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ATRP in Waterborne Miniemulsion via a Simultaneous Reverse and Normal Initiation Process

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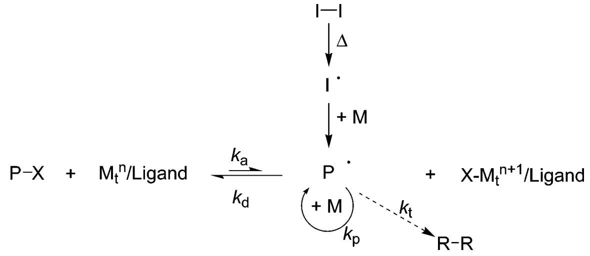
ABSTRACT: Atom transfer radical polymerization with simultaneous reverse and normal initiation process was conducted in a miniemulsion system with the use of highly active transition-metal complexes formed by hydrophobic ligands at concentrations 5−8 times lower than in a typical reverse ATRP process. The molecular weights were essentially determined by the concentration of alkyl halide (used in ~5-fold excess to a standard radical initiator) and much less affected by the concentration of a standard radical initiator (e.g., AIBN) and/or Cu^{II} complex. Controlled polymerizations of methacrylate, acrylate, and styrene were demonstrated by a linear correlation between molecular weights and monomer conversions and relatively low polydispersities ($M_w/M_n < 1.3$). The resulting latexes showed good colloidal stability with an average particle sized around 250−300 nm. Oil-soluble initiator (e.g., AIBN) provided better control over polymerization than water-soluble initiator (e.g., VA-044). Well-defined waterborne 3-arm star polystyrene and poly(*n*-butyl acrylate) were synthesized by adding a trifunctional alkyl halide to a reverse ATRP initiating system.

Introduction

Atom transfer radical polymerization (ATRP) is a robust and versatile technique for the synthesis of well-defined polymers with various architectures and narrow molecular weight distributions.[1−10] Control over the polymerization process is based on creation of a dynamic activation/deactivation equilibrium, between a small fraction of propagating radicals and a large majority of dormant species, via an atom transfer reaction. There are two approaches that have been developed to attain the atom transfer equilibrium (Scheme 1). In a normal ATRP, the initiating radicals are generated from an alkyl (pseudo)halide (RX), which is activated in the presence of a transition-metal complex in its lower oxidation state (e.g., Cu^IBr/ligand). Alternatively, an ATRP reaction can be initiated using a conventional radical initiator (e.g., 2,2′-azobis(isobutyronitrile), AIBN), which decomposes to form radicals that quickly interact with the transition-metal compound in its higher oxidation state (e.g., $Cu^{II}Br_2$/ligand) to form the dormant species (i.e., RX and/or PX).[11−14] The latter approach was named reverse ATRP.

Scheme 1. Two Approaches toward the ATRP Equilibrium



Reverse ATRP has proved to be the better pathway to initiate ATRP in waterborne emulsion[13,15−20] and miniemulsion[21−26] systems. Recently, well-controlled miniemulsion polymerizations (with a reasonable solid levels (≥20%) and low surfactant usage (2.3 wt % Brij 98 with respect to monomer)) were demonstrated using a reverse ATRP. It was started with a $Cu^{II}Br_2$/hexa-substituted TREN catalyst complex and 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) as the radical deactivator and water-soluble radical initiator, respectively.[22] While productivity and colloidal stability were significantly improved, a relatively high amount of catalyst (1−2 equiv of Cu^{II} complex vs initiator, VA-044) was employed in this system, as had been the case in previously reported reverse ATRP reactions.[13,16,21] In such a reverse ATRP system, the degree of polymerization is determined by the initial concentration of normal radical initiator, as expressed by eq 1

$$\mathrm{DP} = \frac{\Delta[\mathrm{M}]}{2f\,[\mathrm{I-I}]_0} \qquad (1)$$

where f is the initiation efficiency of the initiator.

In a standard ATRP, one way to reduce the catalyst concentration, while at the same time maintaining control over the polymerization, is to use a highly active catalyst system (such as tris(2-(dimethylamino)ethyl)-amine, Me_6TREN).[27,28] A controlled polymerization of methyl acrylate was attained while using only 0.1 equiv of CuBr/Me_6TREN, relative to the initiator (i.e., ethyl 2-bromopropionate, 2-EBP). The reaction reached 41% conversion in 1 h at 22 °C under bulk polymerization conditions. However, there is a stoichiometric limitation to similarly reduce the level of catalyst in a reverse ATRP process. Since the initial concentration of the deactivator ($[Cu^{II}Br_2/\mathrm{ligand}]_0$) in a reverse ATRP reaction is intimately related to the amount of normal radical initiator, the level of copper complex in the system cannot be independently regulated for a given targeted degree of polymerization.

