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High Molecular Weight Poly(butyl methacrylate) by Reverse Atom Transfer Radical Polymerization in Miniemulsion Initiated by a Redox System

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ABSTRACT: The reverse atom transfer radical polymerization of butyl methacrylate in miniemulsion, initiated with the redox pair hydrogen peroxide/ascorbic acid and mediated with copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine, produced high molecular weight poly(butyl methacrylate) ($M_n = 989\,900$, PDI = 1.25). The miniemulsion was carried out with 15% solids (based on 100% conversion), 10 wt % of the nonionic surfactant Brij 98 (based on monomer), and 3.8 wt % hexadecane (based on monomer), with the final weight-average particle diameter less than 110 nm. The use of the redox pair to initiate the polymerization also facilitated a relatively fast rate of polymerization. The polymerizations were carried out at 60 °C and typically reached their maximum conversion (with degrees of polymerization up to 6900) of ∼80% in only 8 h. Additionally, the polymerization of methyl methacrylate produced well-defined high molecular weight polymers with a controlled degree of polymerization and narrow molecular weight distribution.

Introduction

Atom transfer radical polymerization (ATRP)[1−4] provides a facile route to the syntheses of polymers with predetermined microstructure and narrow molecular weight distributions. Regardless of how well suppressed the radical reactions are in the ATRP system, the radicals undergo the same side reactions (termination and transfer) that occur in conventional free radical polymerizations. The lifetime of the growing end, and consequently the molecular weight, are limited by the rate of the radical side reactions. Typically, for linear polymers produced by ATRP, the number-average molecular weight (M_n) is limited to ∼200 000, after which the effect of the radical side reactions become significant and the livingness of the system is decreased.[3,4] Well-defined high molecular weight poly(methyl methacrylate) (PMMA) was achieved by Xue et al.[5] using the phenyl 2-bromomethylpropionate/CuCl/4,4′-*n*-nonyl-2,2′-bipyridine initiator/mediating complex in xylene. After 500 min the conversion reached ∼55%, resulting in PMMA with a M_n of 360 000 with a polydispersity index (PDI) of ∼1.20. Recently, Mao et al.[6] produced high molecular weight poly[2-(dimethylamino)ethyl methacrylate] employing *p*-toluenesulfonyl chloride/CuCl/1,1,4,7,10,10-hexamethyltriethylenetetramine as the initiator/mediating complex in a methanol/water mixture. After 24 h at 50 °C the conversion reached 85%, and the resulting polymer had a M_n of 1 100 000 with a PDI of 1.26.

The application of ATRP to an aqueous dispersed system such as an emulsion or miniemulsion process provides advantages such as better mixing, improved heat transfer, and easier removal of residual monomer. Compared to ATRP conducted in emulsion, the miniemulsion process has proven to be far more robust in terms of colloidal stability and maintaining control of the polymerization.[7−13] Miniemulsion eliminates some of the complicating factors thought to negatively impact ATRP latexes made by emulsion polymerization, such as micelle nucleation, simultaneous polymerization within droplets and particles, and stabilization of very small particles at the beginning of the polymerization.[14,15] In addition, nucleation of the miniemulsion droplets that already contain the mediating complex avoids the need to transport the very hydrophobic mediating complex to the polymerization site. Reverse ATRP has proven to be an effective method of adapting ATRP to miniemulsion. It employs the mediating complex in its higher oxidation state, which is not easily oxidized during the high shear required to formulate the 100−200 nm droplets of a miniemulsion. We have previously observed that a thermal initiator which decomposes readily at low temperature is required since miniemulsion ATRP with particles sizes less than 200 nm are typically not colloidally stable above 60 °C.[16] The azo-initiator 2,2′-azobis-[2-(2-dimidazolin-2-yl)propane] dihydrochloride (VA-044) is employed since it has one of the lowest 10 h half-life temperatures commercially available (44 °C). Using VA-044 as the initiator at 60 °C leads to an induction period, in which no polymer is formed, at the beginning of the polymerization. This had been attributed to the time required for the initiator to thermally decompose and consume the copper(II) complex to levels where polymerization can proceed at an appreciable rate.

Initiators used for conventional free radical polymerizations, including azo compounds,[17,18] peroxides[19] and thermal iniferters,[20] have all been successfully applied to reverse ATRP; however, relatively high polymerization temperatures (>90 °C) are required to ensure the rapid decomposition of the initiator. Reverse ATRP employing a redox initiation system would allow the polymerization to be run at lower temperatures, as well as afford a more ideal reverse ATRP initiation, with all the polymer chains initiated almost instantaneously. The use of the redox pair, such as hydrogen peroxide (HPO)/ascorbic acid (AA), was expected to reduce the length of the induction period and lower the polydispersity index of the polymer. In addition to the expected results, the HPO/AA redox initiation system applied to the reverse ATRP of butyl methacrylate (BMA) and methyl methacrylate (MMA) in miniemulsion produced well-defined high molecular weight polymers ranging from 300 000 to 1 000 000. The preliminary results of the investigation are presented here.

