymerization in Miniemulsion. A typical recipe for the preparation of a miniemulsion is listed in Table 2. The macroinitiator, radical deactivator (CuBr$_2$ and ligand), monomer, and costabilizer (hexadecane) were charged to a round-bottom flask and heated with magnetic stirring at 60 °C for 10−20 min to form a homogeneous solution. After cooling to room temperature, AIBN was dissolved in the oil phase with stirring. Then the surfactant solution was added, and the mixture was ultrasonified (Heat Systems Ultrasonics W-385 sonicator; output control set at 8 and duty cycle at 70% for 1 min) in an ice bath to prevent a significant temperature rise resulting from ultrasonification. The resulting miniemulsion exhibited good shelf life stability at room temperature, as evidenced by a lack of visible creaming or phase separation over 1 day of aging. After homogenization, the miniemulsion was transferred to a 25 mL Schlenk flask, where argon was bubbled through the miniemulsion for 30 min at room temperature before it was immersed in an oil bath thermostated at 80 °C. The magnetic stirrer speed was set at 700 rpm. Time zero of the polymerization was marked when the Schlenk flask was immersed in the oil bath. Samples were withdrawn periodically via a pre-degassed syringe to monitor the monomer conversion and molecular weight.

Characterization. The samples were dissolved in THF prior to measuring the monomer conversion using GC (Shimadzu GC-14A gas chromatograph, equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR51 Chromatapac). Samples for molecular weights analysis were dissolved in THF (in the case of miniemulsion samples, samples were dried by air prior to dissolving in THF) and analyzed using GPC, which was equipped with an autosampler (Waters, 717 plus), HPLC pump at 1 mL/min (Waters, 515), and four columns (guard, 10^5 Å, 10^3 Å, and 100 Å; Polymer Standards Services) in series. Toluene was used as an internal standard. A calibration curve based on linear polystyrene standards was used in conjunction with a differential refractometer (Waters, 2410). The particle size was measured using dynamic light scattering (high-performance particle sizer, model HPP5001, Malvern Instruments).

Compositional Analysis. 1. Liquid Adsorption Chromatography at Critical Conditions (LA-CC). The analysis of samples was performed at the critical point of polystyrene (PS) using a Waters 600 controller and pump. The mobile phase was a mixture of tetrahydrofuran and acetonitrile (49%: 51% v/v). The columns used for separation were Macherey &

Table 1. Results for the Synthesis of Macroinitiators via ATRP

expt	macroinitiator	RX	stoichiometry $[M]_0/[RBr]_0/[CuBr-PMDETA]_0$	T (°C)	conv	$M_{n,sec}$ (g/mol)	$M_{n,theo}{}^a$ (g/mol)	M_w/M_n
1	PS-Br	1-PEBr	100/1/1	80	0.62	6700	6400	1.09
2	PMA-Br	MBP	43/1/1	50	0.52	1900	1900	1.12
3	PBA-Br	MBP	100/1/0.4	50	0.57	8000	7300	1.19
4	PS-Br	MBP	100/1/1	80	0.49	6400	5100	1.18
5	Br-PBA-Br	DMDBHD	100/1/0.4	50	0.75	10100	9600	1.15
6	3-arm R-$(PS\text{-}Br)_3$	TB*i*BPE	300/1/1	90	0.45	13800	14100	1.13
7	3-arm R-$(PMA\text{-}Br)_3$	TB*i*BPE	300/1/1	60	0.41	9200	10600	1.08
8	3-arm R-$(PBA\text{-}Br)_3$	TB*i*BPE	300/1/1	60	0.61	23600	23400	1.12

[a] $M_{n,theo} = ([M]_0 \times conv \times M_0)/[RBr]_0$; M_0 is the molar mass of the monomer.

Table 2. Typical Recipe for the Synthesis of Waterborne Block Copolymer via a SR&NI ATRP Process in an Aqueous Miniemulsion[a]

monomer	styrene	2.27 g (2.5 mL)	200 equiv
macroinitiator[b]	PBA	0.874 g	1 equiv
ligand	tNtpy	0.0134 g	0.2 equiv
catalyst	$CuBr_2$	0.0049 g	0.2 equiv
costabilizer	hexadecane	0.08 g	
surfactant	Brij 98	0.0713 g	
deionized water	H_2O	12.33 g	
water-soluble initiator	VA-044	0.0022 g	0.125 equiv

[a] [Brij 98] = 0.58 wt % based on water (2.3 wt % based on the oil phase); [hexadecane] = 3.6 wt % with respect to monomer; [b] See Table 1, expt 3, for the synthesis of macroinitiator.

