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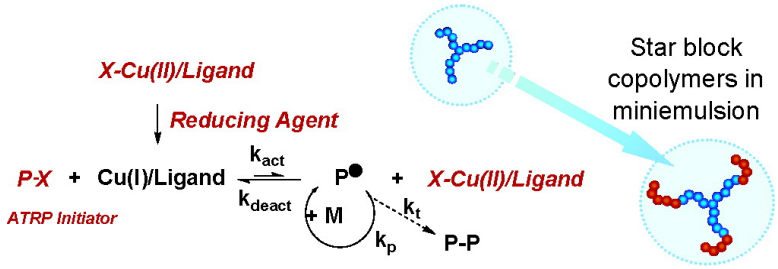

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Preparation of Homopolymers and Block Copolymers in Miniemulsion by ATRP Using Activators Generated by Electron Transfer (AGET)

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Abstract: A new initiating/catalytic system for atom transfer radical polymerization (ATRP) is reported. This system starts with alkyl halides as initiators and transition metal complexes in their oxidatively stable state (e.g., $Cu^{II}Br_2$/ligand) as catalysts. The activators are generated by electron transfer (AGET) without involvement of initiating organic radicals. AGET ATRP has a significant advantage over simultaneous reverse and normal initiation (SR&NI) ATRP, because it provides a simple route for synthesizing pure polymers with complex architectures such as star copolymers, block copolymers, etc. Furthermore, AGET ATRP can be also successfully carried out in miniemulsion. Homopolymers and pure block copolymers were successfully synthesized via ATRP in miniemulsion using AGET ATRP. The final products were analyzed via two-dimensional chromatography, which combines high performance liquid chromatography (HPLC) and gel permeation chromatography (GPC). The resulting chromatograms showed that pure linear block copolymers and star block copolymers were prepared without the presence of any homopolymers.

Introduction

It is challenging to extend controlled/living radical polymerizations (CRP), including atom transfer radical polymerization (ATRP), to aqueous dispersed media.[1,2] The first ATRP emulsion process was attempted in 1998.[3] However, the relatively complicated transport process of the monomer from droplets to micelles limited the level of control attained in the polymerization.[4−9] Recently, miniemulsion, which is also one of the best aqueous dispersed systems for other CRPs,[10−13] has proven successful for ATRP.[14] The preexistence of monomer droplets minimizes the problems associated with monomer transport during the polymerization.[15] Each miniemulsion droplet behaves like a "mini-bulk" system.

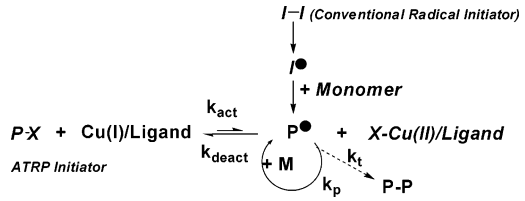
To conduct a successful ATRP in miniemulsion, each component, including the initiator, the monomer, and the catalyst in both oxidation states, should remain stable inside the monomer droplets for the entire polymerization.[16] A stable miniemulsion is created with the aid of a high shearing force, usually sonication, before polymerization is initiated. The sonication procedure presents a problem for a direct ATRP because the activating Cu(I) complex is sensitive to air. It is difficult to avoid oxidation and control the concentration of the activator during the sonication.

Reverse ATRP[17] was therefore applied to the miniemulsion system with the catalyst precursor added to the reaction in the form of Cu(II).[14] To reach the ATRP equilibrium, a conventional radical initiator such as 2,2′-azobisisobutyronitrile (AIBN) was added to generate radicals, which reduced Cu(II) to Cu(I) and generated in situ a halogen-containing initiator. As compared to direct ATRP, a reverse ATRP is more adaptable to miniemulsion because the catalyst oxidation during sonication is less challenging. However, reverse ATRP has some limitations. The amount of catalyst cannot be independently reduced and should be comparable to the radical initiator because the added Cu(II) complex provides the only source of the transferable atoms. Furthermore, a block copolymer cannot be synthesized using a reverse ATRP.