A newly developed simultaneous reverse and normal initiation (SRNI) ATRP process[29] has provided a way to reduce the catalyst concentration without sacrificing

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the level of control over polymerization. It was demonstrated by the use of 0.1 equiv of a highly active catalyst system in its higher oxidation state (e.g., $Cu^{II}Br_2/Me_6TREN$), which is less than 1/10 of that used in a typical reverse ATRP, and a dual initiator system consisting of 0.062 equiv of AIBN and 1 equiv of alkyl halide. A small amount of activating catalyst complex (e.g., $Cu^{I}Br/Me_6TREN$) was generated with the slow decomposition of AIBN. Since the initial concentration of alkyl halide was much higher than that of AIBN, the majority of the polymer chains were initiated by the alkyl halide via a normal ATRP process, and the degree of polymerization was predominately controlled by the concentration of alkyl halide, RX, as expressed by eq 2

$$\mathrm{DP} = \frac{\Delta[\mathrm{M}]}{[\mathrm{RX}]_0 + (2f\ [\mathrm{AIBN}]_0)} \tag{2}$$

Well-defined poly(*n*-butyl acrylate) and polystyrene, with narrow molecular weight distributions ($M_w/M_n < 1.1$), were synthesized by means of the SRNI process.[29]

This paper describes the application of this novel SRNI process to an aqueous dispersed polymerization system. The miniemulsion system that built up upon our previous work[22] was employed for enhancing colloidal stability and facilitating polymerization control, since its droplet nucleation mechanism[30] minimizes the mass transport of radical activator/deactivator through the aqueous phase. The use of air-stable Cu^{II} complex in the starting system, instead of air-sensitive Cu^{I} complex, additionally improves the operation of a miniemulsion polymerization.

Experimental Section

Materials. *n*-Butyl methacrylate (BMA, Aldrich), *n*-butyl acrylate (BA, Aldrich), and styrene (St, Aldrich) were purified by passing through an inhibitor removal column filled with basic aluminum oxide (Aldrich). The monomers were stored at −5 °C for later use. 1,1,1-Tris(4-(2-bromoisobutyryloxy)phenyl)ethane (TBiBPE),[31] tris(2-bis(3-(2-ethylhexoxy)-3-oxopropyl)aminoethyl)amine (EHA_6TREN),[32] bis(2-pyridylmethyl)octadecylamine (BPMODA),[33] and 4,4′4″-tris(5-nonyl)-2,2′:6′,2″-terpyridine (tNtpy)[34] were synthesized according to previously published procedures. Methyl 2-bromopropionate (MBP, Acros), ethyl 2-bromoisobutyrate (EB*i*B, Aldrich), (1-bromoethyl)benzene (1-PEBr, Aldrich), $CuBr_2$ (Aldrich), Brij 98 (Aldrich), hexadecane (HD, Aldrich), 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich), and 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044, Wako Chem. Inc.) were used as received.

Bulk Polymerization. In a typical polymerization, $CuBr_2$, the selected ligand, and any alkyl halide that was present in the solid state (i.e., TBiBPE) were degassed in a Schlenk flask by three nitrogen/vacuum cycles. Then, deoxygenated monomer was added to the flask using previously purged syringes. The solution was stirred for 10−20 min at 60 °C to form a homogeneous solution of the Cu^{II} complex. When a liquid alkyl halide (e.g., MBP) was employed, it was deoxygenated and then injected into the flask under a nitrogen atmosphere at this time. The flask was immersed in an oil bath thermostated at 80 °C. The polymerization was initiated by the injection of deoxygenated AIBN in anisole solution using a purged syringe. Samples were withdrawn periodically to monitor the monomer conversion and molecular weight.

Miniemulsion Polymerization. A typical recipe for the preparation of a miniemulsion is listed in Table 1. The 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, the surfactant solution was added and the mixture was ultrasonicated (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 sonification. The resulting miniemulsion exhibited good shelf life stability at room temperature, as evidenced by a lack of visible creaming or phase separation over 3 days of aging. After homogenization, the miniemulsion was then transferred to a 25 mL Schlenk flask, where pure argon was bubbled through the miniemulsion for 30 min before it was immersed in an oil bath thermostated at 80 °C. The magnetic stirring speed was set at 700 rpm. When using water-soluble azo initiator (e.g., VA-044), the polymerization was initiated by injection of a deoxygenated initiator aqueous solution to the miniemulsion. While, when using a water-insoluble azo initiator (e.g., AIBN), it was predissolved in the homogeneous oil phase at room temperature before homogenization. Time zero for the polymerization was marked when the Schlenk flask was immersed in the oil bath. Samples were withdrawn periodically via a degassed syringe to monitor monomer conversion and molecular weight.

Table 1. Typical Recipe for SRNI ATRP Process in a Miniemulsion System[a]

monomer	BA	5.0 g	200 equiv
alkyl halide	MBP	0.0326 g	1 equiv
ligand	tNtpy	0.0239 g	0.2 equiv
copper(II)	$CuBr_2$	0.0087 g	0.2 equiv
costabilizer	hexadecane	0.18 g	
surfactant	Brij 98	0.115 g	
deionized water	H_2O	19.88 g	
initiator	AIBN	0.004 g	0.125 equiv.

