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# Atom Transfer Radical Polymerization of Methyl Methacrylate in Water-Borne System

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ABSTRACT: The controlled/living polymerization of methyl methacrylate was carried out by atom transfer radical polymerization (ATRP) in a water-borne system. Both the direct and reverse processes were performed in the presence of a copper halide/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) complex and a nonionic surfactant. In direct ATRP, ethyl 2-bromoisobutyrate (EB*i*B) was used as the oil-soluble initiator. Several surfactants with a large range of hydrophile−lypophile balance (HLB) values were tested. The critical micellar concentration (cmc) and the pH of the medium were also measured to determine their effects on the emulsion stability. The direct ATRP most likely proceeds via the suspension mechanism. In reverse ATRP, 2,2′-azobis[2-(2-dimidazolin-2-yl)propane] dihydrochloride (VA-044) was used as the water-soluble initiator, and the results suggest an emulsion polymerization mechanism. In both approaches, the kinetics were followed along with the particle size (measured by laser diffraction and SEM), and the influence of the halogen atom associated with the catalyst (i.e., CuBr or CuCl) was examined. It was demonstrated that utilizing the halide exchange could improve the control over both the molecular weight and end functionality of the polymers.

## Introduction

Controlled living radical polymerization (CRP) has been the focus of numerous studies during the past years, with the goal of obtaining well-defined polymer compositions (homo, random, gradient, block, graft), topologies (linear, star, comb, hyperbranched), or functionalities (end groups, side groups).[1] Most of these reactions were performed in bulk or solution, while those in the more challenging heterogeneous systems[2] were less studied. Recently, several reports concerning emulsion or other aqueous dispersed CRPs by various methods, for example atom transfer radical polymerization (ATRP),[3−8] stable free radical polymerization (SFRP),[9] degenerative transfer polymerization,[10] and reversible addition−fragmentation chain transfer polymerization (RAFT),[11] have been published. In these novel heterogeneous systems, the colloidal stability is of great importance in addition to the control over the polymerization. A deeper understanding of both parameters requires much more research in this area.

In this study, the ATRP of methyl methacrylate (MMA) in water-borne media was explored. The reactions were conducted using either $Cu^{I}$ complexes with alkyl halide initiators or $Cu^{II}$ complexes with azo initiators (i.e., direct and reverse ATRP,[12] respectively). The influence of several factors, such as the surfactant partitioning, the critical micellar concentration, and the particle size, on the stability of the emulsion and the control of the polymerization was investigated.

## Experimental Section

MMA was dried over $CaH_2$ and distilled under vacuum. Deionized water was used without further purification. CuBr and CuCl were purified as previously described.[13] All surfactants were from commercial sources and used as received.

**Direct ATRP in Water.** A 10 mL round-bottom flask equipped with a magnetic stirrer was charged with CuX and 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy). The flask was deoxygenated by several vacuum/nitrogen cycles before adding 1.5 mL of degassed monomer via syringe. The surfactant was added to a 25 mL Schlenk flask and evacuated and back-filled with nitrogen before adding degassed water. At 60 °C and under stirring, the monomer solution was cannula transferred to the surfactant solution. The mixture was stirred (20−30 min) to obtain a stable emulsion before the initiator addition via a microsyringe. Samples were taken periodically for kinetic analysis. The monomer conversion was measured by gas chromatography (Shimadzu GC-14A) and gravimetric methods. In the latter method, the samples were dried in an oven at 70 °C. The monomer conversion was calculated from the percentage of the solid content recovered, with the weights of the surfactant and the catalyst subtracted. The molecular weight was determined by size exclusion chromatography in THF, using a Waters 717plus autosampler and the following Phenogel columns: Polymer Standard Service $10^5$, $10^3$, and 100 Å and guard. Samples were diluted with THF and dried over magnesium sulfate, and the copper complex was removed by passing the solution through an alumina column before filtering it through a 0.2 $\mu$m PTFE filter. The calibration curve was based on linear poly(methyl methacrylate) standards.

**Reverse ATRP in Water.** The surfactant was added to a 25 mL Schlenk flask, and the flask was degassed. 9 mL of water (previously deoxygenated) was added under nitrogen, and the solution was stirred at the polymerization temperature. The $CuX_2$ and the ligand were added to a 10 mL round-bottom flask, which was then subjected to several vacuum/nitrogen cycles. 1.5 mL of previously degassed monomer was then added, and the mixture was heated to form a homogeneous solution. At the same time, the initiator was dissolved in 1.5 mL of degassed water and stirred at room temperature in a 10 mL round-bottom flask. The monomer solution was then added to the surfactant solution via cannula transfer. After a stable emulsion formed, 1 mL of the initiator solution was finally added to the Schlenk flask, and the flask was immersed into an oil bath at 80 °C. Samples were taken

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periodically via syringe to monitor the conversion (GC, gravimetry), molecular weight (SEC), and particle size (laser diffraction).

**Particle Size Measurement.** The latexes were poststabilized with sodium dodecyl sulfate (SDS), and the particle size was measured either by scanning electron microscopy (SEM) using imaging software (visilog, NOESIS S.A.) analysis or by dynamic light scattering (ZetaPlus from Brookhaven). The latex samples were diluted with aqueous 10 mM KCl solution for light scattering and with water for SEM measurement. SEM measurement was performed by casting the samples onto glass slides, which were then cut and mounted on aluminum SEM sample stubs with conductive carbon tape. The samples were coated with approximately 50 nm of gold/palladium (60 s sputter) before imaging to reduce surface charging and specimen damage from electron irradiation in the FE-SEM. SEM images were obtained with an accelerating voltage of 2 keV at 20K× magnification.