These problems were partially solved by the development of the simultaneous reverse and normal initiation (SR&NI) process

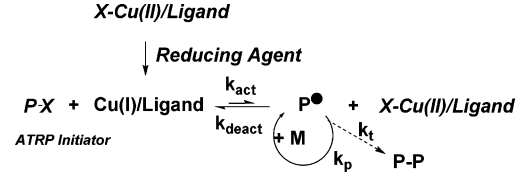
(1) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083−2134.
(2) Cunningham, M. F. *Prog. Polym. Sci.* **2002**, *27*, 1039−1067.
(3) Makino, T.; Tokunaga, E.; Hogen-Esch, T. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 288−289.
(4) Gaynor, S. G.; Qiu, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5951−5954.
(5) Qiu, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2872−2875.
(6) Matyjaszewski, K.; Shipp, D. A.; Qiu, J.; Gaynor, S. G. *Macromolecules* **2000**, *33*, 2296−2298.
(7) Matyjaszewski, K.; Qiu, J.; Shipp, D. A.; Gaynor, S. G. *Macromol. Symp.* **2000**, *155*, 15−29.
(8) Qiu, J.; Pintauer, T.; Gaynor, S. G.; Matyjaszewski, K.; Charleux, B.; Vairon, J.-P. *Macromolecules* **2000**, *33*, 7310−7320.
(9) Jousset, S.; Qiu, J.; Matyjaszewski, K.; Granel, C. *Macromolecules* **2001**, *34*, 6641−6648.
(10) Cunningham, M. F. *C. R. Chim.* **2003**, *6*, 1351−1374.
(11) de Brouwer, H.; Tsavalas, J. G.; Schork, F. J.; Monteiro, M. J. *Macromolecules* **2000**, *33*, 9239−9246.
(12) Asua, J. M. *Prog. Polym. Sci.* **2002**, *27*, 1283−1346.
(13) Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **2002**, *27*, 689−757.
(14) Matyjaszewski, K.; Qiu, J.; Tsarevsky, N. V.; Charleux, B. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 4724−4734.
(15) Sudel, E. D.; El-Aasser, M. S. In *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley and Sons: New York, 1997.
(16) Li, M.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3606−3614.
(17) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7572−7573.

Scheme 1. Proposed Mechanism for the SR&NI Process in ATRP[a]



[a] The activation and deactivation steps proceed with the rate constant k_{act} and k_{deact}. Generated free radicals propagate and terminate with rate constants k_p and k_t. All ingredients present in the initial system are in italic.

Scheme 2. Proposed Mechanism for the AGET Process in ATRP[a]



[a] All ingredients present in the initial system are in italic.

(Scheme 1).[18] In this process, an ATRP initiator, that is, an alkyl halide or a halogen-terminated macroinitiator, is added to the reaction together with a conventional radical initiator. Both of them contribute to the ATRP equilibrium, so that the relative amount of catalysts can be dramatically decreased and the synthesis of block copolymers can be achieved. Indeed, SR&NI was successful for the preparation of homopolymers,[19] linear block copolymers, star-block copolymers,[20] and gradient copolymers with a significantly decreased concentration of catalyst in both bulk and miniemulsion processes. On the other hand, the SR&NI process had an intrinsic deficiency when it was used to synthesize block copolymers. This drawback came from the use of a conventional radical initiator to reduce the catalyst complex, which introduced new free radicals. These free radicals produced homopolymer chains consisting of the second monomer only, which competed with the growth of block copolymers from the macroinitiator. Therefore, the final product contained a small fraction of homopolymer in addition to the desired block copolymer.[20] Pure block copolymers are nearly impossible to obtain by SR&NI ATRP.

To overcome this limitation, and prepare a pure block copolymer in miniemulsion without contamination by homopolymers, a new catalyst activation process was developed. This novel procedure, which we name activator generated by electron transfer (AGET) ATRP (Scheme 2), is an improvement over SR&NI. Instead of employing a conventional radical initiator, a reducing agent is used to react with Cu(II) complex and to generate the activator without an involvement of organic radicals which could initiate new chains. Because this novel AGET process remains tolerant to air during sonication, it may be useful for the commercial miniemulsion ATRP process. Most importantly, because no initiating radicals are introduced during polymerization, no homopolymer is formed when a block copolymer is targeted.

In this paper, we present results of the first miniemulsion AGET ATRP where the activator is generated via electron transfer rather than organic radicals. The success of this AGET technique for the preparation of homopolymers and pure block copolymers was demonstrated by two-dimensional (2D) chromatography analyses of the products.