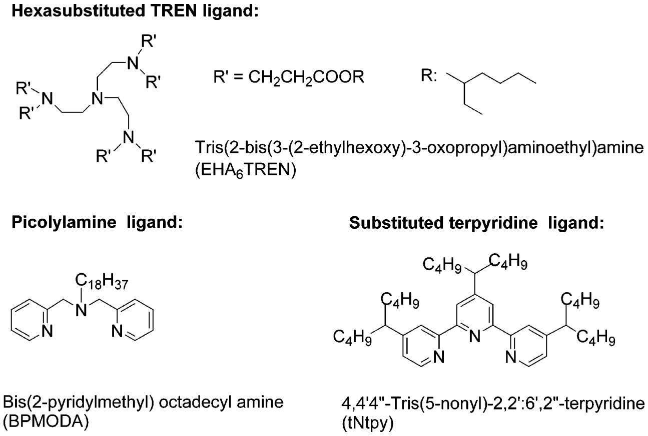
[a] [Brij 98]/[hexadecane] = 2.3/3.6 wt % based on monomer; solid content = 20% (based on 100% conversion); 80 °C.

Characterization. The polymerization samples were dissolved in THF for 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). A gravimetric method was also utilized to monitor the monomer conversion in miniemulsion polymerizations. Samples for molecular weights analysis were dissolved in THF (miniemulsion samples were first dried in the vacuum oven) and analyzed using GPC, which was equipped with 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 the internal standard. A calibration curve based on linear polystyrene standards (for polystyrene samples and poly(*n*-butyl acrylate) samples) or poly(methyl methacrylate) standards (for poly(*n*-butyl methacrylate)) 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).

Results and Discussion

Identification of Suitable Ligands. The development of the SRNI process shows promise as a method that can reduce the catalyst concentration in a reverse ATRP starting with less air-sensitive Cu^{II} complex. It leads to a dramatic reduction in the contamination from catalyst (i.e., copper species) in the final polymer products. The use of a highly active catalyst system is one of the key issues in the development of a well-controlled SRNI ATRP process. As shown in the previously reported work,[29] catalysts formed with Me_6TREN as ligand (0.1 equiv of $Cu^{II}Br_2/Me_6TREN$ in starting system) led to the synthesis of well-defined poly(*n*-butyl acrylate) and polystyrene under bulk homopolymerization conditions. However, Me_6TREN forms a hydrophilic complex, and it would not bring appropriate concentrations of the radical deactivator ($Cu^{II}Br_2/Me_6TREN$) or

Scheme 2. Ligands Used for the Preparation of ATRP Catalyst Complexes



the activator (Cu^IBr/Me_6TREN) into the organic phase for the establishment of an atom transfer equilibrium in a waterborne miniemulsion system. Thus, identification of a highly active catalyst complex formed with a hydrophobic ligand is demanded for the application of SRNI to an ATRP miniemulsion system. In addition to the hexasubstituted TREN ligands (e.g., EHA_6TREN) that were employed in our previous study,[22] substituted terpyridine (e.g., tNtpy) and picolylamine (e.g., BPMODA) ligands were also selected due to their high hydrophobicity and the “triamine” nature of the ligand that was expected to form an active catalyst. The structures of the ligands used in this study are presented in Scheme 2. The ligands were initially examined in bulk polymerization conditions using various monomers (i.e., methacrylate, acrylate, and styrene). The initial system consisted of 0.2 equiv of $CuBr_2$/ligand, 0.125 equiv of AIBN (leading to 0.2 equiv of radicals based on the decomposition efficiency of AIBN of 0.8), and 1 equiv of alkyl halide as initial deactivator, normal radical initiator, and ATRP initiator, respectively.

First, the bulk polymerization of BMA was carried out via SRNI in an ATRP process using catalyst complexes formed with EHA_6TREN, tNtpy, and BPMODA as ligands. After an initial induction period, a relatively linear semilogarithmic plot was observed in each case (Figure 1A). The induction period at the beginning of polymerizations implied that the initial concentration of Cu^{II} complex was high enough to capture all radicals generated by the relatively slow decomposition of AIBN. The molecular weight increased linearly with conversion with higher values than the theoretical ones (Figure 1B). This observation might indicate the occurrence of slow initiation with respect to the fast propagation of BMA in such a SRNI process. The polydispersities were in the range 1.2−1.3. The catalyst complexes formed with EHA_6TREN or BPMODA provided better agreement of experimental molecular weights with the theoretical values and relatively narrower molecular weight distributions (M_w/M_n) than using catalyst complexes formed with tNtpy.

These three types of ligands were also employed in the bulk polymerization of BA using similar reaction conditions. As shown in Figure 2, well-controlled polymerizations, characterized by a linear correlation between molecular weights and monomer conversion, were realized when using either BPMODA or tNtpy as ligands. The polydispersities of the resulting polymers were 1.1. However, the catalyst complex formed with hexasubstituted TREN ligand (e.g., $CuBr_2/EHA_6TREN$) resulted in an uncontrolled polymerization.