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Experimental Section

Materials. *n*-Butyl methacrylate (99%, Aldrich), methyl methacrylate (99%, Aldrich), and 2-ethylhexyl acrylate (98%, Aldrich) were purified by passing each through a column packed with inhibitor remover (Aldrich). The compounds copper(II) bromide ($CuBr_2$, 99%, Aldrich), tris(2-aminoethyl)amine (96%, Aldrich), polyoxyethylene(20) oleyl ether (Brij 98, Aldrich), hexadecane (99%, Aldrich), basic alumina (Aldrich), ascorbic acid (99%, Aldrich), hydrogen peroxide (3 wt % in water, Aldrich), and 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (Wako Chemicals) were used as received. The synthesis of tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine (EHA_6TREN) was adapted from literature methods.[21,22]

Miniemulsion Polymerization. The organic phase was prepared by adding $CuBr_2$ (0.153 g, 6.85×10^{-4} mol), EHA_6TREN (0.901 g, 7.20×10^{-4} mol), hexadecane (1.48 g, 3.8 wt % vs monomer), and BMA (39 g, 0.274 mol, 15 wt % vs deionized water) to a beaker and stirring overnight at room temperature to form a homogeneous solution. The aqueous phase that consisted of the surfactant Brij 98 (3.9 g, 10 wt % vs monomer) and deionized water (221 g) was stirred overnight at room temperature. The organic phase was added to the surfactant solution and stirred for ~30 min prior to passing through a Microfluidizer 110S (Microfluidics International Corp.) operating at an inlet pressure of 275 kPa. The miniemulsion (200 g) was transferred to a 500 mL round-bottom flask fitted with a condenser and was purged with ultrahigh-purity nitrogen for 30 min before being immersed in a 60 °C oil bath with the magnetic stirring speed set to 250 rpm. Fifteen minutes elapsed before the addition of the initiator. The AA (0.0227 g, 1.29×10^{-4} mol) and HPO (0.029 16 g, 2.57×10^{-4} mol) were added to separate Schlenk tubes, mixed with 2 mL of deionized water, and purged with ultrahigh-purity nitrogen for 20 min prior to injection. Using a deoxygenated syringe, the HPO was added prior to the AA, which was added dropwise over 5 min. Samples were withdrawn with a deoxygenated syringe and placed in an ice bath.

Characterization. After the polymerizations were complete the latexes were filtered (Fisherbrand P8 creped) to collect any coagulum. The amount of coagulum, if present, was determined gravimetrically. Monomer conversions were determined gravimetrically. Size exclusion chromatography (SEC) was used to measure the molecular weight distribution of the polymer samples. The dried polymer samples from the miniemulsion were dissolved in tetrahydrofuran (THF) and passed through a column packed with basic alumina to remove the residual copper. The SEC was equipped with a Waters 2960 separation module containing four Styragel columns (100, 500, 10^3, 10^4 Å) maintained at 40 °C, coupled with a Waters 410 differential refractive index (RI) detector (930 nm) and a Wyatt Technology DAWN EOS photometer multiangle light scattering (LS) detector (690 nm, 30 mW Ga−As laser). THF was used as the eluant, and the flow rate was set to 1 mL min^{-1}. The LS detector was calibrated with toluene, normalized with 30 000 g/mol narrow polystyrene standard, and the data were processed using Astra (version 4.90.08) software. A Wyatt Optilab DSP 690 nm refractometer was used determine the d*n*/d*c* values of poly(butyl methacrylate) (PBMA) and PMMA. Before running the samples, the instrument was first calibrated with sodium chloride. Six samples of 1−10 mg mL^{-1} were prepared in THF for each polymer and injected sequentially to construct a curve with slope d*n*/d*c*. The d*n*/d*c* values for PBMA and PMMA were 0.075 and 0.081, respectively. The particle sizes of the latexes reported in this paper were measured using a Matec Applied Sciences Capillary Hydrodynamic Fractionation (CHDF) 2000 unit. The UV detector was set to 220 nm. The eluant was a 20:1 mixture of deionized water and GR500-1X (Matec Applied Sciences). Samples were diluted with the eluant to ~3.5 wt % solids and sonicated for 5 min. Samples were passed through a 0.5 μm pore size filter prior to injection. The marker was a 2 wt % solution of sodium benzoate. To ensure that there were no particles greater than 0.5 μm, the particle size distributions were also measured using a Malvern Mastersizer 2000 equipped with a Hydro 2000S optical unit. The refractive index value for water, PBMA, and PMMA were 1.33, 1.48, and 1.49, respectively.