**Partitioning of Surfactant.** The partitioning of surfactants between MMA and water was measured by gravimetric method. 20 mL of the surfactant solution (5 wt % vs MMA) in deionized water was mixed with 3 mL of MMA. The mixture was stirred at room temperature or 60 °C for 30 min. Then the stirring was stopped and the emulsion kept at the same temperature until phase separation occurred. A sample was taken from the aqueous phase and dried in oven at 70 °C. From the solid content recovered, the amount of the surfactant in the entire water phase was extrapolated. The partitioning of HV25 was also performed in the presence of either $CuBr_2$ or dNbpy. In the former case ($CuBr_2$ without dNbpy), it was assumed that all $CuBr_2$ was in the aqueous phase due to its high solubility in water.[14] In the latter case (dNbpy without $CuBr_2$), it was assumed that all dNbpy was in the organic phase due to its high oil solubility.[7]

## Results and Discussion

### I. Polymerization of MMA by Direct ATRP in Water-Borne System.

Prior to this study, the copper-mediated ATRP of *n*-butyl methacrylate (BMA) in a water-borne system was investigated under various conditions.[4−7] The results pointed out that, in order to achieve a successful polymerization in terms of both the colloidal stability and the control of molecular weights and polydispersities, a nonionic surfactant and a copper halide complex with a hydrophobic ligand should be employed. Therefore, the MMA polymerization was conducted under similar conditions. Ethyl 2-bromoisobutyrate (EB*i*B) and 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) were used as the oil-soluble initiator and hydrophobic ligand, respectively. The typical molar ratios of the components are the following: MMA/EB*i*B/CuBr/dNbpy = 300/1/1/2. All polymerizations were carried out at 60 °C with a monomer-to-water ratio of 15% (v/v) vs water. The surfactant concentration vs the monomer (wt %) was varied.

**Effect of Surfactant Structure.** There are two main criteria for a good surfactant in an ATRP system. A good surfactant should not affect the ATRP activation and deactivation processes and must provide a stable emulsion with a minimum amount of coagulation throughout the polymerization. Nonionic surfactants usually satisfy the first criterion, and our attention mostly focused on the colloidal stability provided by several emulsifiers. The surfactants were selected on the basis of their hydrophile−lypophile balance (HLB) values, which can be varied by the relative lengths of the hydrophilic and hydrophobic moieties of the surfactant. In this study, three types of surfactants with HLB ranging from 12 to 18 were tested: (1) polyoxyethylene oleyl such as Brij series from ICI; (2) alkylphenolethoxylates including Igepal (Rhodia), NP (Sipol), Makon (Stepan), HV (Rewopal), and Triton (Union Carbide); (3) polyoxyethylene sorbitan monolaurate such as Tween (ICI) (Table 1). The surfactant concentration was typically around 10 wt % or higher with respect to MMA. The polymerizations were conducted up to high conversions, and the results are summarized in Tables 2−4.

**Table 1. Chemical Structures of the Surfactants**

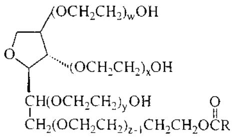
| Surfactant types | Chemical structures | Names |
|---|---|---|
| Polyoxyethylene oleyl | $C_{18}H_{35}(OCH_2CH_2)_nOH$ | Brij 97: n=10<br>Brij 98: n=20 |
| Alkylphenolethoxylate | $C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$ | NP 10: n=10<br>Igepal CO-720: n=12<br>Igepal CO-850: n=20<br>HV25: n=25<br>Makon 30: n=30 |
| | $C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$ | Triton X-405: n=40 |
| Polyoxyethylene sorbitan monolaurate |  | Tween 20: w+x+y+z=20<br>R=lauryl |

**Table 2. Polymerization of MMA by Direct ATRP in Water Using Polyoxyethylene Oleylas Nonionic Surfactants $[MMA]_0/[EB\textit{i}B]_0/[CuBr]_0/[DNbpy]_0 = 300/1/1/2$, MMA/Water = 15/100 (v/v), 60 °C**

| surfactant (HLB) | wt %[a] | time (min) | conv (%) | $M_{n,SEC}$ | $M_{n,th}$ | $M_w/M_n$ | coag (%)[b] |
|---|---|---|---|---|---|---|---|
| Brij 97 | 17.4 | 16 | 26 | 9 320 | 4 770 | 1.36 | |
| (12.4) | | 30 | 30 | 15 560 | 9 000 | 1.32 | |
| | | 60 | 51 | 56 030 | 15 200 | 1.31 | |
| | | 132 | 78 | 74 770 | 23 400 | 1.24 | |
| 40 | | 260 | 92 | 32 100 | 25 550 | 1.26 | 40 |
| Brij 98 | 14.1 | 18 | 16 | 10 120 | 4 980 | 1.18 | |
| (15.3) | | 32 | 23 | 13 000 | 6 800 | 1.18 | |
| | | 62 | 36 | 15 480 | 10 860 | 1.20 | |
| | | 133 | 64 | 22 940 | 19 260 | 1.20 | |
| | | 262 | 83 | 27 150 | 24 780 | 1.20 | 19 |

[a] Weight percentage of the surfactant vs the monomer. [b] Wt % of the coagulum vs the solid content at the final conversion.

The percentage of coagulation was used as an indicator for evaluating the colloidal stability. It was calculated on the basis of the weight ratio of the coagulum to the solid content at the last point of the reaction, i.e., coagulum % = 100% × coagulum/(initial monomer × conversion %). Because of prior success in the emulsion polymerization of BMA,[4] the Brij family was the first set of emulsifiers applied to the MMA polymerization (Table 2). However, with Brij 97 as the surfactant, coagulation occurred during the early stage of the polymerization even at a high surfactant concentration (17.4% vs monomer). The use of Brij 98 allowed for a slight improvement in the colloidal stability. Premature coagulation could only be avoided when the amount of Brij 98 was increased up to 25 wt % vs the monomer.