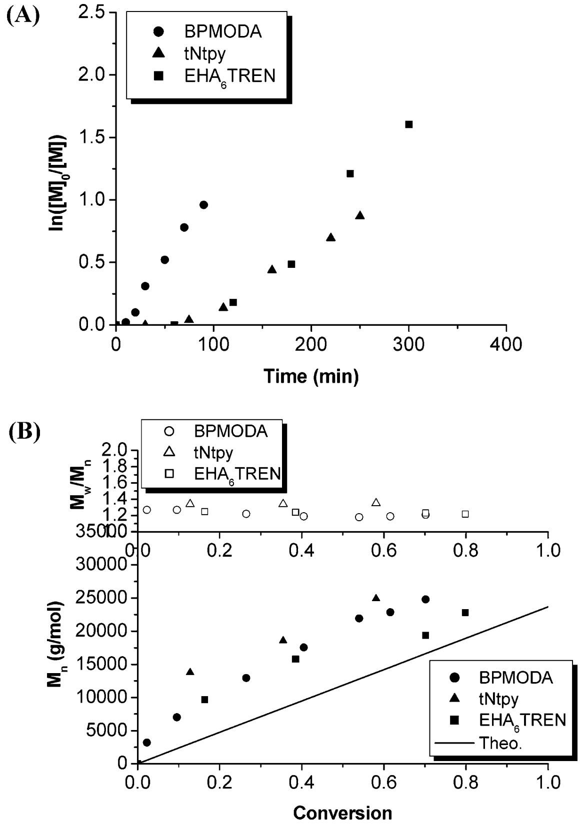


Figure 1. (A) First-order kinetic plot and (B) molecular weight evolution with conversion in ATRP using SRNI for BMA in bulk. $[BMA]/[EB\textit{i}B]/[CuBr_2\text{-ligand}]/[AIBN] = 200/1/0.2/0.125$; ligands: EHA_6TREN, tNtpy, and BPMODA; reaction temperature = 80 °C. Theoretical molecular weights were calculated using eq 2, $f = 0.8$.

Finally, the bulk polymerizations of styrene were performed using catalysts formed with BPMODA and tNtpy as ligands. As shown in Table 2, the polymerization was slow under similar reaction conditions. The experimental molecular weights were lower than the corresponding to theoretical values. However, the polydispersities were quite low ($M_w/M_n = 1.1$).

With the demonstration of successful application of SRNI to bulk ATRP of methacrylate, acrylate, and styrene using hydrophobic ligands for preparation of the catalyst complex, this initiating system was extended to the aqueous dispersed miniemulsion system.

ATRP in Miniemulsion via a Simultaneous Reverse and Normal Initiation (SRNI) Process. A typical ATRP in miniemulsion employing SRNI was conducted under the conditions described in Table 1. Homopolymerizations of *n*-butyl methacrylate, *n*-butyl acrylate, and styrene were carried out using various catalyst systems formed with the ligands depicted in Scheme 1. In addition to the oil-soluble radical initiator AIBN, a water-soluble initiator VA-044 was also used, in the presence of a normal ATRP initiator (i.e., alkyl halide), to get better understanding of this initiating process in a miniemulsion system. In addition, well-defined waterborne 3-arm star polystyrene and 3-arm star poly(*n*-butyl acrylate) were synthesized by the use of trifunctional alkyl halide (i.e., TBiBPE) as a “normal” initiator.

1. Polymerization Reactions. The homopolymerization of *n*-butyl methacrylate was carried out in a

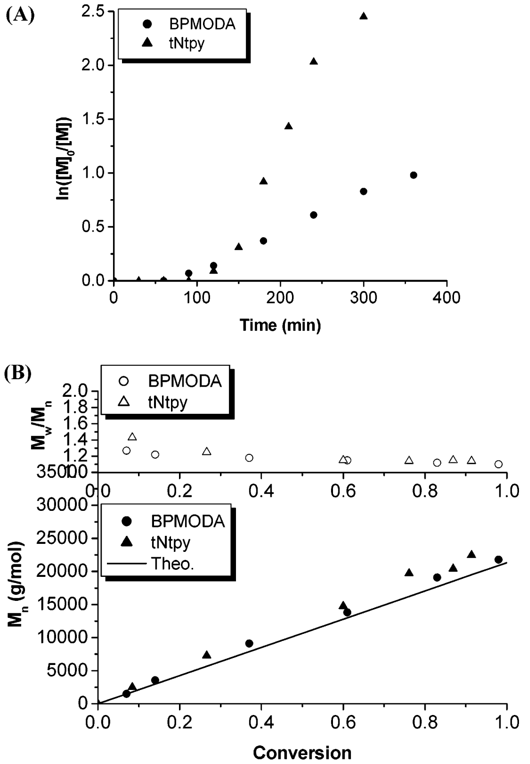


Figure 2. (A) First-order kinetic plot and (B) molecular weight evolution with conversion in ATRP using SRNI for BA in bulk. [BA]/[MBP]/[$CuBr_2$-ligand]/[AIBN] = 200/1/0.2/0.125; ligands: tNtpy and BPMODA; reaction temperature = 80 °C. Theoretical molecular weights were calculated using eq 2, $f = 0.8$.

Table 2. Bulk ATRP of Styrene via SR&NI[a]

ligand	time (h)	conv	$M_{n,sec}$	$M_{n,theo}{}^{b}$	M_w/M_n
BPMODA	0	0			
	20.5	0.45	5400	7800	1.13
	46	0.70	9800	12 100	1.10
tNtpy	0	0			
	6	0.18	2000	3100	1.18
	50	0.28	3900	4850	1.14

[a] [Styrene]/[1-PEBr]/[$CuBr_2$-ligand]/[AIBN] = 200/1/0.2/0.125; reaction temperature = 80 °C. [b] See Figure 1 for the calculation of theoretical molecular weights.