Nagel, Nucleosil 300-5 C18 (particle size 5 μm and column dimensions 250 × 4 mm i.d.) and Nucleosil 1000-7 C18 (particle size 7 μm and column dimensions 250 × 4 mm i.d.). The column oven temperature was set at 32 °C. The mobile phase flow rate was 0.4 mL/min, and the detector used was an evaporative light scattering detector (Polymer Laboratories, PL-ELS 1000). Data collection was done with PSS-WINGPC 7 from Polymer Standards Service (PSS; Mainz, Germany).

2. Two-Dimensional (2D) Chromatography. For the first dimension, the same setup was used as described for the LA-CC analysis, except that the flow rate was set at 0.08 mL/min. Sample fractions from the first dimension were transferred to the second dimension via an eight-port valve system (VICI Valco EHC8W), which consisted of two 200 μL loops. The second dimension consisted of a Waters 515 pump delivering a flow of 5 mL/min. The column used was a Polymer Standards Service SDV linear M, high-speed column (pore size 5 μm, dimensions 50 × 20 mm i.d.). The same detector was used in LA-CC analysis, and the second dimension was calibrated using polystyrene calibration standards. Data acquisition and processing were automatically performed by the Polymer Standards Service software: WINGPC 7 and PSS-2D-GPC software, respectively.

Results and Discussion

Block Copolymerization Using a Simultaneous Reverse and Normal Initiation (SR&NI) Process. In addition to significantly decreasing the catalyst concentration through the use of highly active transition metal complex,[19,26] the SR&NI process also opens a novel and practical synthetic route for the synthesis of well-defined polymers of varying compositions and architectures, such as block or star polymers, via an ATRP process starting with air-stable Cu^{II} complexes. When the small molecule alkyl halide initiator, (RX in Scheme 1) was replaced by a halogenated macroinitiator in a SR&NI ATRP process, chain extension of the macroinitiator was expected to proceed in a controlled manner. Figure 1 shows the GPC traces of a block copolymerization of styrene using bromo-terminated poly(methyl acrylate) as macroinitiator (M_n = 1900 g/mol and M_w/M_n = 1.12), where 1 equiv of macroinitiator and 0.125 equiv of AIBN (leading to 0.2 equiv of free radicals based on the decomposition efficiency of 0.8) were employed as a dual initiator system, and 0.2 equiv of $Cu^{II}Br_2$/BPMODA was added as the initial deactivator. The clear shift of the GPC traces toward the higher molecular weights with monomer conversion indicates that the macroinitiator (PMA) chains were extended with the second monomer (St) in a well-controlled way to form a diblock copolymer, poly(methyl acrylate)-*b*-polystyrene (M_n = 9000 g/mol). The polydispersity (M_w/M_n) of the resulting block polymer was 1.12 (Table 3, run 3).

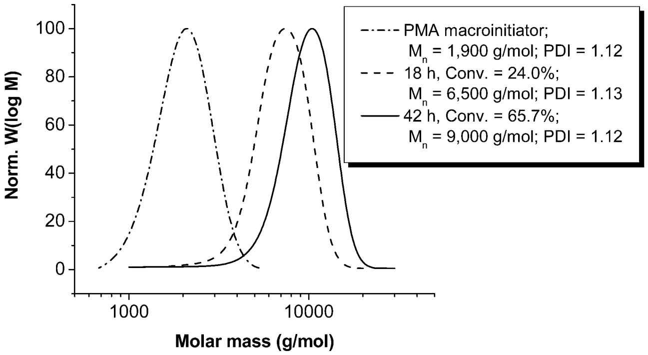


Figure 1. GPC traces of samples obtained in the synthesis of poly(methyl acrylate)-*b*-polystyrene (M_n = 9000 g/mol and M_w/M_n = 1.12, see Table 3, run 3) using PMA as macroinitiator (M_n = 1900 g/mol and M_w/M_n = 1.12, see Table 1, expt 2) via a SR&NI of ATRP process under bulk polymerization conditions; $[St]_0/[PMA\text{-}Br]_0/[CuBr_2-BPMODA]_0/[AIBN]_0$ = 96/1/0.2/0.125; anisole was used as internal standard for GC analysis; 90 °C.