Experimental Section

Materials. *n*-Butyl acrylate (BA, Aldrich), methyl acrylate (MA), and styrene (St) were purified by passing through a column filled with basic aluminum oxide (Aldrich) to remove inhibitor, or antioxidant, to provide consistent kinetics in the presence of oxygen.[21−23] The monomers were stored at −5 °C. 1,1,1-Tris(4-(2-bromoisobutyryloxy)-phenyl)ethane (TBiBPE)[24] and bis(2-pyridylmethyl)octadecylamine (BPMODA)[25] were synthesized according to the procedures previously published. CuBr (Aldrich) was purified by stirring in acetic acid. After filtration, it was washed with 2-propanol and then dried in a vacuum. *N*,*N*′,*N*″,*N*‴-Pentamethyldiethylenetriamine (PMDETA, Aldrich),[26] $CuBr_2$ (Aldrich), ethyl 2-bromoisobutyrate (EBiB, Aldrich), Brij 98 (polyoxyethylene(20) oleyl ether, Aldrich), hexadecane (Aldrich), and ascorbic acid (Aldrich) were used as received.

Preparation of Homopolymers. Before conducting a miniemulsion polymerization, the Cu(II) complex was prepared in a round-bottomed flask by dissolving $CuBr_2$ (0.0218 g, 0.098 mmol), BPMODA (0.0440 g, 0.098 mmol), and hexadecane (0.18 g) in BA (5.0 g, 39 mmol) at 60 °C. The resulting solution was cooled by an ice bath. The EBiB initiator (28.7 μL, 0.196 mmol) was dissolved in the cold solution. The aqueous Brij 98 solution (20 mL, 5 mmol/L) was added to the organic solution before the mixture was subjected to sonication (Heat Systems Ultrasonics W-385 sonicator; output control set at 8 and duty cycle at 70% for 1 min). The resulting homogenized miniemulsion was transferred to a Schlenk flask and purged with argon for 30 min. The flask was then immersed in an oil bath thermostated at 80 °C. An aqueous solution of ascorbic acid was injected into the reaction to initiate the polymerization. Aliquots were taken at intervals to measure the conversion gravimetrically and to examine the evolution of molecular weight.

Preparation of Macroinitiators. Both linear and 3-arm macroinitiators were prepared by direct ATRP in bulk. Table 1 lists the conditions and results for the syntheses of poly(methyl acrylate) (PMA) macroinitiators that were used in the following block copolymerizations. A 10 mL Schlenk flask was charged with CuBr and then degassed and backfilled with nitrogen three times. Pre-deoxygenated PMDETA, monomer, and anisole (as internal GC standard) were added to the flask, respectively. After the solution was magnetically stirred for 10 min to form the Cu^{I}−PMDETA complex, the flask was immersed in an oil bath at the desired temperature. The polymerization was initiated by the injection of pre-deoxygenated alkyl halide. Aliquots were withdrawn periodically to monitor monomer conversion through GC. The reaction was stopped at around 50% conversion. The resulting mixture was diluted with THF and filtered through a neutral aluminum oxide column to remove the copper catalyst. To isolate the macroinitiator, the solvent and unreacted monomer were removed, and the polymer was dried under vacuum to a constant mass.

Preparation of Block Copolymers in Miniemulsion. The macroinitiator, $CuBr_2$, BPMODA ligand, and hexadecane were dissolved in monomer in a round-bottomed flask at 60 °C. After the formation of the Cu(II) complex, the resulting solution was cooled by ice bath. An aqueous Brij 98 solution was added to the cooled organic solution before the mixture was subjected to sonication (Heat Systems Ultrasonics

(18) Gromada, J.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 7664−7671.
(19) Li, M.; Min, K.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 2106−2112.
(20) Li, M.; Jahed, N. M.; Min, K.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 2434−2441.
(21) Acar, A. E.; Yagci, M. B.; Mathias, L. J. *Macromolecules* **2000**, *33*, 7700−7706.
(22) Gnanou, Y.; Hizal, G. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *42*, 351−359.
(23) Nanda, A. K.; Hong, S. C.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2003**, *204*, 1151−1159.
(24) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526−6535.
(25) Xia, J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2434−2437.
(26) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697−7700.