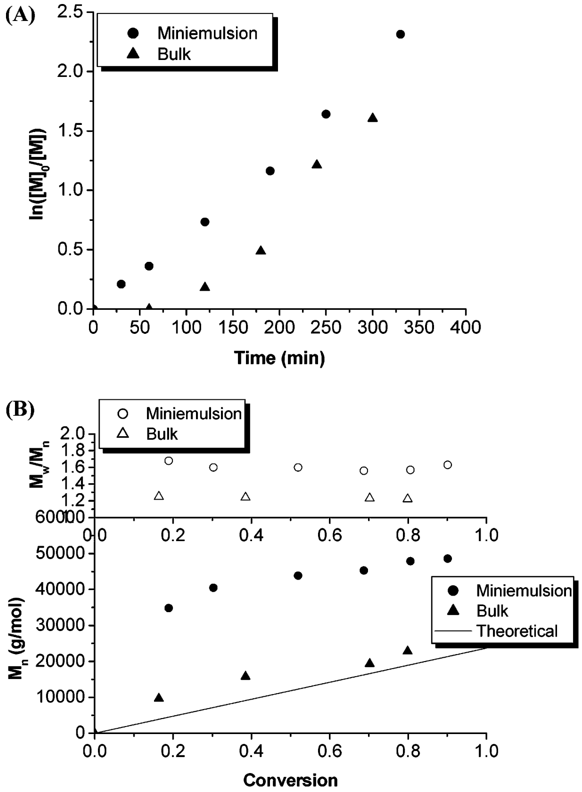


Figure 3. (A) First-order kinetic plot and (B) molecular weight evolution with conversion in ATRP using SRNI for BMA in miniemulsion and bulk systems. [BMA]/[EB*i*B]/[$CuBr_2$-EHA_6TREN]/[AIBN] = 200/1/0.2/0.125; reaction temperature = 80 °C. Miniemulsion system: [Brij 98]/[hexadecane] = 2.3/3.6 wt % based on monomer; solid content = 20% (based on 100% conversion). Theoretical molecular weights were calculated using eq 2, $f = 0.8$.

miniemulsion system using SRNI in an ATRP process, where 0.2 equiv of $CuBr_2$ complexed with EHA_6TREN (or BPMODA), 0.125 equiv of AIBN, and 1 equiv of EB*i*B were used as catalyst, radical initiator, and normal ATRP initiator, respectively. The ratio of [$CuBr_2$/ligand]/[AIBN] = 1.6 would lead to the complete reduction of the initial Cu^{II} complex into Cu^{I} species, based on the decomposition efficiency of AIBN of 0.8.[29] While affording a well-controlled polymerization of *n*-butyl methacrylate under bulk conditions, the catalyst system formed with a hexasubstituted TREN ligand (i.e., $CuBr_2$/EHA_6TREN) led to uncontrolled polymerization in miniemulsion system, as shown in Figure 3. The molecular weight increased only slightly with monomer conversion with a relatively high value at the beginning of polymerization (M_n = 34 800 g/mol at 19% conversion). This implied that the presence of 0.2 equiv of $CuBr_2$/EHA_6TREN complex in the starting system was not sufficient for immediate deactivation of the radicals generated by the decomposition of AIBN in the monomer droplets. The disappearance of the initial induction period, which was over 60 min in the corresponding bulk system, provided additional evidence for an AIBN-initiated conventional free radical polymerization mechanism at the early stage of the polymerization. Partitioning of the catalyst into the aqueous medium and/or preference for the higher oxidation state of the metal complex formed with such a ligand might be responsible for the poorly controlled polymerization. However, well-controlled polymerization of *n*-butyl methacrylate was realized in a miniemulsion system using catalysts formed with BPMODA as ligand. As shown in Figure 4, comparable kinetic behaviors, with linear semilogarithmic plots after the initial induction period, were noted in both bulk and miniemulsion systems. This implied that the miniemulsion polymerization behaved as a bulk polymerization under current reaction conditions, where each growing particle could be treated as an individual “minireactor”. The long hydrocarbon chain (C_{18}) of BPMODA restricted the diffusion of radical activator (CuBr/BPMODA)/deactivator ($CuBr_2$/BPMODA) from the organic phase to the aqueous media. The evolution of molecular weights also demonstrated a similar tendency for bulk and miniemulsion cases, both showing a linear correlation with respect to monomer conversions. The positive deviations from the theoretical values could be caused by the low initiation efficiency or the inherent error from molecular weight analysis by using PMMA as calibration standards. The polydispersities were relatively low with M_w/M_n of 1.21 in the bulk case and 1.28 in the miniemulsion case. There was little coagulum throughout the polymerization. The average diameter of the final latex was 252 nm with particle size distribution (D_v/D_n) of 1.17.