Block copolymerization was also carried out in a miniemulsion with ~20% solid (based on 100% conversion), where 0.58 wt % Brij 98 (with respect to water) and 3.6 wt % hexadecane (with respect to monomer) were used as surfactant and costabilizer, respectively, to provide colloidal stability and diffusional stability of the miniemulsion. A halogenated macroinitiator, poly(*n*-butyl acrylate) (PBA, M_n = 8000 g/mol and M_w/M_n = 1.19), was chain extended with styrene monomer to form a waterborne block copolymer, PBA-*b*-PS, with molecular weight of 17 400 g/mol and a narrow molecular weight distribution (M_w/M_n = 1.11) (Table 3, run 7). The small peaks at low molecular weights in GPC traces (Figure 2) may result from the presence of nonionic surfactant, Brij 98, in the dried latex samples. The resulting latex particles showed good colloidal stability with an intensity-average particle size of 245 nm measured by dynamic light scattering. Little coagulum was observed throughout the course of the polymerization. Table 3 summarizes the results obtained from the synthesis of block copolymers. Well-defined linear diblock, triblock, and star-shaped block copolymers with relatively low polydispersity were produced via ATRP by

Table 3. Results for the Synthesis of Block Copolymer via SR&NI in ATRP

system	run	block copolymer	macroinitiator[b]	ligand	stoichiometry $[M]_0/[MI]_0/$ $[Cu\ Br_2\text{-}L]_0/[AIBN]_0$	conv	$M_{n,sec}$ (g/mol)	$M_{n,theo}$[c] (g/mol)	M_w/M_n
bulk	1	PS-*b*-PBA	PS (expt 1)	Me_6TREN	200/1/0.1/0.0625	0.82	24 200	25 800	1.26
	2	PS-*b*-PBA	PS (expt 1)	BPMODA	200/1/0.1/0.0625				
	3	PMA-*b*-PS	PMA (expt 2)	BPMODA	96/1/0.2/0.125	0.66	9 000	7 400	1.12
	4	PS-*b*-PMA	PS (expt 4)	BPMODA	200/1/0.2/0.125	0.47	12 100	13 100	1.27
	5	3-arm R-(PS-*b*-PMA)$_3$	PS (expt 6)	BPMODA	205/1/0.6/0.375	0.81	36 700	22 700	1.25
	6	3-arm R-(PMA-*b*-PS)$_3$	PMA (expt 7)	BPMODA	300/1/0.6/0.375	0.72	24 700	23 600	1.41
mini-emulsion[a]	7	PBA-*b*-PS	PBA (expt 3)	tNtpy	200/1/0.2/0.125	0.68	17 400	19 800	1.11
	8	PS-*b*-PBA	PS (expt 1)	tNtpy	200/1/0.2/0.125	0.89	17 500	25 700	1.32
	9	PS-*b*-PBA-*b*-PS	PBA (expt 5)	tNtpy	200/2/0.4/0.25	0.98	24 500	28 000	1.18
	10	3-arm R-(PMA-*b*-PS)$_3$	PMA (expt 7)	BPMODA	300/1/0.6/0.375	0.72	22 100	23 200	1.37
	11	3-arm R-(PS-*b*-PBA)$_3$	PS (expt 6)	BPMODA	300/1/0.6/0.375	0.99	38 700	37 600	1.20

[a] [Brij 98] = 0.58 wt % with respect to water (2.3 wt % with respect to the oil phase); [hexadecane] = 3.6 wt % with respect to monomer; 20% solid content based on 100% conversion. [b] See experiments in Table 1 for the synthesis of macroinitiators. [c] See eq 1 for the calculation of the theoretical molecular weights.

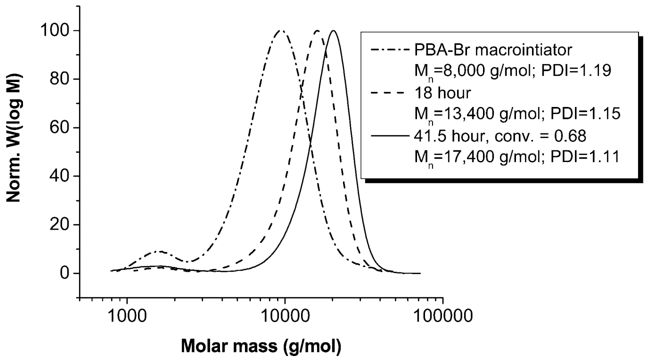


Figure 2. GPC traces of samples obtained in the synthesis of waterborne poly(*n*-butyl acrylate)-*b*-polystyrene (M_n = 17 400 g/mol and M_w/M_n = 1.11, see Table 3, run 7) using PBA as macroinitiator (M_n = 8000 g/mol and M_w/M_n = 1.19, see Table 1, expt 3) via a SR&NI of ATRP process in aqueous miniemulsion; $[St]_0/[PBA\text{-}Br]_0/[CuBr_2\text{-}tNtpy]_0/[AIBN]_0$ = 200/1/0.2/0.125; 80 °C; miniemulsion conditions: [Brij 98] = 0.58 wt % with respect to water (2.3 wt % with respect to the oil phase); [hexadecane] = 3.6 wt % with respect to monomer.