The second class of surfactants (alkylphenolethoxylate) has been successfully used in the conventional emulsion polymerization of MMA,[15,16] resulting in stable latexes. To determine the best surfactant from this series, several emulsifiers with a wide range of HLB (from 13.2 to 18) were examined (Table 3). In the presence of surfactants with low HLB (<15, entries 1 and 2), the amount of coagulum was significant. More-

**Table 3. Polymerization of MMA by Direct ATRP in Water Using Alkylphenolethoxylates as the Nonionic Surfactants; $[MMA]_0/[EB\textit{i}B]_0/[CuBr]_0/[DNbpy]_0 = 300/1/1/2$, MMA/Water = 15/100 (v/v), 60 °C**

| surfactant (HLB) | wt % | time (min) | conv (%) | $M_{n,SEC}$ | $M_{n,th}$ | $M_w/M_n$ | coag (%) |
|---|---|---|---|---|---|---|---|
| NP 10 (13.2) | 10.3 | 16 | 13 | 7 950 | 3 940 | 1.24 | |
| | | 31 | 25 | 10 080 | 7 470 | 1.24 | |
| | | 62 | 44 | 12 020 | 13 280 | 1.24 | |
| | | 130 | 62 | 14 830 | 18 450 | 1.26 | |
| | | 248 | 97 | 17 410 | 28 980 | 1.26 | 40 |
| Igepal CO-720 (14.2) | 10.1 | 18 | 15 | 9 630 | 4 390 | 1.27 | |
| | | 35 | 36 | 12 350 | 10 780 | 1.27 | |
| | | 60 | 55 | 15 390 | 16 460 | 1.27 | |
| | | 220 | 87 | 28 190 | 26 100 | 1.26 | 40 |
| Igepal CO-850 (16.0) | 10.5 | 29 | 17 | 12 000 | 5110 | 1.24 | |
| | | 62 | 30 | 15 360 | 9 020 | 1.27 | |
| | | 124 | 53 | 20 790 | 15 920 | 1.27 | |
| | | 183 | 77 | 25 540 | 23 030 | 1.25 | |
| | | 250 | 82 | 27 880 | 24 440 | 1.26 | 18 |
| HV25 (16.6) | 10.7 | 15 | 12 | 9 160 | 3 540 | 1.23 | |
| | | 30 | 22 | 11 120 | 6 520 | 1.26 | |
| | | 60 | 36 | 14 520 | 10 860 | 1.26 | |
| | | 126 | 59 | 20 460 | 17 730 | 1.27 | |
| | | 260 | 86 | 26 880 | 25 830 | 1.33 | 17 |
| Makon 30 (17) | 10.1 | 29 | 20 | 11 310 | 5 970 | 1.20 | |
| | | 60 | 34 | 14 390 | 10 160 | 1.34 | |
| | | 128 | 48 | 19 480 | 14 340 | 1.40 | |
| | | 190 | 67 | 23 410 | 20 010 | 1.41 | |
| | | 265 | 81 | 26 860 | 24 200 | 1.42 | 20 |
| Triton X-405 (17.9) | 10.5 | 21 | 13 | 11 510 | 3 890 | 1.15 | |
| | | 41 | 25 | 14 390 | 7 550 | 1.15 | |
| | | 103 | 50 | 19 690 | 14 280 | 1.17 | |
| | | 150 | 68 | 23 330 | 20 380 | 1.18 | |
| | | 192 | 83 | 24 610 | 24 680 | 1.18 | 30 |

**Table 4. Polymerization of MMA by Direct ATRP in Water Using Polyoxyethylene Sorbitan Monolaurate as the Nonionic Surfactant; $[[Mma]_0/[EB\textit{i}B]_0/[CuBr]_0/[DNbpy]_0 = 300/1/1/2$, MMA/Water = 15/100 (v/v), 60 °C**

| surfactant %, HLB | wt % | time (min) | conv (%) | $M_{n,SEC}$ | $M_{n,th}$ | $M_w/M_n$ | coag (%) |
|---|---|---|---|---|---|---|---|
| Tween 20 (16.7) | 10.0 | 26 | 23 | 12 050 | 6 960 | 1.19 | |
| | | 115 | 55 | 20 720 | 16 370 | 1.19 | |
| | | 158 | 68 | 24 210 | 20 320 | 1.19 | |
| | | 200 | 81 | 26 450 | 24 290 | 1.20 | 34 |

over, the control of the polymerization was poor, especially in the presence of NP 10. The semilogarithmic plots of conversion vs time suggest the loss of active species. Compared with the predicted molecular weights, the actual values were higher at low conversion and lower after 40% conversion, indicating some side reactions including transfer, which will be discussed later. As a general trend, in the presence of surfactants with higher HLB (16 and 17, entries 3−5), the colloidal stability was improved to some extent, and the side reactions leading to large deviation of the molecular weights from the predicted ones were less significant. As HLB further increases, such as in the case of Triton X-405 (HLB = 17.9), the stability of the emulsion decreased again.

In the presence of Tween 20, a surfactant with a HLB number close to the best alkylphenol ethoxylate (HLB = 16.7) yet has a distinct chemical structure, the polymerization was reasonably well controlled, but the emulsion stability turned out to be poor (Table 4). This result shows that while the HLB number could be useful in the preselection of an appropriate nonionic surfactant, it is not a universal property to predict the emulsion stability. This is because it is based exclusively on the weight percent of polyoxyethylene or polyol in the surfactant molecule, while disregarding the size (total molecular weight), the chemical nature of the hydrophobic and hydrophilic moieties, and the structural features (degree of branching and chain length distribution, etc.) of the latter. These factors have also been demonstrated to play important roles in stabilizing the emulsions.[17]

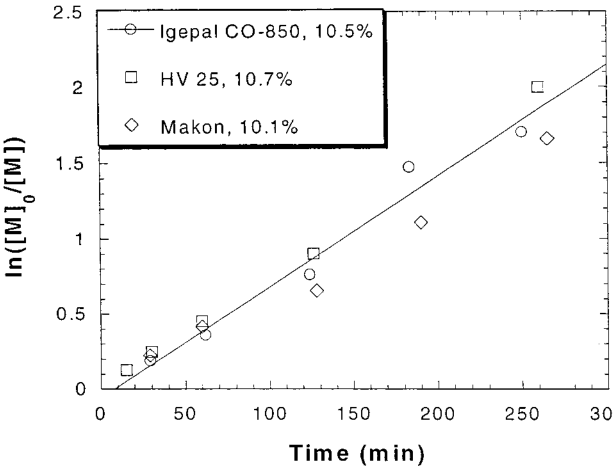


**Figure 1.** First-order plots for the direct ATRP of MMA in water with various surfactants. $[MMA]_0/[EB\textit{i}B]_0/[CuBr]_0/[dNbpy]_0 = 300/1/1/2$, MMA/water = 15/100 (v/v), 60 °C.