Table 1. Syntheses of Macroinitiators via Direct ATRP

macroinitiator	RBr	stoichiometry [MA]:[RBr]:[CuBr/PMDETA]	*T* (°C)	conv.	$M_{n,GPC}$ (g/mol)	M_w/M_n
PMA-Br	EBiB	200:1:0.5	50	0.61	10 200	1.07
3-arm R-(PMA-Br)$_3$	TBiBPE	300:1:1	60	0.54	14 600	1.13

W-385 sonicator; output control set at 8 and duty cycle at 70% for 1 min). The resulting homogenized suspension was transferred to a Schlenk flask and purged with argon for 30 min. The flask was then immersed in an oil bath thermostated at 80 °C. An aqueous solution of ascorbic acid was injected into the flask to initiate the reaction. Aliquots were taken at intervals to measure the conversion gravimetrically and to examine the evolution of molecular weight.

Measurements. Conversion was determined by gravimetry in the case of miniemulsion polymerization, and by GC in the case of bulk polymerization using a Shimadzu GC-14A gas chromatograph, equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR51 Chromatapac. Molecular weights were determined by GPC equipped with an autosampler (Waters, 717 plus), HPLC pump at 1 mL/min (Waters, 515), and four columns (guard, 100 Å, 10^3 Å, and 10^5 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).

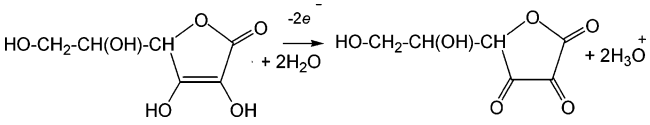
Compositional Analysis. 1. High Performance Liquid Chromatography (HPLC) under Critical Conditions. The analysis of samples was performed under the critical condition for polystyrene (PS) using a Waters 600 controller and pump. The mobile phase was a mixture of tetrahydrofuran (THF) and acetonitrile (49%/51%, v/v). The columns used for separation were Macherey & Nagel, Nucleosil 300-5 C18 (particle size 5 μm, pore size 300 Å, and column dimensions 250 × 4 mm i.d.) and Nucleosil 1000-7 C18 (particle size 7 μm, pore size 1000 Å, and column dimensions 250 × 4 mm i.d.). The column oven temperature was set at 32 °C. The mobile phase flow rate was 0.5 mL/min. An evaporative light scattering detector (ELSD, Polymer Laboratories, PL-ELS 1000, nitrogen flow 1.2 L/min, evaporator temperature 90 °C) was used. Dilute polymer solutions were made in THF/acetonitrile of 50%/50% v/v (2 mg/mL), and each time a 5 μL sample was used for analysis. Data acquisition was accomplished with PSS-WINGPC 7 from Polymer Standards Service (PSS; Mainz, Germany).

2. Two-Dimensional (2D, HPLC-GPC) Chromatography. For the first dimension HPLC, the same analytical condition was used as described for the HPLC analysis under the critical condition for PS, except that the flow rate was set at 0.08 mL/min instead of 0.5 mL/min. Sample fractions from the first dimension were transferred to the second dimension (GPC) via an eight-port valve system (VICI Valco EHC8W), which consisted of two 200 μL loops. The second dimension (GPC) consisted of a Waters 515 pump delivering a flow rate of THF at 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 ELSD detector was used as in HPLC analysis, and the second dimension was calibrated using polystyrene homopolymer standards. Dilute polymer solutions were prepared in THF/acetonitrile 50%/50% v/v (5 mg/mL), and a 5 μL sample was used for analysis. Data acquisition and processing were automatically performed by the Polymer Standards Service software, WINGPC 7 and PSS-2D-GPC software, respectively.

Results and Discussion

1. Synthesis of Homopolymers. Because of its tolerance to air, AGET is a convenient technique to conduct ATRP in miniemulsion. Ascorbic acid was adopted as the reducing agent for the AGET ATRP in miniemulsion because of its water-solubility. During screening reactions, hydrophobic reducing agents were floating over the miniemulsion and therefore could not successfully enter droplets, reduce the catalyst, and activate the polymerization. On the contrary, a water-soluble reducing agent, such as ascorbic acid, easily dissolves in the aqueous phase of miniemulsion and reduces the Cu(II) complexes, either at the surface of monomer droplets or in the aqueous phase. During the redox reaction, ascorbic acid is involved in a two-electron oxidation to yield dehydroascorbic acid (Scheme 3).[27] Because the resulting Cu(I) complexes are more hydrophobic than Cu(II) complexes, the reduction process essentially drives the active catalysts back into the droplets, which provides an additional handle to control the polymerization.