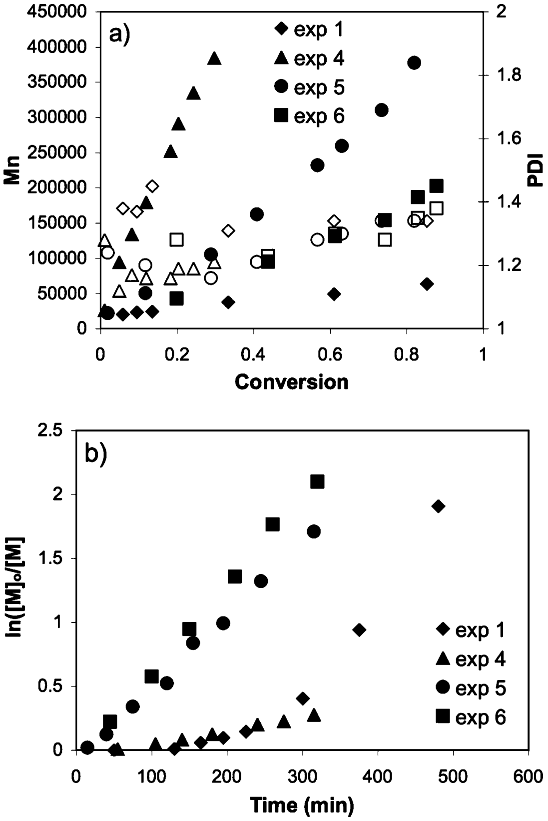

Figure 1. Evolution of number-average molecular weight (M_n, filled symbols) and polydispersity index (PDI, open symbols) with conversion (a) and the kinetic plots (b) for the reverse atom transfer radical polymerization of butyl methacrylate (BMA) at 60 °C in miniemulsion. [Brij 98]:[hexadecane] = 10:3.8 wt % based on monomer; 15% solid content; $[BMA]_0$:[copper(II) bromide tris[2-di(2-ethylhexyl acrylate)-aminoethyl]amine $(CuBr_2\text{-}EHA_6TREN)]_0$ = 400:1; experiment 1: $[CuBr_2\text{-}EHA_6TREN]_0$:[2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride$]_0$ = 1:1; experiment 4: $[CuBr_2\text{-}EHA_6TREN]_0$:[hydrogen peroxide (HPO)$]_0$:[ascorbic acid (AA)$]_0$ = 1:0.25:0.25; experiment 5: $[CuBr_2\text{-}EHA_6TREN]_0:[HPO]_0:[AA]_0$ = 1:0.5:0.25; experiment 6: $[CuBr_2\text{-}EHA_6TREN]_0:[HPO]_0:[AA]_0$ = 1:1:0.25.

Results and Discussion

Reverse ATRP Initiated with the Water-Soluble Azo-Initiator VA-044. The polymerization of BMA was carried out in a miniemulsion system using the reverse ATRP process with VA-044 as the radical initiator and $CuBr_2\text{-}EHA_6TREN$ as the mediating complex. The ratio of $[BMA]_0:[CuBr_2\text{-}EHA_6TREN]_0:[VA\text{-}044]_0$ = 400:1:1 (experiment 1) afforded a well-controlled polymerization (Figure 1a) after an inhibition period of ~130 min (Figure 1b). After 480 min the conversion was 85%, and the polymer had a M_n of 67 900 with a PDI of 1.34. The weight-average particle diameter was 82 nm with a standard deviation of 34 nm. The evolution of the molecular weight and the rate of the polymerization is consistent with earlier reports of copper-mediated ATRP in aqueous dispersed systems using nonionic surfactants.[8−10,23−27]

Redox Initiation System for Reverse ATRP. The use of the HPO/AA redox pair to initiate ATRP, which controls the polymerization through a reversible redox process, creates a potentially complex system. The AA is oxidized by HPO forming hydroxyl radical and ascorbate radical intermediates that initiate the polymerization. Dehydroascorbic acid, a product of the reaction between AA and HPO, can be hydrolyzed to products that are reducing agents,[28] and reactions of these

Table 1. Summary of Experiments for the Reverse Atom Transfer Radical Polymerization of Butyl Methacrylate (BMA) and Methyl Methacrylate (MMA) in Miniemulsion[a] at 60 °C Initiated with the Redox Pair Hydrogen Peroxide (HPO)/Ascorbic Acid (AA)

expt	monomer	$[\text{monomer}]_0$:$[\text{CuBr}_2]_0$:$[\text{HPO}]_0$:$[\text{AA}]_0$	conv[b] (%)	M_n[c] (g mol^{-1})	PDI[d]	D_w[e] (nm)	SD[f]
5	BMA	400:1:0.5:0.25	82	377 500	1.34	103	24
7	BMA	800:1:0.5:0.25	83	604 600	1.29	99	27
8	BMA	1200:1:0.5:0.25	83	989 900	1.24	113	19
9	BMA	800:1:0.4:0.20	80	850 800	1.23	102	20
10	BMA	800:1:0.6:0.30	78	447 600	1.23	107	26
11	MMA	800:1:0.5:0.25	69	333 400	1.22	89	16
12	MMA	1136:1:0.5:0.25	70	502 200	1.27	99	24
13	MMA	1685:1:0.5:0.25	59	629 200	1.17	97	21

[a] [Brij 98]:[hexadecane] = 10:3.8 wt % based on monomer; 15% solid content. [b] conv = conversion, determined gravimetrically. [c] M_n = number-average molecular weight, determined from size exclusion chromatography. [d] PDI = polydispersity index, determined from size exclusion chromatography. [e] D_w = weight-average particle diameter, determined with capillary hydrodynamic fractionation (CHDF 2000). [f] SD = standard deviation of the weight-average particle diameter, determined with capillary hydrodynamic fractionation (CHDF 2000).