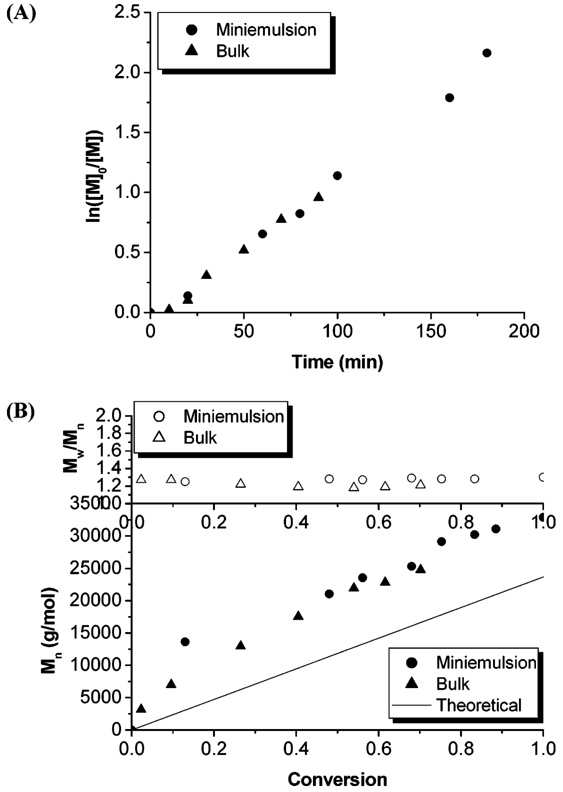


Figure 4. (A) First-order kinetic plot and (B) molecular weight evolution with conversion in ATRP using SRNI for BMA in miniemulsion and bulk systems. [BMA]/[EB*i*B]/[$CuBr_2$/BPMODA]/[AIBN] = 200/1/0.2/0.125; reaction temperature = 80 °C. Miniemulsion system: [Brij 98]/[hexadecane] = 2.3/3.6 wt % based on monomer; solid content = 20% (based on 100% conversion). Theoretical molecular weights were calculated using eq 2, $f = 0.8$.

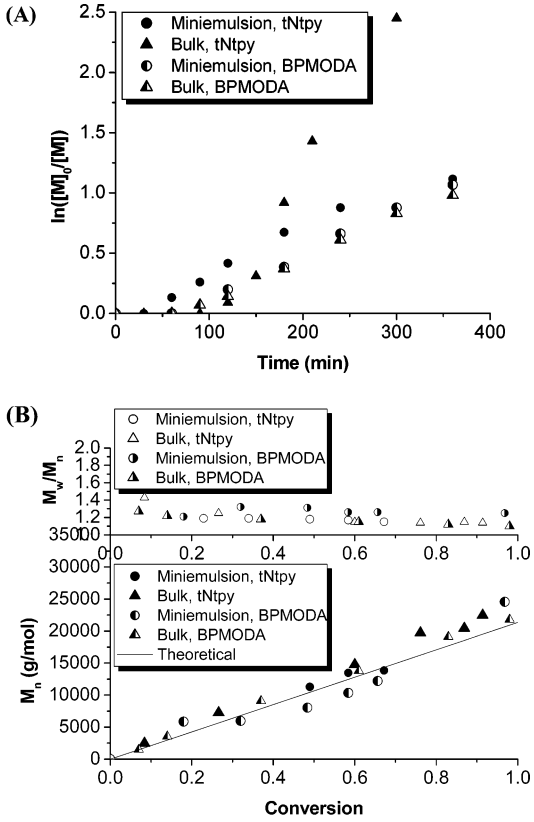


Figure 5. (A) First-order kinetic plot and (B) molecular weight evolution with conversion in ATRP using SRNI for BA in miniemulsion and bulk systems. [BA]/[MBP]/[$CuBr_2$-ligand]/[AIBN] = 200/1/0.2/0.125; ligands: tNtpy and BPMODA; reaction temperature = 80 °C. Miniemulsion system: [Brij 98]/[hexadecane] = 2.3/3.6 wt % based on monomer; solid content = 20% (based on 100% conversion). Theoretical molecular weights were calculated using eq 2, $f = 0.8$.

Figure 5 shows the semilogarithmic plots and molecular weight evolution for ATRP of BA employing a SRNI process in both miniemulsion and bulk systems, using copper complexed with BPMODA (or tNtpy) as catalyst. In the case of polymerizations conducted with catalysts formed with BPMODA, the linear semilogarithmic plots, following an initial induction period, were almost identical in both the bulk and miniemulsion systems. This phenomenon further confirms that the use of a highly hydrophobic ligand (e.g., BPMODA) and an oil-soluble radical initiator (e.g., AIBN) in a SRNI ATRP miniemulsion system enables the reaction to proceed in the same way as the corresponding bulk polymerization. However, this was not the case when using catalysts formed with tNtpy. A shorter induction period and slower polymerization rate were observed in the miniemulsion system as compared to those of the corresponding bulk system. This observation can be explained by assuming limited diffusion of the copper complex from the organic phase to the aqueous phase, resulting in a slight decrease in the initial concentration of deactivator, $CuBr_2$/tNtpy, in the monomer droplets. While it was still sufficient with respect to the slow formation of free radicals by decomposition of AIBN, the lower concentration of deactivator resulted in a shorter initial induction period. A slower polymerization rate could be attributed to a lower concentration of activator (CuBr/tNtpy) in the growing particles. Nevertheless, the majority of the catalyst was present in the organic phase throughout the polymerization due to the hydrophobic nature of the ligand, tNtpy. A well-controlled miniemulsion polymerization can be recognized by linear increase of molecular weights with monomer conversions, low polydispersities, and good agreement of experimental molecular weights with theoretical values. The particle diameter of the final latex was 270 nm (with BPMODA as ligand) and 305 nm (with tNtpy as ligand) with particle size distribution (D_v/D_n) of 1.15 and 1.22, respectively.