Scheme 3. Reduction Mechanism of Ascorbic Acid in Water



Before the polymerization is initiated, most of the Cu(II) species remain in the monomer droplets because of complexation with a highly hydrophobic ligand such as BPMODA, but some are also present in the aqueous medium. Therefore, when ascorbic acid is added to the miniemulsion, it can immediately interact with and reduce the small fraction of the Cu(II) complex that is present in the water phase and those complexes near the surface of the monomer droplets. To eliminate the early nonstationary period, the ascorbic acid was slowly added during 10 min. This resulted in the reaction attaining more linear kinetics than that obtained when all of the ascorbic acid was added at the very beginning of the reaction.

To leave some excess of Cu(II) species to regulate ATRP, the substoichiometric amount of the reducing agent was used. The optimal amount of the acid depends on partition coefficients of the complexes, ATRP equilibrium constants, targeted molecular weights, etc. Too small amount of ascorbic acid would lead to a very slow polymerization, whereas too large amount would lead to the reduced level of control.

Figure 1 shows the results of experiments conducted where the amount of ascorbic acid was adjusted to obtain an appropriate rate of reaction, without generating too many radicals at the beginning. The experimental results suggested that the best ratio of ascorbic acid to Cu(II) complex is ~0.4:1. With this ratio, the polymerization was sufficiently fast and did not show significant coupling reactions (Figure 2). The small curvature of the kinetic plot could indicate a possible loss of the bromine end groups through hydrolysis or a progressive migration of the catalyst to the aqueous phase.

2. Synthesis of Linear Block Copolymers. AGET should be a more efficient technique than SR&NI for the synthesis of pure block copolymers. In SR&NI, the appearance of some homopolymer was inevitable, even if the amount of conventional radical initiator was reduced to a low level.[19] AGET ATRP does not require a conventional radical initiator to be introduced into

(27) Sawyer, D. T.; Sobkowiak, A.; Roberts, J. J. L. *Electrochemistry for Chemists*, 2nd ed.; John Wiley & Sons: New York, 1995.

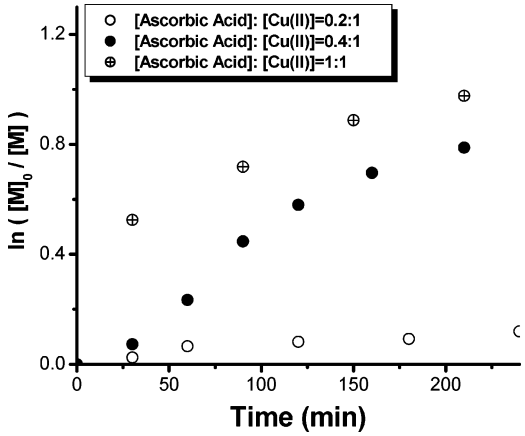


Figure 1. The first-order kinetic plot for polymerization of BA in an AGET ATRP in miniemulsion using variable amounts of ascorbic acid as a reducing agent. [BA]:[EBiB]:[$CuBr_2$/BPMODA] = 200:1:0.5; reaction temperature = 80 °C; [Brij 98]:[hexadecane] = 2.3/3.6% based on monomer; solid content = 20% (based on 100% conversion).

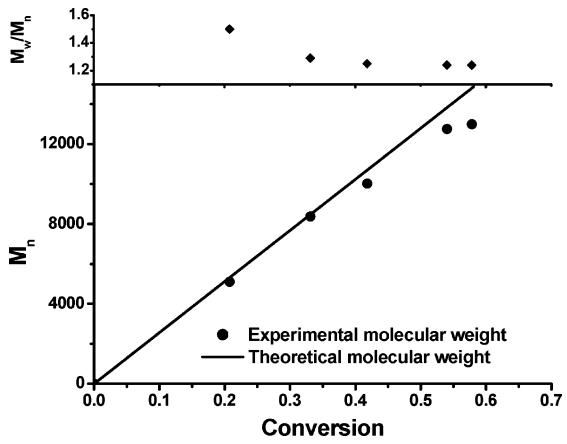


Figure 2. Molecular weight evolution with conversion in an AGET ATRP for BA in miniemulsion. [BA]:[EBiB]:[$CuBr_2$/BPMODA]:[ascorbic acid] = 200:1:0.5:0.2; reaction temperature = 80 °C; [Brij 98]:[hexadecane] = 2.3/3.6% based on monomer; solid content = 20% (based on 100% conversion).