secondary products could influence the reverse ATRP process. In addition to the generation of primary radicals from the reaction between AA and HPO, both AA and HPO can react with other species in the system. Jakubowski and Matyjaszewski developed a process called activator generated by electron transfer (AGET) ATRP using a reducing agent, tin(II) 2-ethylhexanoate, in combination with a copper(II) complex (in the presence of an alkyl halide initiator) to produce well-defined polymers.[29] The system has also been successfully applied to miniemulsion[30] and microemulsion[31] processes using AA as the reducing agent. In another process, referred to as activators regenerated by electron transfer (ARGETATRP),[32] the presence of a reducing agent regenerates the copper(I) complex from the copper(II) complex, allowing for a significant reduction in the amount of copper in the system. As well, the decomposition of peroxides by copper(I) complexes occurs,[33] and this reaction has been used to initiate ATRP.[34,35]

When BMA was polymerized with 1.0 equiv of the CuBr_2-EHA_6TREN complex relative to the HPO/AA redox initiating system, $[\text{BMA}]_0$:$[\text{CuBr}_2\text{-EHA}_6\text{TREN}]_0$:$[\text{HPO}]_0$:$[\text{AA}]_0$ = 400:1:1:1 (experiment 3), there was inefficient deactivation of the radicals generated in the system, evident from the uncontrolled polymerization that reached complete conversion in less than 30 min with the polymer obtaining a M_n of 424 000 with a PDI of 2.3. A reduction in the amount of initiator (HPO/AA) relative to the copper(II) complex, $[\text{BMA}]_0$:$[\text{CuBr}_2\text{-EHA}_6\text{TREN}]_0$:$[\text{HPO}]_0$:$[\text{AA}]_0$ = 400:1:0.25:0.25 (experiment 4, Figure 1), resulted in a controlled polymerization that unexpectedly produced high molecular weight polymer (M_n = 384 600, PDI = 1.21). The rate of the polymerization was slow, attaining only 30% conversion after 360 min. As shown in Figure 1, the effect of the $[\text{HPO}]_0$:$[\text{AA}]_0$ ratio was investigated by maintaining $[\text{BMA}]_0$:$[\text{CuBr}_2\text{-EHA}_6\text{TREN}]_0$:$[\text{AA}]_0$ at 400:1:0.25 and varying $[\text{HPO}]_0$. All the polymerizations were controlled, and a trend of decreasing molecular weight was seen when the ratio of $[\text{HPO}]_0$:$[\text{AA}]_0$ was increased from 1:1 (experiment 4) to 2:1 (experiment 5) to 4:1 (experiment 6), indicating that more polymer chains were created. The M_n increased linearly with conversion and the PDI remained low. The molecular weight vs conversion data do not pass through the origin, and the rapid increase of molecular weight at the beginning of the polymerization is a trend that is common in reverse ATRP systems.[7,10,11,16] This indicates that chains are either initiated slowly (unlikely with redox initiation) or more probably in a miniemulsion system; chains initiated in the aqueous phase do not all immediately enter droplets/particles, thereby resulting in a lower number of chains at low conversions.

From the kinetic plots of $\ln([M]_0/[M])$ vs time shown in Figure 1b it can be seen that employing the redox initiating system significantly reduced the inhibition period when compared to the VA-044 initiated system. The inhibition time of less than 20 min is attributed to the initiation of the majority of the polymer chains early in the polymerization, which consumes the copper(II) complex to levels where polymerization can proceed at an appreciable rate. An increase in the $[\text{HPO}]_0$:$[\text{AA}]_0$ ratio from 1:1 (experiment 4) to 2:1 (experiment 5) to 4:1 (experiment 6) increased the rate of the polymerization. An increase in the rate of the polymerization is expected when the number of propagating chains is increased and the copper(II) complex loading is held constant. This is attributed not only to the increase in the number of polymer chains but also to the subsequent increase in the ratio of copper(I) complex to copper(II) complex during the polymerization. A $[\text{HPO}]_0$:$[\text{AA}]_0$ ratio of 2:1 (experiment 5) resulted in the polymerization obtaining 82% conversion in 315 min compared to 30% conversion in 360 min when the $[\text{HPO}]_0$:$[\text{AA}]_0$ ratio was 1:1 (experiment 4). However, increasing the $[\text{HPO}]_0$:$[\text{AA}]_0$ ratio to 4:1 (experiment 6), which resulted in approximately double the number of polymer chains relative to experiment 5, had only a minimal effect on the rate of the polymerization.

High Molecular Weight PBMA. The ratio of $[\text{BMA}]_0$:$[\text{CuBr}_2\text{-EHA}_6\text{TREN}]_0$:$[\text{HPO}]_0$:$[\text{AA}]_0$ = 400:1:0.5:0.25 produced well-controlled polymers at high rates of polymerization; subsequently, this ratio was studied in further detail. As seen in Table 1, varying the amount of copper/initiator relative to BMA targeted high molecular weight polymer. Figure 2a illustrates that the M_n increased with conversion while the PDI remained relatively low. The evolution of the molecular weight distributions with conversion in Figure 3 (experiment 8) further demonstrates that the polymerization was controlled. The entire molecular weight distribution shifted to higher molecular weight during the polymerization, and the distributions remain narrow. At low conversion the molecular weight distribution is broad, and there is a slight shoulder in the SEC trace at a conversion of 23%, attributed to variation in number of activation/deactivation cycles that polymer chains undergo at low conversions. There is no low molecular weight tail indicating that all the polymer chains are created during the early stages of the polymerization and that termination and transfer reactions involving the polymer chains are minimal. Xue et al.[5] reported a low molecular weight tail in the SEC distribution when the molecular weight of the PMMA reached 367 000, attributed to slow propagation of a fraction of the chains.