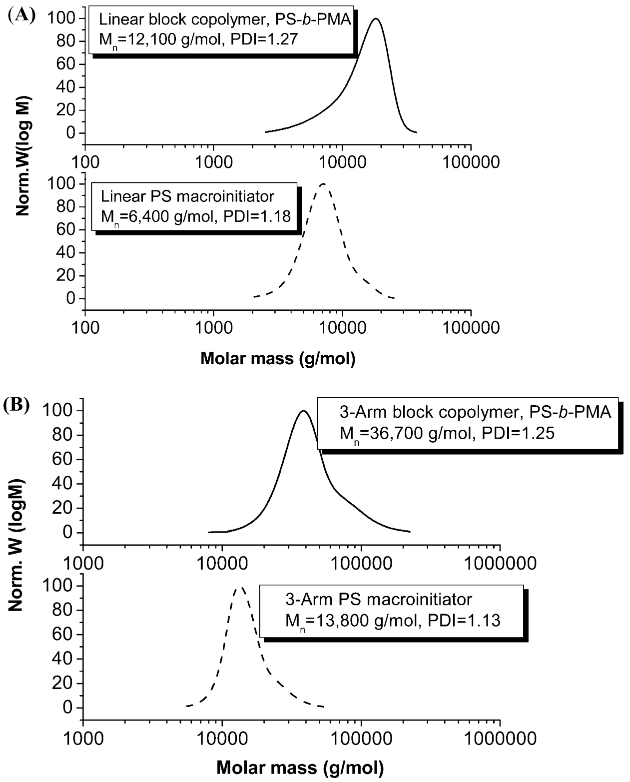


Figure 3. GPC traces of (A) linear monofunctional PS macroinitiator (M_n = 6400 g/mol and M_w/M_n = 1.19, see Table 1, expt 4) and the resulting linear block copolymer (M_n = 12 100 g/mol and M_w/M_n = 1.27, see Table 3, run 4); reaction conditions: $[MA]_0/[PS\text{-}Br]_0/[CuBr_2\text{-}BPMODA]_0/[AIBN]_0$ = 200/1/0.2/0.125; 80 °C; bulk, and (B) 3-arm trifunctional PS macroinitiator (M_n = 13 800 g/mol and M_w/M_n = 1.13, see Table 1, expt 6) and the resulting block copolymer (M_n = 36 700 g/mol and M_w/M_n = 1.25, see Table 3, run 5), reaction conditions: $[MA]_0/[PS\text{-}Br]_0/[CuBr_2\text{-}BPMODA]_0/[AIBN]_0$ = 205/1/0.6/0.375; 80 °C; bulk.

the SR&NI process using halogenated mono-, di-, and trifunctional macroinitiators (Table 1), respectively, in both bulk and miniemulsion systems.

Macroinitiators with higher chain-end functionality facilitate the formation of block copolymer with higher block efficiency. The halogenated macroinitiators employed in our study were synthesized by bulk ATRP, and the polymerizations were stopped at around 50% conversion in order to achieve high chain-end functionality. Nevertheless, the loss of active alkyl halide at the polymer chain end may occur during either polymerization or the subsequent purification, resulting in less than 100% end functionality. A linear diblock copolymer, PS-*b*-PMA (M_n = 12 100 and M_w/M_n = 1.27), was synthesized by chain extension of a PS macroinitiator (M_n = 6400 and M_w/M_n = 1.18) with methyl acrylate using SR&NI ATRP (Table 3, run 4). The GPC trace of resulting copolymer showed a tailing toward low molecular weight (Figure 3A). Further analysis of the macroinitiator and resulting copolymer using 2D chromatography (Figure 4A,B) indicated that there was 18 wt % (29 mol %) unreacted PS macroinitiator remaining in the final product after the block copolymerization reaction. These nonextended chains are the result of some nonhalogenated polymer chains due to the loss of chain-end functionality during macroinitiator preparation. However, when a multifunctional macroinitiator, such as 3-arm macroinitiator, is employed, the chance of obtaining totally unreacted macroinitiator is much lower. The statistical loss of chain-end functionality predominantly leads to the formation of 2-arm or 1-arm block copolymer. This expectation was confirmed during the synthesis of a 3-arm block copolymer using a 3-arm trifunctional PS as macroinitiator. No tailing toward low molecular weight is detected in the GPC traces (Figure 3B), and the lack of any detectable macroinitiator response in 2D chromatography clearly supports the absence of unreacted macroinitiator in the resulting block copolymers (Figure 4C,D), which could be a