the system. The Cu(I) complex is produced in situ through an electron transfer rather than organic radical reduction of the Cu(II) complex. On one hand, AGET retains the main advantage of a SR&NI process: an air-insensitive Cu(II) complex as the form of active catalyst precursor is initially added to the reaction, which allows easy manipulation of the process streams, especially for miniemulsion. On the other hand, this procedure inherits the advantage of direct ATRP, in which all radicals are generated exclusively from the alkyl halide, or macroinitiator if a block, graft, or comb copolymer is targeted; that is, the final products will only consist of the desired segmented copolymer with no homopolymer as impurity. Thus, AGET might be the best technique to synthesize pure block copolymers in miniemulsion ATRP.

2D Chromatography Analysis. Conventional gel permeation chromatography (GPC) has some limitation in evaluating the purity of a block copolymer. Copolymer distribution varies not only in molar mass, but also in chemical composition and/or functionality. Therefore, complete characterization of the copolymers requires chromatographic separations in more than one dimension. 2D chromatography is a powerful technique that can be employed to evaluate the purity of complex polymer systems. HPLC-GPC 2D chromatography is an appropriate analytical tool that allows an independent evaluation of chemical composition, or functionality, in addition to molar mass. The polymer mixtures are initially separated according to their chemical compositions in the dimension of HPLC, and then the eluents are transferred to the GPC dimension and further separated according to their molar masses or hydrodynamic volumes.[28] It was earlier shown that 2D chromatography allows for efficient separation for block copolymers, homopolymers, and coupling products.[20,29]

To determine the amount of homopolymer produced during AGET ATRP in a miniemulsion synthesis of a poly(MA-*b*-St) copolymer, the critical condition for polystyrene (PS) was utilized in the HPLC analysis. Under the critical condition for PS, the entropic and enthalpic interactions between PS and the packing column are compensated and the elution volume of PS in the column is independent of the size of its polymer chains. Therefore, the PS chains become chromatographically invisible; that is, the chromatographic behavior of PS under this critical condition does not depend on its hydrodynamic size but on its chemical composition or functionality. Thus, the elution volume of the poly(MA-*b*-St) copolymer is solely determined by the molar mass of PMA segment in the copolymer. In addition, under the critical conditions for PS, the elution behavior of PMA segment appeared as size exclusion mode, meaning the poly(MA-*b*-St) copolymer chains with longer PMA segment would have smaller elution volume and elute earlier.

Figure 3 shows the 2D chromatograms of the linear macroinitiator PMA (Figure 3A) and linear block copolymer poly(MA-*b*-St) (Figure 3B) synthesized by AGET ATRP in miniemulsion. According to these two chromatograms, the PMA macroinitiator and the final poly(MA-*b*-St) copolymer have different molecular weights but similar elution volumes (4.52 mL). The comparable elution volume confirmed that the PS segment is chromatographically invisible in the HPLC analysis under the critical condition for PS. The elution volume of PS homopolymer under its critical condition (4.88 mL) is independent of its molecular weight. Therefore, because there was no peak at 4.88 mL in the contour of the final linear block copolymer product (Figure 3B), no homopolystyrene was formed during this AGET ATRP miniemulsion reaction. The small region in the copolymer chromatogram (Figure 3B) with an elution volume of 4.24 mL was ascribed to star−star coupling products, because a smaller elution volume corresponds to a larger PMA segment. This was confirmed by the molecular weight determination from the GPC dimension, in which the small shoulder peak had a molecular weight of 22 000 g/mol, higher than that of the main product poly(MA-*b*-St) (15 400 g/mol). Integration of each peak in the 2D chromatogram of copolymer provided semi-quantitative composition information of the final product. The coupling product corresponded to ~1 wt % of the final product, which showed a high yield of linear block copolymer by AGET ATRP in miniemulsion.

(28) Pasch, H.; Trathnigg, B. *HPLC of Polymers*; Springer: Berlin, 1997.
(29) Lutz, J.-F.; Jahed, N.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1939−1952.