As expected, a decrease in the amount of copper/initiator relative to the initial amount of monomer resulted in an increase in the molecular weight of the polymer. The $[\text{BMA}]_0$:$[\text{CuBr}_2\text{-EHA}_6\text{TREN}]_0$ ratios of 400, 800, and 1200 produced polymers with M_n of 377 500, 604 600, and 989 900 and PDI of 1.34, 1.29, and 1.24, respectively. The trend of decreasing PDI with a higher targeted molecular weight could be attributed to the

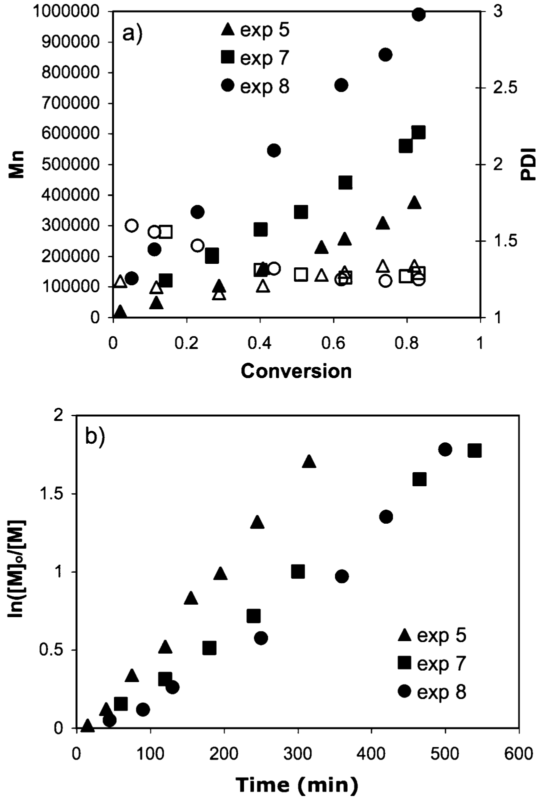

Figure 2. Effect of varying the ratio of butyl methacrylate (BMA) to copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine ($CuBr_2$-EHA_6TREN). Evolution of number-average molecular weight (M_n, filled symbols) and polydispersity index (PDI, open symbols) with conversion (a) and the kinetic plots (b) for the reverse atom transfer radical polymerization of BMA at 60 °C in miniemulsion. [Brij 98]:[hexadecane] = 10:3.8 wt % based on monomer; 15% solid content; [hydrogen peroxide]:[ascorbic acid] = 0.5:0.25; experiment 5: $[BMA]_0$:$[CuBr_2$-$EHA_6TREN]_0$ = 400:1; experiment 7: $[BMA]_0$: $[CuBr_2$-$EHA_6TREN]_0$ = 800:1; experiment 8: $[BMA]_0$: $[CuBr_2$-$EHA_6TREN]_0$ = 1200:1.

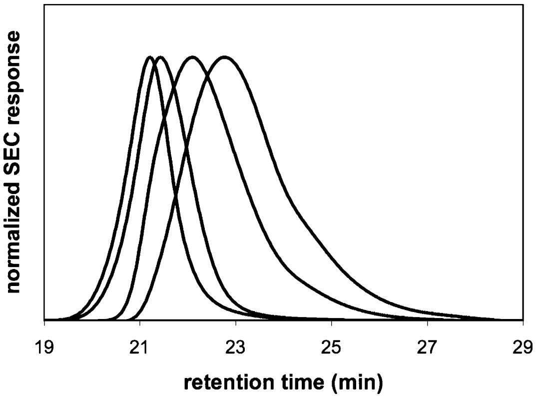

Figure 3. Size exclusion chromatography (SEC) traces for the reverse atom transfer radical polymerization of butyl methacrylate (BMA) at 60 °C in miniemulsion. [Brij 98]:[hexadecane] = 10:3.8 wt % based on monomer; 15% solid content; $[BMA]_0$:[copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine$]_0$:[hydrogen peroxide$]_0$:[ascorbic acid$]_0$ = 400:1:0.5:0.25 (experiment 8). Conversion increases from right to left; conversion = 11%, number-average molecular weight (M_n) = 222 500, polydispersity index (PDI) = 1.56; conversion = 23%, M_n = 345 000, PDI = 1.47; conversion = 74%, M_n = 859 000, PDI = 1.24; conversion = 83%, M_n = 989 900, PDI = 1.24.

decreased concentration of radicals that would result in less termination or from the expected decrease in PDI with increasing molecular weight in ATRP systems. After an induction period of less than 20 min, the kinetic plots of $\ln([M]_0/[M])$ vs time in Figure 2b were relatively linear up to 70% conversion, which demonstrates the first-order dependence of monomer consumption with respect to time. The induction period suggests that the initial concentration of $CuBr_2$-EHA_6TREN was sufficient to capture all the radical generated by the redox initiation system.