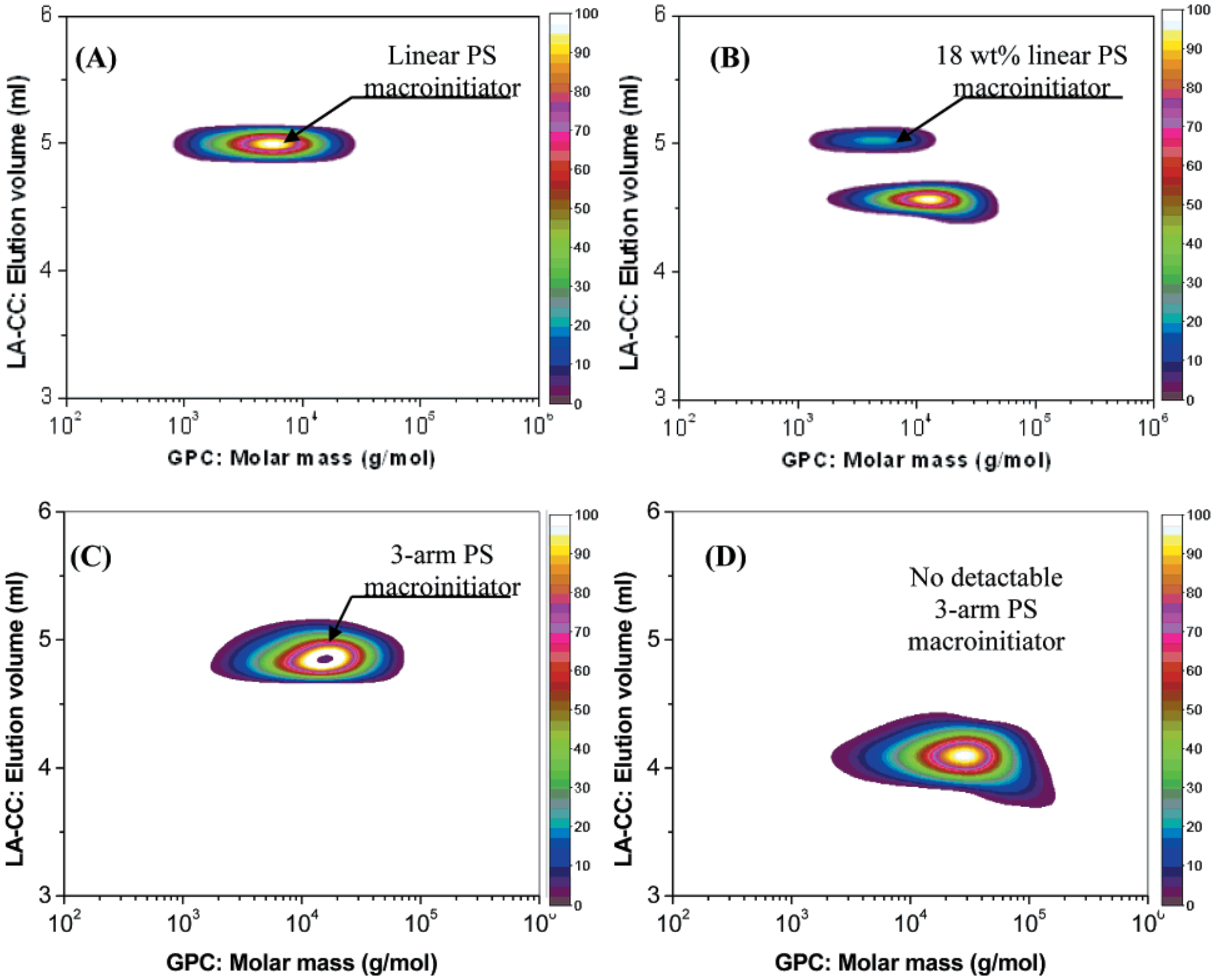


Figure 4. 2-Dimensional contour plots of (A) linear PS macroinitiator (M_n = 6,400 g/mol and M_w/M_n = 1.19, see Table 1, expt 4); (B) the resulting linear block copolymer (M_n = 12 100 g/mol and M_w/M_n = 1.27; see Table 3, run 4); (C) 3-arm PS macroinitiator (M_n = 13 800 g/mol and M_w/M_n = 1.13; see Table 1, expt 6); and (D) the resulting block copolymer (M_n = 36 700 g/mol and M_w/M_n = 1.25; see Table 3, run 5). First dimension is liquid adsorption chromatography at the critical condition (LC-CC) of PS, and second dimension is gel permission chromatography (GPC); see Figure 4 for polymerization conditions.