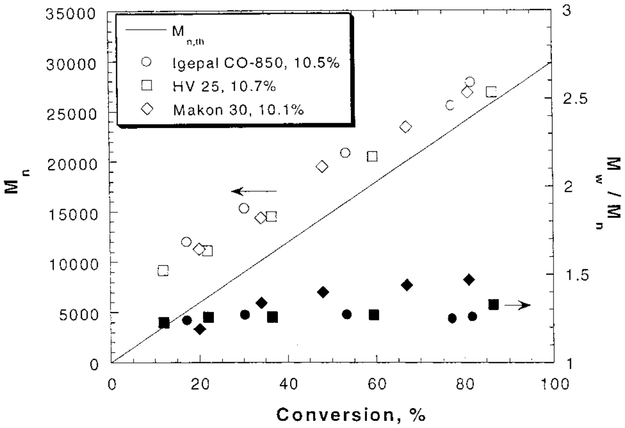


**Figure 2.** Dependence of molecular weights and polydispersities on monomer conversion for the direct ATRP of MMA in water with various surfactants. $[MMA]_0/[EB\textit{i}B]_0/[CuBr]_0/[dNbpy]_0 = 300/1/1/2$, MMA/water = 15/100 (v/v), 60 °C. Surfactant/MMA ≈10 wt %.

Regardless of the latex stability, the “living” character of the polymerization was observed with almost all the nonionic surfactants examined. The results shown in Figure 1 and Figure 2 are from the experiments performed in the presence of Igepal CO-850 (HLB = 16.0), HV25 (HLB = 16.6), and Makon 30 (HLB = 17). The surfactant concentrations were 10 wt % vs the monomer.

The concentrations of the active species remained nearly constant throughout the course of the polymerizations, as evidenced from the straight semilogarithmic plots (Figure 1). The molecular weights gradually increased with monomer conversion (Figure 2) and roughly followed the theoretical calculations. However, up to 50% higher molecular weights than the theoretical values at lower conversion were observed in most cases.

Since all previous samples were analyzed without precipitation, the presence of the surfactant might affect the molecular weight determinations especially at low conversion where overlap on SEC may occur. One experiment was then conducted under the following conditions: $[MMA]_0/[EB\textit{i}B]_0/[CuBr]_0/[dNbpy]_0 = 300/1/1/2$, MMA/water = 15/100 (v/v), 60 °C, HV25/MMA = 10 wt %. The samples were analyzed by SEC both without removing the surfactant (as previously) and after precipitation from methanol.

A slight difference in the molecular weights was found at low conversion; the molecular weights of the precipitated samples were approximately 10% lower than those obtained without surfactant removal. In the presence of the surfactant, the molar mass from the SEC analysis might be overestimated because low molecular weight PMMA underneath the HV25 peak were not taken into account in the overall molecular weight determination. Above 30% conversion, the two sets of molecular weights could be regarded as identical.

This 10% experimental error is too small to account for the up to 50% deviation of molecular weight observed in Figure 2. One possible reason could be due to a slow initiation that results in fewer chains formed at low conversion. However, this is not obvious from the kinetic plots, the linearity of which indicates constant active species throughout the polymerization. Another reason could be attributed to the lack of persistent radical effect[18] arising from the $Cu^{II}$ species partitioning in the aqueous phase.[7] $Cu^{II}$ species are produced in situ from the atom transfer reaction and act as the radical deactivator to suppress the radical termination. If a significant amount of $Cu^{II}$ species escapes from the polymerization site at the beginning of the polymerization, the termination between primary radicals may become extensive enough so that the number of initiated chains is fewer than expected. If this is true, the molecular weight at higher conversion should also be much greater than the theoretical values due to the loss of chains. This is not observed in Figure 2 since the molecular weights are approaching the theoretical line. However, it is also possible that some side reactions may cancel the effect of low initiation efficiency. As is known in MMA solution polymerization, the EB*i*B/CuBr/dNbpy initiating system is usually associated with side reactions such as chain transfer, although their exact natures have not been identified.[19] The same situation may also hold in the water-borne system. When NP 10 was used as the surfactant, the large molecular weight discrepancy between the observed and calculated values, as described earlier, is presumably caused by these side reactions as well. The reason that the effect of side reactions in the presence of NP 10 is more significant than for other surfactants is still unclear.

**Other Factors Affecting Colloidal Stability and Particle Size.** The aforementioned experiments showed that the best colloidal stability and molecular weight control was obtained in the presence of HV25 as the surfactant. Figure 3 shows typical SEC traces of polymer samples taken at various intervals. The molecular weight distribution continuously shifts to the higher molar mass region with increasing monomer conversion.

The surfactant concentration has a significant influence on the emulsion stability. Increasing the amount of HV25 from 10.7 to 12.5 wt % with respect to the monomer reduced the coagulation from 17% to 10%. No coagulation was observed when the surfactant was increased to 18% vs monomer.

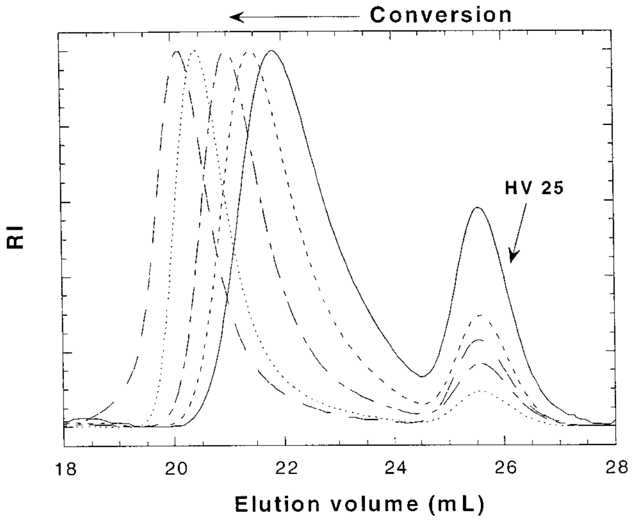


**Figure 3.** SEC chromatograms of the polymerization of MMA by direct ATRP in water with HV25 as the surfactant. $[MMA]_0/[EB\textit{i}B]_0/[CuBr]_0/[dNbpy]_0 = 300/1/1/2$, MMA/water = 15/100 (v/v), HV25/MMA = 10.7 wt %, 60 °C.