From the basic ATRP mechanism, Matyjaszewski et al. developed a rate law that is first order with respect to time,[36] which can be used when there is an excess of copper(II) complex and if it assumed that the concentrations of the other species remain constant (eqs 1 and 2).[37,38] This simple mechanistic model allows an apparent rate constant (k^{app}) of the polymerization to be estimated and the relative rate of the polymerizations to be compared; however, no specific mechanistic information is drawn from the data. The model neglects the persistent radical effect on the kinetics for ATRP, which was first developed by Fischer[39] and has since been refined by Tang et al.[38] As well, the reduction of the termination rate during the polymerization due to the gel effect is neglected.[40]

$$R_p = k_p[M][P^*] = k_p[M]K_{eq}[\text{chain}]\frac{[Cu(I)]}{[Cu(II)]} = k^{app}[M] \tag{1}$$

$$\ln\left(\frac{[M]_0}{[M]}\right) = k^{app}t \tag{2}$$

$$\frac{k^{app}}{[\text{chain}]} = k_pK_{eq}\frac{[Cu(I)]}{[Cu(II)]} \tag{3}$$

The k^{app} was determined from the slope of the kinetic plot between approximately 10−70% conversion. As seen in Table 2, the k^{app} of the polymerization was found to decrease as higher molecular weight polymer was targeted. The $[BMA]_0$:$[CuBr_2$-$EHA_6TREN]_0$ ratios of 400, 800, and 1200 resulted in a k^{app} of 9.3×10^{-5}, 7.5×10^{-5}, and 4.9×10^{-5} s^{-1}, respectively. The decrease in k^{app} results from the decrease in the number of polymer chains in the system (Table 2) which influences the rate of the polymerization (eq 1). The fast rate of polymerization for the redox initiated systems is highlighted by a comparison of the k^{app} per polymer chain (eq 3, Table 2). Typically, the redox initiated systems have an apparent rate constant per polymer chain which is greater than 5 times that of the VA-044 systems. Since the k_p and K_{eq} values should not be influenced by the initiation system, the conclusion is that the HPO/AA system yields an advantageous ratio of [Cu(I)]/[Cu(II)] that allows the polymerization to proceed at higher rates and to much higher molecular weights, while preserving control, than has previously been observed. While the exact nature of this behavior is currently not understood, it is possible that the concentration of the deactivating species ($CuBr_2$-EHA_6TREN) is regulated by the presence of the AA. This kinetic analysis also allowed for a comparison between the redox initiated systems, for which the apparent rate constant per polymer chain increased as the number of chains in the system decreased.

The desired molecular weight of the polymer can be targeted by selecting the $[BMA]_0$:$[CuBr_2$-$EHA_6TREN]_0$ ratio. The theoretical M_n weight cannot be readily determined since the number of species that produce a polymer chain are not accurately known; however, an initiator efficiency ([polymer chains]/$[\text{initiator}]_0$) can be calculated. The initiator efficiency for the VA-044 systems is 0.36 and 0.38 for experiment 1 and 2, respectively. These values are typical of the VA-044 initiated reverse ATRP and consistent with the initiation efficiency of nonionic azo-initiators,[41] although we note that VA-044 is cationic. For redox initiated systems it can be seen from Table 2 that for every mole of HPO (when $[HPO]_0$:$[AA]_0$ = 2:1) ~0.3

Table 2. Summary of the Kinetic Parameters for the Reverse Atom Transfer Radical Polymerization of Butyl Methacrylate (BMA) and Methyl Methacrylate (MMA) in Miniemulsion[a] at 60 °C Initiated with the Redox Pair Hydrogen Peroxide (HPO)/Ascorbic Acid (AA)

expt	monomer	VA-044[b] (mol × 10^{-4})	HPO (mol × 10^{-4})	$CuBr_2$ (mol × 10^{-4})	k^{app} [c] (s^{-1} × 10^{-5})	chain[d] (mol × 10^{-5})	chain/HPO	$CuBr_2$/chain	k^{app}/chain
1	BMA	5.15		5.15	11.7	37.5		1.4	0.31
2	BMA	2.58		5.15	2.8	19.4		2.7	0.14
5	BMA		2.57	5.15	9.3	6.5	0.25	7.9	1.43
7	BMA		1.29	2.58	7.5	4.1	0.32	6.3	1.83
8	BMA		0.86	1.72	4.9	2.5	0.29	6.9	1.96
9	BMA		1.03	2.58	7.8	2.8	0.27	9.2	2.76
10	BMA		1.54	2.58	8.0	5.2	0.34	5.0	1.54
11	MMA		1.83	3.66	5.9	6.0	0.32	6.3	0.98
12	MMA		1.29	2.58	6.3	4.1	0.31	5.3	1.54
13	MMA		0.87	1.74	3.4	2.7	0.31	6.3	1.25

[a] [Brij 98]:[hexadecane] = 10:3.8 wt % based on monomer; 15% solid content. [b] VA-044 = 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride. [c] k^{app} = apparent rate constant. [d] Moles of polymer chains = moles(monomer) × molar mass(monomer) × conversion/number-average molecular weight.