mixture of 3-arm, 2-arm, and 1-arm block copolymers. In general, the use of a multifunctional macroinitiator results in higher block efficiency (with less unreacted macroinitiator) than that with a monofunctional macroinitiator at a same level of end-group functionality. For example, the end-group functionality of linear monofunctional macroinitiator was 90 mol %, which led to 10 mol % of unreacted macroinitiator remaining in the final product of block copolymerization. However, in the case of using 3-arm trifunctional macroinitiator with the same chain-end functionality, there would be only 0.1 mol % ($0.1^3 = 0.001$) unreacted macroinitiator in the final product. Statistically, the resulting block copolymer should be composed of 72.9 mol % ($0.9^3 = 0.729$) of 3-arm, 24.3 mol % ($0.9 \times 0.9 \times 0.1 \times 3 = 0.243$) of 2-arm, and 2.7 mol % ($0.9 \times 0.1 \times 0.1 \times 3 = 0.027$) of 1-arm block copolymers. Therefore, the use of multifunctional macroinitiator is a practical way to increase the block efficiency.

In addition to block copolymers produced by the chain extension of halogenated macroinitiators via a normal ATRP mechanism, the use of a small amount of thermal radical initiator (e.g., AIBN) in the dual initiator system results in the formation of some linear homopolymer chains of the monomer employed for the second block via a reverse ATRP mechanism (step D in Scheme 1). Considering the dual radical sources (majority from the halogenated macroinitiator and a minor amount from AIBN) and assuming these two kinds of radicals have the same activation/deactivation equilibrium constant, the theoretical molecular weights can be calculated by eq 1.

$$M_{n,th} = M_{n,MI} + \frac{[M]_0 \times \text{conversion}}{[MI]_0 + 2f_{AIBN}[AIBN]_0} M_0 \qquad (1)$$

where $M_{n,MI}$ is the molecular weight of macroinitiator and M_0 is the molar mass of the second block monomer. Decreasing the AIBN concentration, and correspondingly Cu^{II}/BPMODA, would led to less linear homopolymer being present in the resulting block copolymers, but this approach is greatly restricted by the catalytic activity of copper complex. The use of 0.1 equiv of $Cu^{II}Br_2/Me_6TREN$ and 0.0625 equiv of AIBN accordingly resulted in a well-controlled block copolymerization (Table 3, run 1). However, the polymerization did not proceed at all when using 0.1 equiv of BPMODA as ligand to replace Me_6TREN in the above formulation (Table 3, run 2). Therefore, the use of highly active copper complexes is preferred when one desires to increase the blocking efficiency in the SR&NI process.

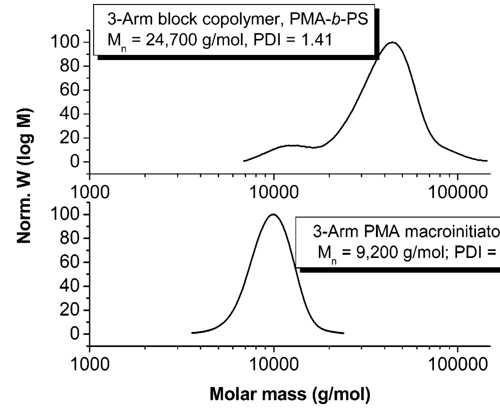


Figure 5. GPC traces of 3-arm trifunctional PMA macroinitiator ($M_n = 9200$ g/mol and $M_w/M_n = 1.08$; see Table 1, expt 7) and the resulting block copolymer ($M_n = 24\,700$ g/mol and $M_w/M_n = 1.41$; see Table 3, run 6); reaction conditions: $[S]_0/[PMA\text{-}Br]_0/[CuBr_2{-}BPMODA]_0/[AIBN]_0 = 300/1/0.6/0.375$; 80 °C; bulk,