It is known that, in a conventional emulsion polymerization using an ionic surfactant, both the changes in pH and ionic strength have a great impact on the colloidal stability. Even if these effects are minimized in the presence of nonionic surfactants, a possible large pH variation during the polymerization cannot be ignored. To check this, the pH in the direct ATRP system was monitored throughout the polymerization. It was found that the medium became slightly more acidic with increasing conversion: from 6.3 at the beginning to 5.7 at the end. This slight change in pH over the course of the polymerization should not have an effect on the latex stability.

To better understand the parameters affecting the latex stability, the partitioning of HV25 both at room temperature and at 60 °C was determined by gravimetry. The partitioning was performed in the absence of $CuBr_2$ and dNbpy or in the presence of either $CuBr_2$ or dNbpy. It was found that without additives or with dNbpy present the emulsion was too stable to phase separate or the phase separation was poor. But the presence of $CuBr_2$ ($2.5 \times 10^{-3}$ M in the aqueous phase) improved the phase separation, and the partitioning can be roughly evaluated. At room temperature with 5% HV25, more than 95 wt % of the surfactant was found in the aqueous phase, in the form of both single molecule and aggregates. However, at 60 °C HV25 remaining in the aqueous phase decreased to 13 wt % of the total amount. This is not surprising since the dehydrating surfactant at high temperature tends to dissolve in the organic phase. As a result, not only the amount of surfactant effectively stabilizing the particles is well below the apparent concentration but also the thickness of the adsorbed layer is reduced as a consequence of the penetration of the oil/water interface by the stabilizing surfactant. This would cause a significant loss of colloidal stability, particularly with large particles that are subjected to greater attraction between each other than smaller particles.

The particle diameters obtained via direct ATRP ($[MMA]_0/[EB\textit{i}B]_0/[CuBr]_0/[dNbpy]_0 = 300/1/1/2$, MMA/water = 15/100 v/v, HV25/water = 12.5 wt %) were measured by both dynamic light scattering and scanning electron microscopy (SEM). The light scattering measurement was carried out within 24 h after the polymerization, and the final average particle size was around 800 nm for samples poststabilized with SDS. In comparison, the samples without SDS showed much larger diameters (>1500 nm), indicating particle coagulation during the storage period. The SEM measurement was performed after longer storage time. The samples were also poststabilized with SDS and well-shaken before cast on the glass slide. The mean average particle sizes, however, were much smaller than measured by light scattering, ranging from 100 to 300 nm. Considering the long-standing time of the samples, it is likely that most large particles already settled down before sampling on the glass slide despite the presence of SDS and therefore were not taken for the SEM measurement. In other words, the small values obtained from SEM might only represent those small particles remaining in the dispersed state. A hint of this possibility also comes from the broad distribution of the particle sizes (up to 2 $\mu$m) revealed by the SEM images.

The use of an oil-soluble initiator and the large average particle size obtained with a broad size distribution suggest that the direct ATRP of MMA in the water-borne systems most likely proceeds via a (micro)-suspension process. The monomer droplets containing the oil-soluble initiator and the catalyst system act as small individual reactors. Because of the partitioning of the nonionic surfactant at the polymerization temperature, a significant amount of the surfactant is probably dissolved in the monomer droplets. Consequently, the amount of the surfactant remaining in the aqueous phase and at the surface of the droplets does not stabilize the growing particles, as evidenced by premature coagulation (40% conversion). In the conventional emulsion polymerization using similar nonionic surfactants, water-soluble initiators are used, and the monomer droplets mostly act as monomer reservoir instead of polymerization sites. In this case, the fraction of surfactant dissolved in the monomer droplets is released into the aqueous phase as the monomer droplets gradually disappear during the polymerization. The newly released surfactant is responsible for the final stable emulsion.[16,20]

To improve the latex stability, the effect of adding sodium dodecyl sulfate (SDS) during the course of the polymerization was studied. The polymerization was performed in the presence of 5% HV25, and a small amount of SDS was added at 30% monomer conversion. The emulsion stability was improved, but the control of the polymerization was lost when 1.5 or 3 mol equiv of SDS vs CuX was added. Conversely, when 0.5 equiv was added, the polymerization was still controlled, but the stability remained poor. This phenomenon is attributed to the reaction of SDS with the $Cu^{II}$ complex, removing the deactivator that controls the polymerization from the reaction medium.[21]

**Improving the Polymerization Control by Utilizing Halogen Exchange.** As mentioned earlier, when EB*i*B/CuBr/dNbpy was used as the initiating system for a MMA polymerization, at low conversion, the molecular weights deviated significantly from the expected values. This phenomenon could be associated with the aqueous partitioning of the catalyst. Since copper chloride complexes usually have higher organic solubilities than their bromide counterparts, replacing CuBr with CuCl might lead to better results. In case that slow initiation did contribute to the poor molecular weight control, the new initiating/catalyst system EB*i*B/CuCl/dNbpy may also overcome this problem. Such a halogen exchange strategy was previously applied to the homogeneous ATRP of MMA in bulk or in solution to improve the molecular weight control.[22] In water-borne media, first-order kinetics with respect to monomer was observed using the mixed halide system. Compared to the EB*i*B/CuBr system, the polymerization rate was slower due to the less active C−Cl end group. The plot of the molecular weights vs conversion was in better agreement with the theoretical line, and the polydispersities were reduced (Figure 4).

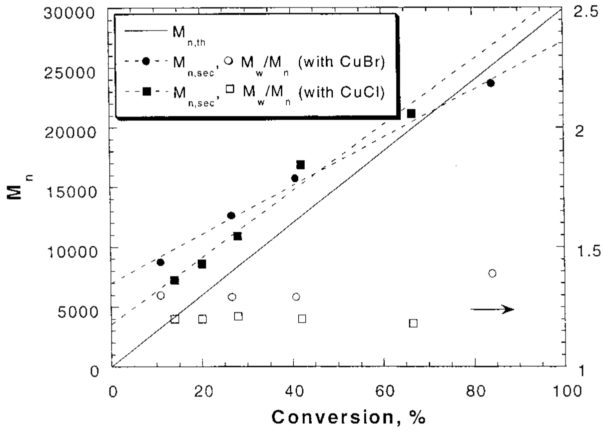


**Figure 4.** Dependence of molecular weights and polydispersities on monomer conversion for the direct ATRP of MMA in water. $[MMA]_0/[EBiB]_0/[CuX]_0/[dNbpy]_0$ = 300/1/1/2, MMA/water = 15/100 (v/v), HV25/MMA = 5 wt %, 60 °C.