Controlled polymerizations were successfully carried out by ATRP using a SRNI process in miniemulsion systems with $^{1}/_{5}-^{1}/_{8}$ amount of added radical deactivator ($CuBr_2$/ligand) as compared to that added in a typical reverse ATRP process.[21,22] Latex particles with average volume diameter of 250–300 nm were formed. With the use of a dual initiator system consisting of large fraction of standard ATRP initiator (~90% alkyl halide) and minor fraction of normal radical initiator (~10% AIBN), the molecular weight of the final polymer was greatly determined by the initial ratio of monomer to alkyl halide rather than the concentration of AIBN and Cu^{II} complex. The polydispersities of the resulting polymers were in the range 1.1–1.3. The metal complex formed with BPMODA and tNtpy as ligands have been identified as suitable catalysts for this new initiating process in the miniemulsion system due to their hydrophobicity and high catalytic activities.

2. Hydrophilicity of the Standard Radical Initiator. A small amount (0.2 equiv) of oil-soluble radical initiator (e.g., AIBN), along with same equivalent of highly active Cu^{II} complex (e.g., $CuBr_2$/ligand), was initially employed in the development of the dual

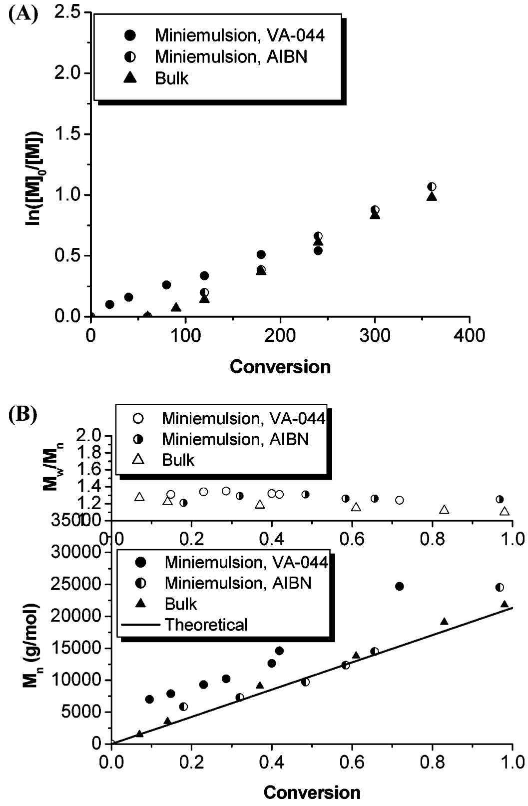


Figure 6. (A) First-order kinetic plot and (B) molecular weight evolution with conversion in ATRP using SRNI for BA in miniemulsion and bulk systems with different radical initiators, I−I: VA-044 or AIBN. [BA]/[MBP]/[$CuBr_2$−BP-MODA]/[I−I] = 200/1/0.2/0.125: reaction temperature = 80 °C. Miniemulsion system: [Brij 98]/[hexadecane] = 2.3/3.6 wt % based on monomer; solid content = 20% (based on 100% conversion). Theoretical molecular weights were calculated using eq 2, $f = 0.8$.

initiating system for SRNI process. All the components of such a SRNI system are hydrophobic, including the alkyl halide, copper complexes, AIBN, and monomer. They are restricted in the monomer droplets upon homogenization of the oil phase and aqueous surfactant solution. The kinetics of the miniemulsion polymerization is similar to that of the corresponding bulk polymerization. To broaden the scope of the SRNI ATRP miniemulsion process, a water-soluble diazo compound, VA-044, was employed as the radical initiator while the other ingredients were unchanged. A comparison of the kinetics and molecular weight evolution of the resulting BA polymerization is depicted in Figure 6. The relatively fast decomposition of VA-044 in the aqueous phase resulted in the formation of a large number of oligomeric radicals prior to the establishment of the atom transfer equilibrium, as evidenced by the lack of a detectable induction period at the beginning of the polymerization. Under these conditions, the chance for radical−radical termination reactions increased leading to low initiation efficiency. In addition, the observed behavior may be related to the fast initiator decomposition and its water solubility. As demonstrated in Figure 6B, the use of VA-044 as the radical initiator resulted in higher molecular weight than theoretical values, indicating a lower number of growing chains.

3. Synthesis of Well-Defined Waterborne 3-Arm Star Polymers. Atom transfer radical polymerization provides one of the most efficient synthetic routes for preparation of polymers with both controlled molecular weight and desired complex architecture.[6,35] The synthesis of well-defined multiarm star polymers was demonstrated using either core-first or arm-first approach.[36−43] Both multifunctional small-molecule initiators[31,44] and macroinitiators were used in the normal ATRP processes.[45] It is interesting to extend star polymer synthesis to aqueous (mini)emulsion. A reverse ATRP process, starting with metal complex in its higher oxidation state (e.g., Cu^{II}/ligand), is preferred in a miniemulsion system and proved to be a practical approach for the synthesis of well-defined waterborne polymers.[22] However, the use of standard radical initiators (e.g., AIBN, VA-044) does not allow the synthesis of polymers with a more complex architecture, such as multiarm polymers. The successful application of SRNI to reverse ATRP miniemulsion systems opens a novel and practical route for producing waterborne polymers with well-defined polymer architecture.