mol of polymer chains is produced. To produce a well-controlled polymerization, a greater than 5-fold excess of initial $CuBr_2$-EHA_6TREN relative to the moles of polymer chains produced is required. Compared to the VA-044 initiated systems in which the initial moles of $CuBr_2$-EHA_6TREN relative to the moles of polymer chains are 1.4 (experiment 1) and 2.7 (experiment 2), it would be expected that such a large excess of $CuBr_2$-EHA_6-TREN would result in no polymer formation, or very slow rates of polymerization. Attempts at targeting high molecular weight polymers with VA-044 as the initiator have so far been unsuccessful. Targeting high molecular weight polymer ($[BMA]_0$:$[CuBr_2\text{-}EHA_6TREN]_0$:$[VA\text{-}044]_0$ = 1000:1:1) led to poor control of the polymerization. The amount of the copper(II) complex was increased in an attempt to improve control over the polymerization ($[BMA]_0$:$[CuBr_2\text{-}EHA_6TREN]_0$:$[VA\text{-}044]_0$ = 1000:3:1); however, after 24 h no polymer had formed. It appears that the use of the HPO/AA redox pair is required to create well-controlled, high molecular weight polymer at relatively high rates of polymerization; however, the reason for this interesting behavior is unknown and currently under investigation.

Typically, the final latexes were monomodal and ranged in particle size from 90 to 110 nm, with less than 2 wt % coagulum at the end of the polymerization. The particle sizes were confirmed with a Malvern Mastersizer 2000, which also verified the absence of large particles in the system. All the experiments exhibited some initial phase separation. A clear, colorless monomer layer was present from the beginning of the experiment until the system reached ~75% conversion. Instability of the miniemulsion early in living radical polymerizations has been reported,[16,42] but its presence does not lead to coagulum formation in these systems.

Effect of the Initiator Concentration. The relationship between the initial concentration of $CuBr_2$-EHA_6TREN and the initiator (HPO/AA) was studied. If the amount of copper remains constant, an increase in the concentration of initiator should produce more chains that would result in a lower M_n. Table 2 summarizes the experimental results of varying the initiator concentration (maintaining $[HPO]_0$:$[AA]_0$ = 2:1) on the system. The plots of M_n and PDI are displayed in Figure 4a. All the polymerizations were well-controlled, with the M_n increasing linearly with conversion and the PDI remaining low. As well, there was no low molecular weight tail in the molecular weight distribution. From Figure 4a it can be seen that the molecular weight of the polymer was dependent on the amount of initiator, with a higher initiator concentration resulting in lower molecular weight polymer due to the increased number of polymer chains (Table 2). The molecular weight of the polymer responded to changes in the amount of the redox initiator as would be expected for a typical reverse ATRP process.

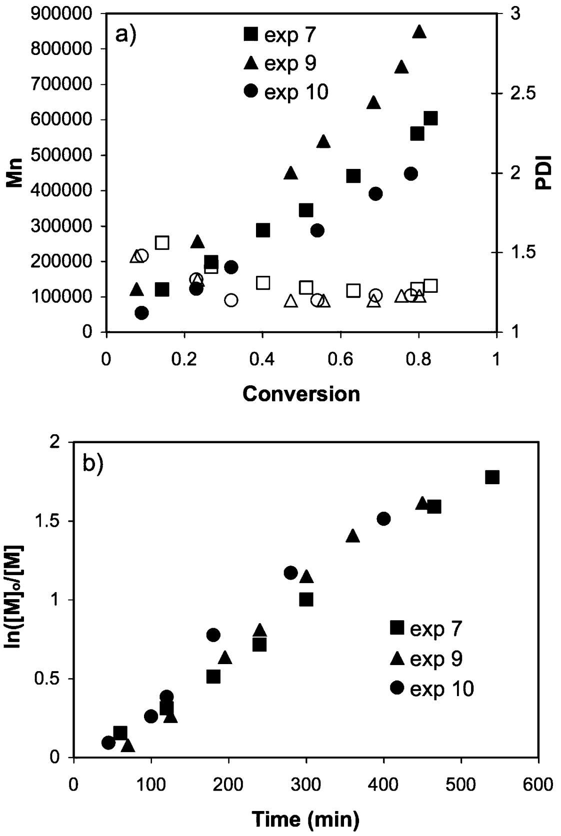

Figure 4. Effect of the amount of the redox initiator hydrogen peroxide (HPO)/ascorbic acid (AA) on the evolution of number-average molecular weight (M_n, filled symbols) and polydispersity index (PDI, open symbols) with conversion (a) and the kinetic plots (b) for the reverse atom transfer radical polymerization of butyl methacrylate (BMA) at 60 °C in miniemulsion. [Brij 98]:[hexadecane] = 10:3.8 wt % based on monomer; 15% solid content; $[BMA]_0$:[copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine $(CuBr_2\text{-}EHA_6TREN)]_0$ = 800:1; experiment 7: $[CuBr_2\text{-}EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0$ = 1:0.5:0.25; experiment 9: $[CuBr_2\text{-}EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0$ = 1:0.4:0.2; experiment 10: $[CuBr_2\text{-}EHA_6TREN]_0$:$[HPO]_0$:$[AA]_0$ = 1:0.6:0.3.