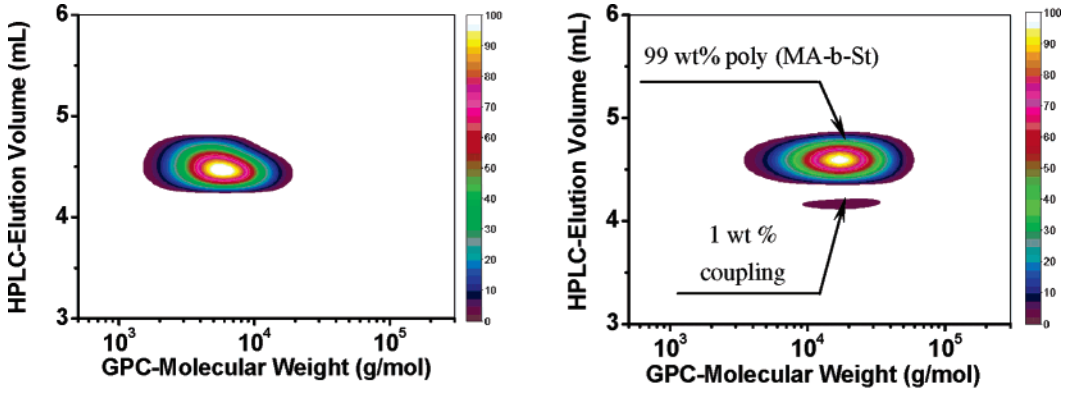


Figure 3. 2D chromatograms of linear PMA macroinitiator (A) and block copolymer poly(MA-*b*-St) (B) synthesized by AGET ATRP in miniemulsion. The first dimension is HPLC under the critical condition for PS, and the second dimension is GPC with PS standard as calibration. Polymerization conditions: $[St]_0:[PMA]_0:[CuBr_2/BPMODA]_0:[\text{ascorbic acid}]_0 = 200:1:0.4:0.16$; 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.

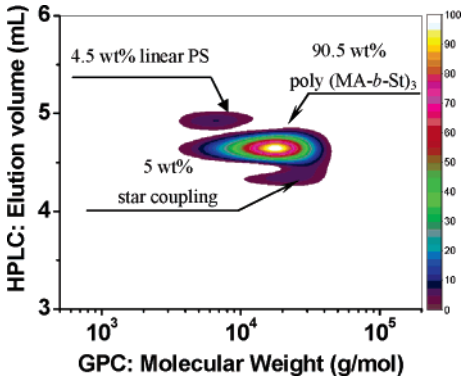


Figure 4. 2D chromatogram of star block copolymer poly(MA-*b*-St)$_3$ synthesized using 3-arm trifunctional PMA macroinitiator by SR&NI ATRP in miniemulsion. The first dimension is HPLC under the critical condition for PS, and the second dimension is GPC with PS standard as calibration. Polymerization conditions: $[St]_0:[(PMA\text{-}Br)_3]_0:[CuBr_2/BPMODA]_0:[AIBN]_0 = 300:1:0.6:0.375$; 80 °C. Miniemulsion conditions: [Brij 98] = 0.58 wt % with respect to water (2.3 wt % with respect to the organic phase); [hexadecane] = 3.6 wt % with respect to monomer.

3. Synthesis of Star Block Copolymers. Star block copolymers have enhanced rheological and mechanical properties.[30−32] ATRP via SR&NI in miniemulsion was successful in the synthesis of star block copolymers;[20] however, the limitation of SR&NI was also clearly observed. Figure 4 shows a typical 2D chromatogram of a 3-arm star block copolymer poly(MA-*b*-St)$_3$ obtained from a SR&NI process in miniemulsion.[20] The peak at 4.56 mL in HPLC represents the main desired 3-arm star block copolymer, and the shoulder peak at 4.25 mL is attributed to star−star coupling reactions, because the molecular weight of this shoulder peak is twice higher than that of the main peak. In addition, a small peak at elution volume of 4.88 mL was identified as a homopolymer of PS. The PS standard was used as the calibration for the GPC dimension, and the compositional information of the resulting block copolymers was provided by the integration of the intensity of each peak in the 2D contour. The polymer composition was: 90.5 wt % of 3-arm star block copolymer, 5 wt % of a copolymer resulting from star−star coupling reactions, and 4.5 wt % of linear homopolymer PS. The homopolymer PS detected in 2D chromatography, as discussed above, resulted from use of a conventional radical initiator (e.g., AIBN) to activate the catalyst. Thus, 2D chromatography analysis demonstrated the limitation of a SR&NI process in preparation of a pure block copolymer.