Compositional Analysis of the Resulting Block Copolymers. According to the proposed mechanism of a SR&NI in ATRP process (Scheme 1), the polymers resulting from chain extension of a halogenated macroinitiator may contain a majority of block copolymer chains, a few homopolymer chains due to the use of small amount of AIBN, and unreacted macroinitiator from nonhalogenated polymer precursor. A 3-arm block copolymer, R-(PMA-*b*-PS)$_3$ ($M_n = 24\,700$ g/mol and $M_w/M_n = 1.41$), was produced by chain extension of a 3-arm trifunctional macroinitiator, R-(PMA)$_3$ ($M_n = 9200$ g/mol and $M_w/M_n = 1.08$), via a SR&NI in ATRP under bulk polymerization conditions (Table 3, run 6). Figure 5 shows the GPC traces of the macroinitiator and the resulting block copolymer. Bimodality was noted in the GPC traces of the block copolymer. Normally, the presence of a small peak at low molecular weight is considered as the presence of unreacted macroinitiator in a controlled chain extension polymerization; however, it is not the case here. Figure 6 illustrates the 2D chromatography analysis of the above 3-arm block copolymer, where the first dimension (1D) is liquid adsorption chromatography under critical conditions (LC-CC) for PS and the second dimension is the normal GPC. When the block copolymer species were introduced to the 1D chromatographic system at critical conditions of PS, the individual polymer fractions elute with respect to differences in their chemical composition (e.g., PMA block length), while PS homopolymer and PS segment in the block copolymer are “chromatographically invisible” with a same elution volume/time. The two sharp elution peaks in 1D LC-CC (Figure 6A) at elution volume of 4.56 and 4.88 mL correspond to 3-arm block copolymer and linear PS, respectively. The small peak at elution volume of 4.25 mL was identified as the product of star−star coupling, which appeared at double the molecular weight of the 3-arm block copolymer in the subsequent second dimension GPC analysis. No detectable 3-arm PMA macroinitiator, which would appear at elution volume of 4.40 mL in 1D LC-CC and molecular weight of 9200 g/mol in the following GPC analysis, was observed. Integrating the intensity of each response in the 2D contour plot (Figure 6B) provided the compositional analysis of the resulting block copolymers. In addition to 88 wt % 3-arm block copolymer, 11 wt % linear PS and 1 wt % of a block copolymer resulting from star−star coupling were also present in the final product. Similar 2D chromatography analysis was applied to the waterborne 3-arm block copolymer, R-(PMA-*b*-PS)$_3$ (Table 3, run 10), which was produced by chain extension of 3-arm macroinitiator, R-(PMA)$_3$ (Table 1, expt 7), via a SR&NI in ATRP in a stable aqueous miniemulsion. The final polymer sample consisted of 90.5 wt % of 3-arm block copolymer, R-(PMA-*b*-PS)$_3$, 4.5 wt % of linear PS, and 5 wt % of star−star coupling.

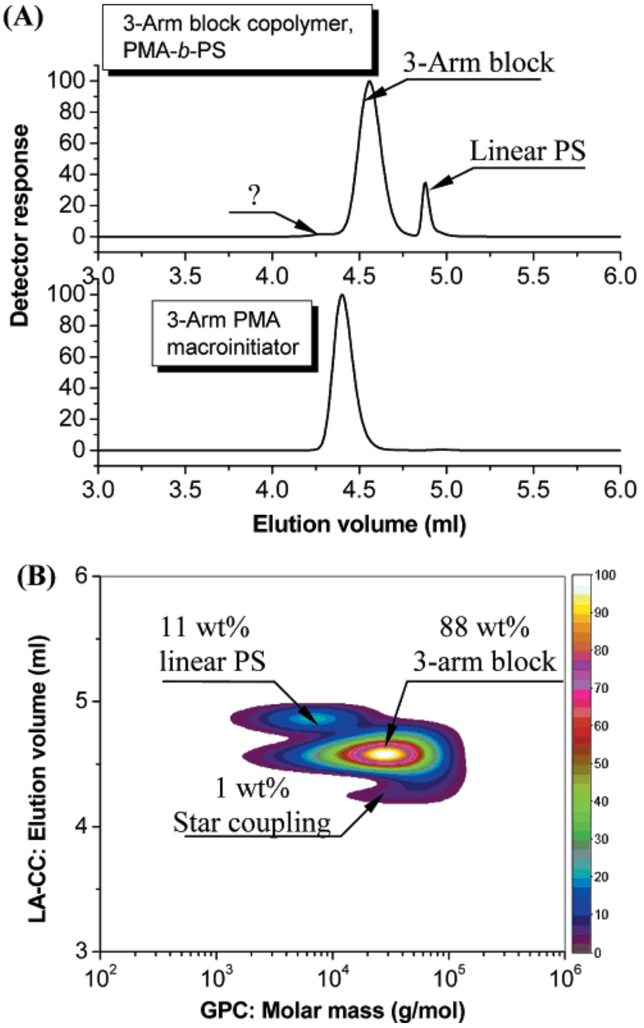


Figure 6. (A) Liquid adsorption chromatography at the critical condition (LC-CC) of PS for 3-am PMA macroinitiator ($M_n = 9200$ g/mol and $M_w/M_n = 1.08$; see Table 1, expt 7) and the resulting block copolymer ($M_n = 24\,700$ g/mol and $M_w/M_n = 1.41$; see Table 3, run 6); and (B) 2-dimensional contour plots with first dimension of LC-CC of PS and second dimension of normal GPC for the resulting block copolymer ($M_n = 24\,700$ g/mol and $M_w/M_n = 1.41$, see Table 3, run 6); see Figure 5 for polymerization conditions.