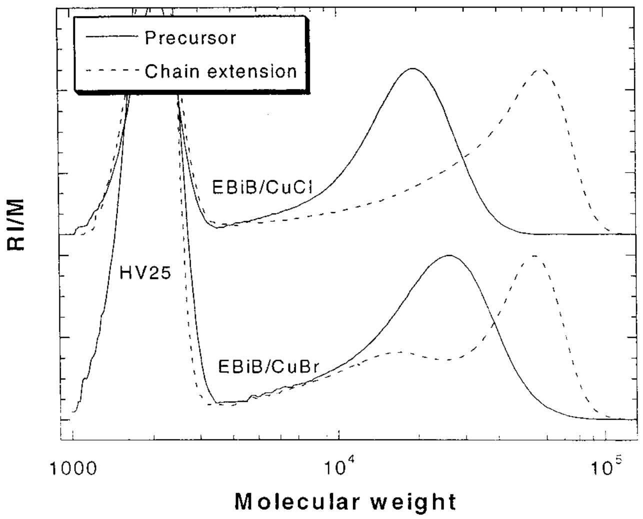


**Figure 5.** Number molecular weight distribution of the polymers obtained by chain extension in direct ATRP in water. Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuX]_0/[dNbpy]_0$ = 240/1/1/2, MMA/water = 15/100 (v/v), HV25/ MMA = 12.5 wt %, for 4 h at 60 °C (precursor polymer) before adding new MMA to the latex.

The halogen exchange approach also helped to improve the end group functionality of the polyMMA prepared under water-borne conditions, as shown by chain extension experiments. After 4 h of polymerization a second feed of MMA was added to the latex. The polymerization was not interrupted until the increase of the molecular weight was sufficient to evaluate the end functionality by SEC.

The number-average molecular weight distribution, represented by the ratio of the differential refractive index to the molecular weight (RI/M) vs the logarithmic

**Table 5. Polymerization of MMA by Reverse ATRP in Water Using HV25 as the Surfactant; $[MMA]_0/[VA\text{-}044]_0/[CuX_2]_0/[dNbpy]_0 = 750/1/1.5/3$; MMA/Water = 15/100 (v/v), 80 °C**

| | wt %[a] | time (min) | conv (%) | $M_{n,SEC}$ | $M_w/M_n$ | $M_{n,th}$ | $f$[b] | coag |
|---|---|---|---|---|---|---|---|---|
| $CuBr_2$ | 5.1 | 59 | 20 | 16 030 | 1.26 | 7 500 | 0.5 | |
| | | 89 | 35 | 25 560 | 1.22 | 13 130 | | |
| | | 138 | 48 | 36 080 | 1.20 | 18 000 | | |
| | | 189 | 61 | 43 020 | 1.20 | 22 880 | | |
| | | 226 | 70 | 48 970 | 1.21 | 26 250 | | some |
| | 10.2 | 34 | 14 | 8 660 | 1.20 | 5 250 | 0.7 | |
| | | 64 | 25 | 18 150 | 1.25 | 9 380 | | |
| | | 121 | 46 | 23 500 | 1.35 | 17 250 | | |
| | | 182 | 67 | 33 580 | 1.36 | 25 130 | | |
| | | 236 | 80 | 45 270 | 1.35 | 30 000 | | none |
| $CuCl_2$ | 10.3 | 63 | 25 | 13 840 | 1.21 | 9 380 | 0.8 | |
| | | 118 | 50 | 27 160 | 1.27 | 18 750 | | |
| | | 183 | 72 | 32 900 | 1.33 | 27 000 | | |
| | | 240 | 79 | 39 280 | 1.30 | 29 630 | | none |

[a] Weight percentage of HV25 vs the monomer. [b] Initiator efficiency calculated by $f = M_{n,th}/M_{n,SEC}$.

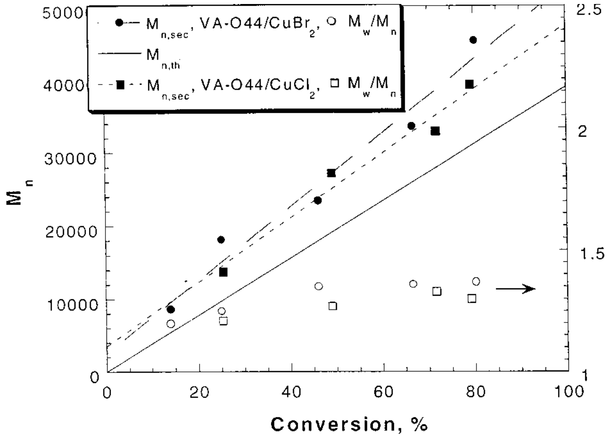


**Figure 6.** Dependence of molecular weights and polydispersities on monomer conversion for the reverse ATRP of MMA in water. $[MMA]_0/[VA\text{-}044]_0/[CuX_2]_0/[dNbpy]_0 = 750/1/1.5/3$, MMA/water = 15/100 (v/v), HV25/water = 10.3 wt %, 80 °C.

molecular weight, allows evaluation of the fraction of dead chains at the end of the monomer consumption.[23] Indeed, we estimate that 63% of the polymeric chains (the percentage is estimated using Gaussian multipeak analysis) are dead at 80% conversion of the first polymerization stage when EB*i*B/CuBr was used as the initiating system. On the other hand, the fraction of dead chains was significantly reduced in the presence of a mixed-halide system (Figure 5).

**II. Polymerization of MMA by Reverse ATRP in the Water-Borne System.** Another way to approach the atom transfer equilibrium is to start from a conventional water-soluble radical initiator and a $Cu^{II}$ complex; the activator, $Cu^IX$, and the alkyl halide are generated in situ.[6,7,12,24] This process is called the reverse ATRP. In the current investigation, the azo-initiator VA-044 was chosen, and the ligand used was still dNbpy. All the experiments were performed using HV25 as the surfactant at various concentrations.