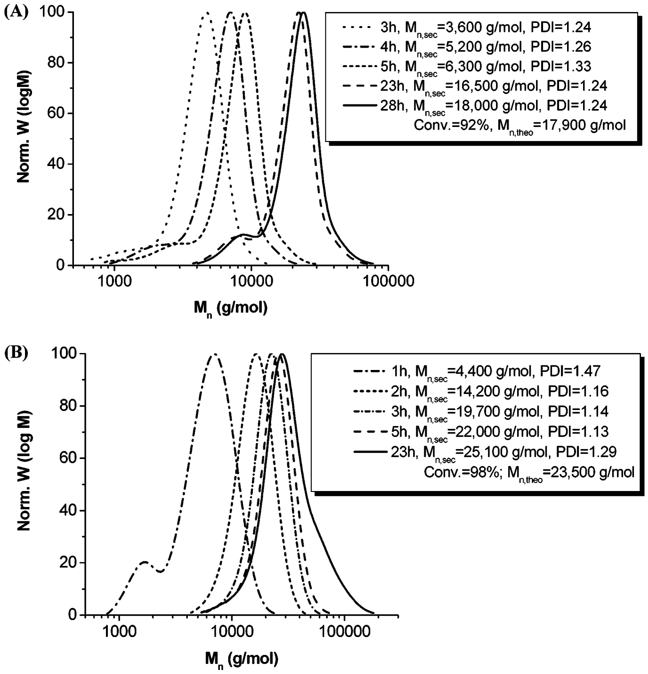


Figure 7. GPC traces of waterborne (A) 3-arm star polystyrene and (B) 3-arm star poly(n-butyl acrylate) produced in a miniemulsion system via a SRNI ATRP process. [Monomer]/[TBiBPE]/[$CuBr_2$-tNtpy]/[AIBN] = 300/1/0.6/0.375 (100/1/0.2/0.125 for each arm); reaction temperature = 80 °C.; [Brij 98]/[hexadecane] = 2.3/3.6 wt % based on monomer; solid content = 20% (based on 100% conversion).

The synthesis of a waterborne 3-arm star polystyrene and a 3-arm star poly(n-butyl acrylate) was performed using a dual initiator system, consisting of 0.375 equiv of AIBN and 1 equiv of a trifunctional alkyl halide, (TBiBPE), in conjunction of 0.6 equiv of a $CuBr_2$/BPMODA catalyst system. GPC traces of samples taken at different reaction time are presented in Figure 7. It can be observed that curves shifted smoothly toward higher molecular weight, and the polydispersities were relatively low ($M_w/M_n < 1.3$). Peaks at molecular weight of 1000−2000 g/mol correspond to the nonionic surfactant, Brij 98. A small peak at ∼3 times smaller molecular weight observed in polystyrene system (Figure 7a) is attributed to linear chains originating from the initiation by AIBN. Apparently, it is less resolved for poly(n-butyl acrylate). In conclusion, the application of the SRNI process to ATRP enables the synthesis of well-defined waterborne polymers with complex architectures.

Conclusion

Atom transfer radical polymerization of methacrylate, acrylate, and styrene were successfully conducted via a SRNI process in miniemulsion system with the use of highly active transition-metal complexes formed by hydrophobic ligands at concentrations 5−8 times lower than in a typical reverse ATRP process. Well-defined poly(*n*-butyl methacrylate), poly(*n*-butyl acrylate), and polystyrene were obtained using 0.2 equiv of highly active transition-metal complexes formed by hydrophobic ligands (e.g., $Cu^{II}Br_2$/BPMODA and $Cu^{II}Br_2$/tNtpy), 0.125 equiv of AIBN (leading to 0.2 equiv of radicals based on the decomposition efficiency of AIBN of 0.8), and 1 equiv of alkyl halide (e.g., EB*i*B, MBP, and 1-PEBr). Controlled polymerizations were demonstrated by a linear correlation of molecular weights with monomer conversion and relatively low polydispersities (M_w/M_n < 1.3). The experimental molecular weights were in good agreements with the theoretical values, which were essentially determined by the initial ratio of monomer to alkyl halide rather than the concentration of AIBN and Cu^{II} complex. It was found that oil-soluble initiator (e.g., AIBN) exhibited better control over polymerization than water-soluble initiator (e.g., VA-044). This can be explained by the low initiation efficiency resulting from the radical−radical termination reactions when using VA-044. The application of SRNI to reverse ATRP system opened a novel and practical route for the synthesis of waterborne polymers with well-defined polymer architecture. Waterborne 3-arm star polystyrene and poly(*n*-butyl acrylate) with low polydispersities (M_w/M_n) were synthesized by adding a trifunctional alkyl halide to a reverse ATRP initiating system.

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