The AGET technique could overcome the limitation of the SR&NI process and provide pure block copolymers. Because the addition of a conventional radical initiator was avoided, the products of the polymerization remained as pure as in a direct ATRP. The final product was analyzed by 2D chromatography, as shown in Figure 5.

The copolymerization in miniemulsion was much faster than in bulk, which indicated a gradual diffusion of Cu(II) complex out of the monomer droplets to water. Star−star coupling reactions were present, especially for styrene polymerization.[33] To suppress the coupling reactions, it was critical to control the amount of ascorbic acid. The contribution of coupling reaction increased with conversion but could be reduced by stopping the polymerization at a lower conversion. Figure 5A and B shows 2D chromatograms of two samples prepared under the same reaction conditions but at different conversions. As shown by the 2D chromatogram (Figure 5A), star−star coupling was significant at 43% conversion; the weight fraction of the star−star coupling product was 13 wt %. However, at 20% conversion (Figure 5B), there was only one single peak in the 2D chromatogram, which represented a poly(MA-*b*-St)$_3$ star block copolymer with the molecular weight of 19 400 g/mol, when PS standards were used for calibration. The weight fraction of star−star coupling products was less than 1 wt %, as shown in Figure 5B by a circle. In addition, no homopolymer was detected at any conversion, which further proved that AGET is an efficient procedure for the preparation of a pure star block copolymer.

Conclusions

A miniemulsion ATRP via a novel AGET process starting from an oxidatively stable catalyst complex was successful for the preparation of pure linear and star-shaped block copolymers. AGET is specifically advantageous in miniemulsion processes because the Cu(II) species is not affected by air during

(30) Ishizu, K.; Uchida, S. *Prog. Polym. Sci.* **2000**, *24*, 1439−1480.
(31) Matyjaszewski, K. *Polym. Int.* **2003**, *52*, 1559−1565.
(32) Hadjichristidis, N.; Pispas, S.; Floudas, G. *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*; John Wiley & Sons: Hoboken, NJ, 2003.
(33) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218−7225.

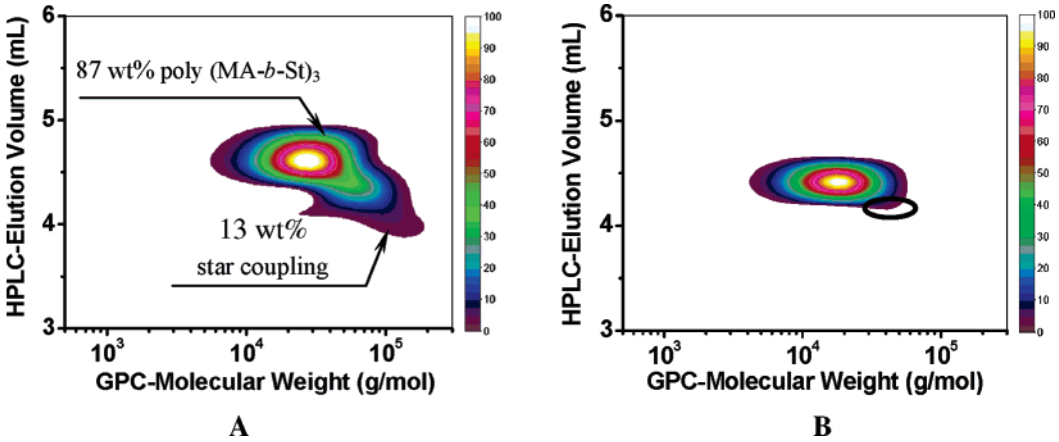


Figure 5. 2D chromatograms of star block copolymers poly(MA-*b*-St)$_3$ synthesized using 3-arm trifunctional macroinitiator (PMA-Br)$_3$ by AGET ATRP in miniemulsion at conversions 43% (A) and 20% (B). The first dimension is HPLC under the critical condition for PS, and the second dimension is GPC with PS standard as calibration. Polymerization conditions: $[St]_0:[(PMA\text{-}Br)_3]_0:[CuBr_2/BPMODA]_0:[ascorbic\ acid]_0 = 400:1:0.6:0.24$; 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.

sonication. In contrast to SR&NI, AGET does not require a conventional radical initiator. The resulting polymers were examined by 2D chromatography, with the first dimension as HPLC under critical conditions for PS and the second dimension as regular GPC. No homopolymers were detected when linear block copolymers or star block copolymers were targeted. Star−star coupling of star block copolymers could be minimized at lower monomer conversion.

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