Representative polymerization results obtained with VA-044/$CuBr_2$ and VA-044/$CuCl_2$ as the initiating system are presented in Table 5. A similar polymerization was observed whether $CuCl_2$ or $CuBr_2$ was used. In both cases, an induction period was observed, during which the color of the emulsion changed from green to brown. A similar phenomenon was previously observed for BMA polymerization, and the induction period was attributed to the establishment of the atom transfer equilibrium in the organic phase as well as the transportation of $Cu^{II}$ species through the aqueous phase.[7,8] The linear development of the molecular weights with monomer conversion (Figure 6) indicated that the number of chains remained constant throughout the course of the reaction. Side reactions were negligible in both cases. The initiator efficiency was in the same range as the one observed for the polymerization of BMA.[6]

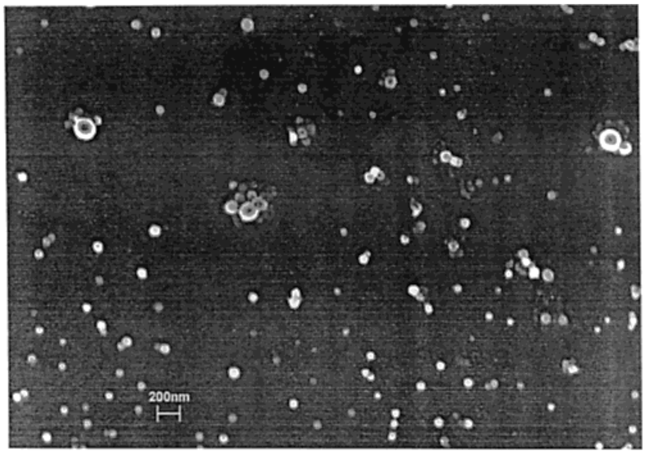


**Figure 7.** SEM analysis on polyMMA obtained by reverse ATRP. $[MMA]_0/[VA\text{-}044]_0/[CuBr_2]_0/[dNbpy]_0 = 760/1/1.5/3$, MMA/water = 15/100 (v/v), HV25/MMA = 10.0 wt %.

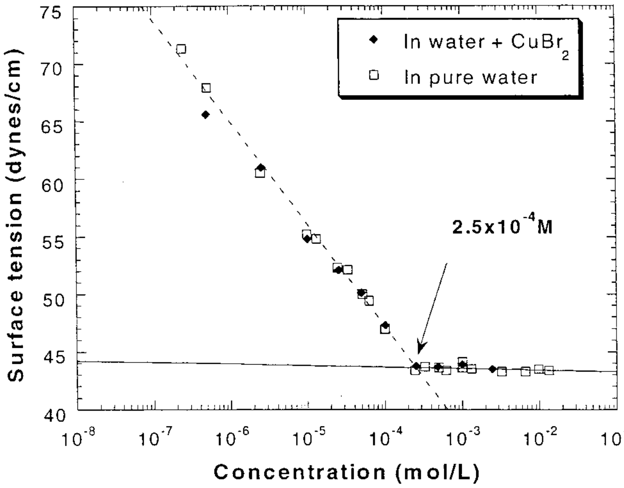


**Figure 8.** The cmc determination of HV25 in pure water and in the presence of $CuBr_2$ by surface tension measurements.

Using the reverse process increased the colloidal stability, and no coagulation was noticed in the presence of 10 wt % HV25. Latex poststabilized with SDS exhibited unimodal particle size distributions and nearly constant average particle diameters with monomer conversion: $D_n = 43-48$ nm by light scattering and 53 ± 15 nm by SEM (Figure 7).

Particle sizes obtained by reverse ATRP are much smaller than those obtained from the direct process. This observation prompted us to examine the nature of the initial emulsion. The critical micellar concentration (cmc) of HV25 in water was measured at room temperature by surface tension using a DuNouy tensiometer (Figure 8). The cmc value was estimated to be $2.5 \times 10^{-4}$ M and was not affected by the presence of $CuBr_2$ ($2.6 \times 10^{-3}$ M) in water. The cmc at higher temperature was not measured but was expected to be

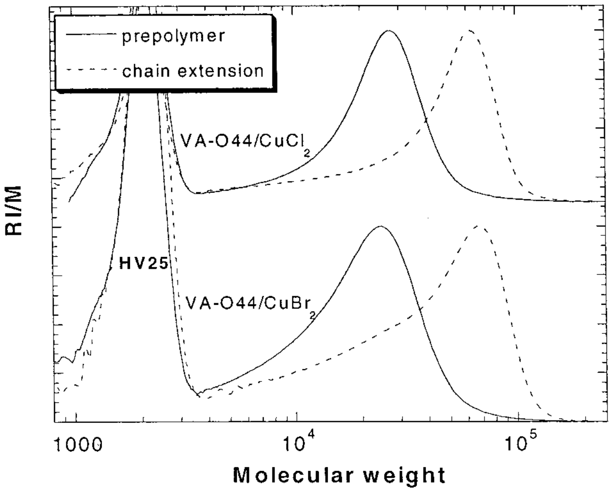


**Figure 9.** Number distribution of molecular weight of the polymers obtained by chain extension in reverse ATRP. Polymerization conditions: $[MMA]_0/[VA\text{-}044]_0/[CuX_2]_0/[dNbpy]_0 = 520/1/1.5/3$, MMA/water = 15/100 (v/v), HV25/MMA = 10.0 wt %, for 4 h at 80 °C (precursor polymer) before adding new MMA to the latex.

lower because of the reduced solubility of the surfactant in water.

Combined with the earlier results from the HV25 partitioning study, under these experimental conditions, the surfactant concentration in the aqueous phase is probably well above the cmc where a large number of micelles might exist. Since a water-soluble initiator is used, micellar nucleation cannot be excluded, and droplet nucleation seems to be a minor event, as opposed to the direct ATRP. In other words, an emulsion polymerization process is very likely occurring. Indeed, radicals are generated in the aqueous phase followed by addition of the monomer in the continuous phase. PMMA oligomers become surface active and enter the existing micelles, or homogeneous nucleation takes place. The relatively low initiator efficiency can be explained by the irreversible termination of radicals in the aqueous phase at the early stage of the polymerization.[7] Chain end functionality of these polymers was evaluated by the PMMA chain extension experiments, and the SEC traces are presented in Figure 9. Chain end functionality of the PMMA was improved by using reverse ATRP. PMMA prepared with the VA-044/CuCl$_2$ system also exhibited higher chain end functionality than those synthesized with the VA-044/CuBr$_2$ system.