The kinetic plots for the different initiator concentrations are shown in Figure 4b. The plots are first order with respect to monomer consumption up to ~70% conversion, except for the high initiator experiment (experiment 10) which shows curvature for the entire duration of the polymerization. The k^{app} for the high (experiment 10), medium (experiment 7), and low (experiment 9) initiator concentrations were 8.0 × 10^{-5}, 7.5 × 10^{-5}, and 7.8 × 10^{-5} s^{-1}, respectively. The expected trend of increased polymerization rate with increased initiator concentration, due to the increase in the number of polymer chains in combination with the increase in the ratio of copper(I) complex

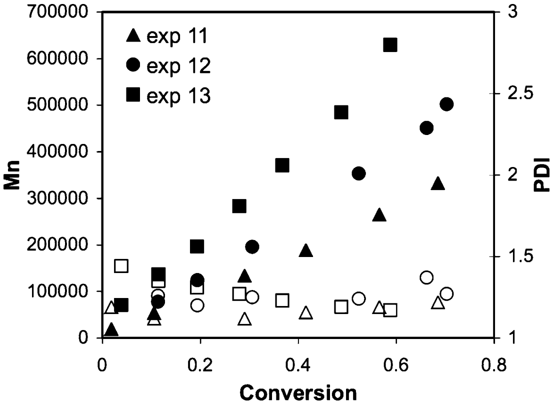

Figure 5. Effect of varying the ratio methyl methacrylate (MMA) to copper(II) bromide tris[2-di(2-ethylhexyl acrylate)aminoethyl]amine ($CuBr_2$-EHA_6TREN). Evolution of number-average molecular weight (M_n, filled symbols) and polydispersity index (PDI, open symbols) with conversion for the reverse atom transfer radical polymerization of MMA at 60 °C in miniemulsion. [Brij 98]:[hexadecane] = 10:3.8 wt % based on monomer; 15% solid content; [hydrogen peroxide]:[ascorbic acid] = 0.5:0.25; experiment 11: $[MMA]_0$:$[CuBr_2\text{-}EHA_6TREN]_0$ = 800:1; experiment 12: $[MMA]_0$: $[CuBr_2\text{-}EHA_6TREN]_0$ = 1136:1; experiment 13: $[MMA]_0$: $[CuBr_2\text{-}EHA_6TREN]_0$ = 1685:1.

to copper(II) complex (eq 1), was not observed. Contrary to this expected trend, when based on the k^{app} per polymer chain (eq 3, Table 2), the rate increased as the amount of the initiator decreased. The reason for this is unknown, but the results are consistent with the observations from the high molecular weight set of experiments (experiments 5, 7, and 9).

Reverse ATRP of MMA Initiated with HPO/AA. A similar study was carried out with MMA, with the total solids content maintained at 15 wt %. Figure 5 is a plot of the M_n and PDI vs conversion. The molecular weight increased linearly with conversion, while the PDI remained relatively low, with no low molecular weight tail in the SEC trace. The M_n ranged from 333 400 to 629 200, depending on the conditions of the polymerization (Table 1). From Table 2, the numbers of polymer chains for the MMA polymerizations were similar to their BMA counterpart (experiments 7 and 12, experiment 8 and 13); as well, the initiator efficiency was ~0.3 mol of growing polymer chains per mole of HPO. The use of MMA resulted in some coagulum formation during the polymerization, ranging from 5 to 9 wt % based on total solids. The final particle diameter distribution was monomodal, and the resulting latex showed no further instability after 3 weeks on the shelf. Compared to BMA, the polymerizations had lower final conversions (typically 70%), attributed in part to the coagulum formation that would cause the measured conversion to be lower than the actual conversion.

Conclusions

The miniemulsion reverse ATRP using $CuBr_2$-EHA_6TREN as the mediating complex and HPO/AA as the initiator has been carried out for BMA and MMA. The use of the HPO/AA redox pair as the initiator enables the production of well-controlled polymers with M_n ranging from 300 000 to 1 000 000. A polymer with M_n of 989 900 and a PDI of 1.25 can be produced in ~8 h of reaction time at 60 °C. The origin of the high molecular weight polymers is currently unknown; however, the polymerizations behave like a typical reverse ATRP system. Kinetic analyses suggest the HPO/AA system provides an advantageous ratio of [Cu(I)]/[Cu(II)] compared to conventional initiators. The molecular weight of the polymer can be controlled by varying the initial amount of initiator (HPO/AA); as well, the desired molecular weight can be predetermined by selecting the initial ratio of monomer to $[CuBr_2\text{-}EHA_6TREN]_0/[HPO]_0/[AA]_0$.

The kinetics of HPO/AA initiated reverse ATRP appear to be complex. The overall rates of the polymerizations initiated with HPO/AA were similar to the VA-044 initiated polymerizations. However, when the k^{app} was based on the number of polymer chains in the system, there was a greater 5-fold increase in the rate of the HPO/AA initiated polymerization compared to the VA-044 initiated polymerization. As well, there appears to be a trend of increasing k^{app} when the number of chains in the system decreased. This includes the set of experiments where the amount of HPO/AA was increased while the amount of $CuBr_2$-EHA_6TREN remained constant, for which the opposite trend was expected.

The latexes had weight-average particle diameters typically less than 110 nm. All of the final particle diameter distributions were monomodal, and the resulting latex showed no further instability after 3 weeks on the shelf. The formation of coagulum was minimal during the polymerization of BMA (less than 2 wt % based on total solids), while the polymerization of MMA resulted in coagulum formation that ranged between 5 and 9 wt % based on total solids.

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