As discussed above, the small peak at low molecular weight in the GPC traces of 3-arm block copolymer R-(PMA-*b*-PS)$_3$ (Figure 5) was related to the presence of linear PS due to the use of a small amount of AIBN in the formulation. However, no separated peak was observed at low molecular weight range in the GPC traces of 3-arm block copolymer R-(PS-*b*-PMA)$_3$ (Figure 3B), which was synthesized by chain extension of 3-arm macroinitiator, R-(PS-Br)$_3$, via SR&NI in ATRP. It suggested that the proportion of linear homopolymer PMA in the 3-arm block copolymer R-(PS-*b*-PMA)$_3$ is lower than that of homopolymer PS in the 3-arm block copolymer R-(PS-*b*-PMA)$_3$. This could be either due to

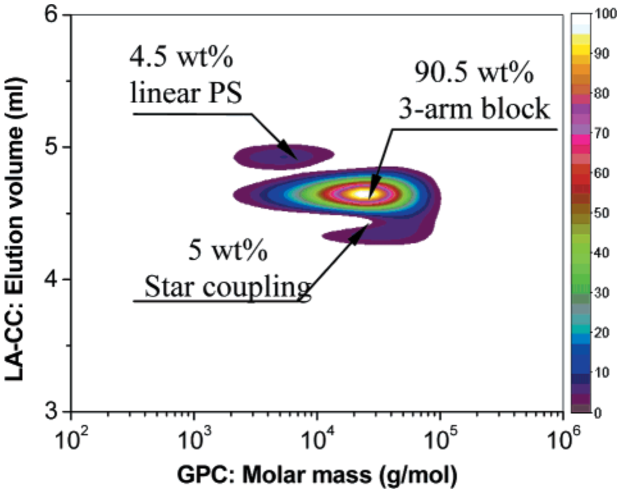


Figure 7. 2-Dimensional contour plots of the resulting waterborne block copolymer (M_n = 22 100 g/mol and M_w/M_n = 1.37; see Table 3, run 10) synthesized using 3-arm trifunctional PMA macroinitiator (M_n = 9200 g/mol and M_w/M_n = 1.08; see Table 1, expt 7) via SR&NI ATRP in an aqueous styrene miniemulsion. First dimension is liquid adsorption chromatography at the critical condition (LC-CC) of PS, and second dimension is gel permission chromatography (GPC). Polymerization conditions: $[S]_0/[PMA\text{-}Br]_0/[CuBr_2\text{-}BPMODA]_0/[AIBN]_0$ = 300/1/0.6/0.375; 80 °C. Miniemulison conditions: [Brij 98] = 0.58 wt % with respect to water (2.3 wt % with respect to the oil phase); [hexadecane] = 3.6 wt % with respect to monomer.

the incomplete resolution of linear PMA from the 3-arm block copolymer, R-(PS-*b*-PMA)$_3$, or due to the lower efficiency of initiation of MA by AIBN. Indeed, the rate constant of addition of AIBN derived radicals to MA are 8 times lower than to styrene.[52−54]

Conclusion

Simultaneous reverse and normal initiation (SR&NI) was used as an improved ATRP process to form well-defined linear and star-shaped block copolymers in both bulk and stable aqueous miniemulsion. In addition to significantly decreasing the catalyst concentration to 5−10 times lower than in a typical reverse ATRP process through the use of highly active ATRP catalyst, a dual initiator system consisting of a large majority of halogenated macroinitiator and a small amount of free radical initiator (e.g., AIBN) allowed the addition of transition metal complexes in the oxidatively stable higher oxidation state (e.g., $Cu^{II}Br_2$/ligand), while the predominant initiating species was a normal halogen-containing macroinitiator. The resulting final products of the block copolymerization were analyzed using 2-dimensional chromatography with the first dimension of liquid adsorption chromatography at critical condition of PS and the second dimension of normal GPC. It was showed that the final product was essentially composed of block copolymers formed by initiation of the halogenated macroinitiator via a normal ATRP mechanism. However the presence of low amounts of linear homopolymer generated by AIBN initiated species via a reverse ATRP mechanism was also detected. The use of multifunctional (e.g., 3-arm star-shaped) macroinitiator was proved to be a practical way to increase the block efficiency.

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