## Conclusions

The direct (RX/Cu$^I$X) and reverse (I–I, Cu$^{II}$X$_2$) ATRP of MMA under water-borne conditions were successfully demonstrated. In the direct process, several surfactants were screened and HV25 ($C_9H_{19}C_6H_4(OCH_2CH_2)_{25}OH$) gave the best results in terms of both molecular control ($M_n$ vs conversion and polydispersity) and colloidal stability. Nevertheless, coagulation could not be entirely avoided except at high surfactant concentrations. The suspension type mechanism and hence the large particles size generated could account for the poor latex stability. This may limit the application of this technique unless more effective stabilizers are found in the future or the colloidal stability is not of critical importance for the application. Potentially, using a water-soluble and surface-active alkyl halide may improve the colloidal stability by promoting micellar or homogeneous nucleation. An alternative approach to solve the colloid stability problem can be the miniemulsion technique, i.e., by applying strong shear force such as ultrasonication and cosurfactant. This technique has been proved successful in BMA water-borne systems,[8] which allows the use of the oil-soluble initiator and radical mediator to obtain small particles.

When the reverse ATRP was used, the polymerization of MMA was well controlled. The colloidal stability was significantly enhanced (no coagulation in the presence of 10% HV25) because of the smaller size of the generated particles. A micellar and/or a homogeneous nucleation mechanism with minor droplet nucleation was hence suggested. Chain end functionality was improved when I–I/CuCl$_2$ was used as the catalyst system. Chain end functionalization efficiency could be classified in the following order according to the process used: I–I/Cu$^{II}$Cl$_2$ > RBr/Cu$^I$Cl ≥ I–I/Cu$^{II}$Br$_2$ > RBr/Cu$^I$Br.

A full optimization of this system requires additional studies and a better understanding of the role of each component.

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## References and Notes

(1) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638. Matyjaszewski, K., Ed. *Controlled Radical Polymerization;* ACS Symposium Series Vol. 685; American Chemical Society: Washington, DC, 1998. Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901. Matyjaszewski, K., Ed. *Controlled/Living Radical Polymerization: Progress in ATRP, NMP, and RAFT;* ACS Symposium Series Vol. 768; American Chemical Society: Washington, DC, 2000.

(2) Lovell, P. A., El-Aasser, M. S., Eds. *Emulsion Polymerization and Emulsion Polymers*; John Wiley and Sons: Chichester, 1997. Gilbert, R. G. *Emulsion Polymerization. A Mechanistic Approach*; Academic Press: London, 1995.

(3) Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576. Moineau, G.; Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1998**, *31*, 542. Shipp, D. A.; McMurtry, G. P.; Gaynor, S. G.; Qiu, J.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 448.

(4) Gaynor, S. G.; Qiu, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5951.

(5) Qiu, J.; Shipp, D.; Gaynor, S. G.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 418.

(6) Qiu, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2872.

(7) Qiu, J.; Pintauer, T.; Gaynor, S. G.; Matyjaszewski, K.; Charleux, B.; Vairon, J.-P. *Macromolecules* **2000**, *33*, 7310.

(8) Matyjaszewski, K.; Qiu, J.; Tsarevsky, N.; Charleux, B. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 4724.

(9) Bon, S. A. F.; Bosveld, M.; Klumperman, B.; German, A. L. *Macromolecules* **1997**, *30*, 324. Marestin, C.; Noel, C.; Guyot, A.; Claverie, J. *Macromolecules* **1998**, *31*, 4041. Prodpran, R.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *Polym. Mater. Sci. Eng.* **1999**, *80*, 534. Lansalot, M.; Farcet, C.; Charleux, B.; Vairon, J.-P.; Pirri, R.; Tordo, P. *ACS Symp. Ser.* **2000**, *768*, 138.

(10) Lansalot, M.; Farcet, C.; Charleux, B.; Vairon, J.-P. *Macromolecules* **1999**, *32*, 7354. Butte, A.; Storti, G.; Morbidelli, M. *Macromolecules* **2000**, *33*, 3485.

(11) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. G.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559. Kanagasabapathy, S.; Claverie, J.; Uzulina, I. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 1080. Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.;

Biadatti, T.; Bouhadir, G. *Macromol. Symp.* **2000**, *150*, 23. Uzulina, I.; Kanagasabapathy, S.; Claverie, J. *Macromol. Symp.* **2000**, *150*, 33.
(12) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7572.
(13) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.
(14) Lide, D. R., et al., Eds. *Handbook of Chemistry and Physics*, 79th ed.; CRC Press: Boca Raton, FL, 1998−1999.
(15) Emelie, B.; Pichot, C.; Guillot, J. *Makromol. Chem., Suppl* **1985**, *10/11*, 43.
(16) Zujkov, A. V.; Solovyev, J. V. *Acta Polym.* **1979**, 30.
(17) Schick, M. J., Ed. *Nonionic Surfactants. Physical Chemistry*; Marcel Dekker: New York, 1987. Shinoda, K.; Friberg, S. *Emulsions and Solubilization*; Wiley: New York, 1986.
(18) Fischer, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1885.
(19) Matyjaszewski, K.; Wang, J.-L.; Grimaud, T.; Shipp, D. A. *Macromolecules* **1998**, *31*, 1527. Wang, J.-L.; Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 6507.
(20) Piirma, I.; Chang, M. *J. Polym. Sci., Part A: Polym. Chem.* **1982**, *20*, 489. Ozdeger, E.; Sudol, E. D.; El-Aaser, M. S.; Klein, A. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, 35.
(21) Gaynor, S. G.; Qiu, J.; Shipp, D.; Matyjaszewski, K. *Polym. Mater. Sci. Eng.* **1999**, *80*, 536.
(22) Matyjaszewski, K.; Shipp, D. A.; Wang, J.-L.; Grimaud, T.; Patten, T. E. *Macromolecules* **1998**, *31*, 6836.
(23) Matyjaszewski, K.; Shipp, D. A.; McMurtry, G. P.; Gaynor, S. G.; Pakula, T. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 2023.
(24) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7692.

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