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Emulsion atom transfer radical polymerization of 2-ethylhexyl methacrylate

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Abstract

The emulsion atom transfer radical polymerization (ATRP) of 2-ethylhexyl methacrylate (EHMA) was carried out with ethyl 2-bromoisobutyrate (EBiB) as an initiator and copper bromide (CuBr)/4,4′-dinonyl-2,2′-bipyridyl (dNbpy) as a catalyst system. The effects of surfactant type and concentration, temperature, monomer/initiator ratio, and $CuBr_2$ addition on the system livingness, polymer molecular weight control, and latex stability were examined in detail. It was found that the polymerization systems with Tween 80 and Brij 98 as surfactants at 30 °C gave the best latex stability. The polymer samples prepared under these conditions had narrow molecular weight distributions ($M_w/M_n = 1.1$–1.2) and linear relationships of number-average molecular weight versus monomer conversion.

Keywords: Atom transfer radical polymerization (ATRP); Emulsion polymerization; Latex

1. Introduction

Control over polymer molecular weight and its distribution during synthesis has been a challenging task in polymer research. The advent of controlled/living radical polymerization provides a new way to synthesize polymers with controlled molecular weights. This approach is more versatile in monomer types and is more tolerant to impurities than living ionic polymerizations. An attractive process is the emulsion living radical polymerization. The advantages of an emulsion polymerization include the absence of organic solvent in final products, which is usually the most voluminous pollutant in polymerization processes, and the ease of separation of other contaminants via aqueous phase using ion exchange resins.

All of the major types of controlled radical polymerizations have been used in the emulsion system, namely emulsion stable free radical polymerization (SFRP), emulsion atom transfer radical polymerization (ATRP), and emulsion reversible addition fragmentation chain transfer polymerization (RAFT). For example, emulsion SFRP was carried out for homo- and copolymerization of styrene using *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2′-dimethyl propyl) at 90 °C [1]. Emulsion RAFT was applied for various types of methacrylates [2,3]. Emulsion ATRP has been challenging due to poor latex stability [4,5]. This difficulty led to the use of reverse emulsion ATRP, which employed a conventional radical initiator system and resulted in smaller and more stable latex particles, but had higher polydispersity indexes (PDI) and lower initiator efficiencies [6,7].

Makino et al. [8] reported the emulsion ATRP of methyl methacrylate (MMA) with ethyl 2-bromoisobutyrate (EBiB) as an initiator, copper bromide (CuBr)/bipyridine as a catalyst and sodium dodecyl sulfate (SDS) as a surfactant. High polydispersity index (about 1.55) but good latex stability was observed. The high polydispersity was attributed to the reaction of SDS with the polymerization system [2]. Gaynor et al. [4] studied the emulsion ATRP of butyl methacrylate (BMA), butyl acrylate (BA), MMA and styrene using CuBr with a variety of ligands and surfactants such as polyethylene glycol (PEG, MW 1000 and 4600 g/mol) and Brij 97 (polyoxyethylene (10) oleyl ether) and Brij

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98 (polyoxyethylene (20) oleyl ether), but not ionic surfactants because of interactions with copper salts. It was found that the systems with dinonyl-(dNbpy) or dialkyl bipyridine (dAbpy) as the ligand and Brij 98 as the surfactant gave polydispersity values of about 1.3. Wan et al. [9] studied the emulsion ATRP of styrene with various initiators such as 1-phenyl ethyl bromide, CCl_4 and $PhCH_2Cl$, and the ligand 2,2′-oxybis (*N*,*N*-dimethylethylamine), and reported polydispersity values of 1.18–1.5 but with molecular weights six-to-ten times higher than the theoretical values. An additional peak of high molecular weight (dead polymer peak) of one and half a million grams per mole was observed. Qiu et al. [6] studied the effects of ligand types on the emulsion ATRP of BA and BMA using EBiB/CuBr and concluded that d5Nbpy and dAbpy gave low polydispersity values of ~ 1.2 and dipyridyl octadecyl amine gave a polydispersity index of 1.1. Chambard et al. [10] studied the emulsion ATRP of MMA using Brij 98 as a surfactant and two different ligands, 2-pyridine carbaldehyde 3,3-diphenylpropylimine (dPP) and 4,4′-diheptyl 2,2′-bipyridine (dHbpy). dHbpy was better than dPP for the control of polydispersity.

Qiu et al. [11] studied the reverse emulsion ATRP with dialkyl bipyridine as a ligand. Stable latexes with low polydispersity indexes (1.2–1.4) were obtained. Qiu et al. [7] also measured the partitioning coefficients of copper salts (CuBr and $CuBr_2$) and the ligand d5Nbpy in water and BMA and concluded that the ligand and its copper I salt complex dissolved preferably in the organic phase while the copper II salt favored the water phase. Jousset et al. [5] studied both direct and reverse emulsion ATRP of MMA and tried various types of surfactants and found Brij 98 was the best choice for the latex stability in the direct ATRP. Li et al. [12] used a simultaneous direct and reverse ATRP to improve the initiation efficiency in the reverse ATRP. Peng et al. [13] investigated the effects of Brij 35 on latex stability in a reverse emulsion ATRP and found that a high concentration level of copper II salt resulted in a large particle size.

Miniemulsion ATRP has also been investigated by several groups. In this technique, a high stabilizer content and a small initial droplet size help to stabilize the ATRP system. Matyjaszewski et al. [14] studied the miniemulsion ATRP of BMA using hexadecane as a hydrophobe and Brij 98 as a surfactant. Strong sonication was applied to make a fine emulsion at the beginning of polymerization. The resulting polymers had polydispersity indexes lower than 1.5 and a linear relationship of M_n versus conversion. Okubo et al. [15] investigated the direct miniemulsion ATRP at 30 and 40 °C and obtained stable polymer latexes of poly (iBMA) with polydispersity indexes of 1.1. Tween 80 (polyoxyethylene sorbitan monooleate) was used as a surfactant. Lie et al. [16] used a miniemulsion technique to synthesize block copolymers from multifunctional macroinitiators based on MMA, BA and St in a simultaneous direct and reverse ATRP. It appeared that a good latex stability and control of molecular weight could be achieved with the nonionic surfactants such as Brij 98 and Tween 80, and with the ligands that have adequate hydrophobicity such as dialkyl bipyridine.

In this paper, we report the experimental results for the emulsion ATRP of 2-ethylhexyl methacrylate (EHMA). Poly(EHMA) has been the subject of several investigations recently [17,18]. We are particularly interested in its potential applications as adhesives. The polymer has a low T_g value of -10 °C. It is polar compared to hydrocarbon-based elastomers and has a good oil resistance and adhesion to various substrates. It can readily copolymerize with other methacryaltes. The objectives of this work are to investigate the control of molecular weight and latex stability of poly(EHMA) in the emulsion ATRP, and to examine the effects of various parameters on the polymerization behavior. In general, one of the advantages of having a controlled molecular weight and narrow polydispersity product is the low content of volatile organic compounds (VOC). It is particularly important for a low-molecular-weight product. If the product is made by a conventional free radical polymerization, it contains a large number fraction of small molecules that can be volatile. An emulsion polymerization process is chosen in this work because of its industrial significance. The basic polymerization recipe was ethyl 2-bromo isobutyrate (EBiB) as an initiator, copper (I) bromide (CuBr) as a catalyst, and 4,4′-dinonyl-2, 2′-bipyridyl (dNbpy) as a ligand. Cu^IBr salt of 5% is replaced by copper (II) bromide ($Cu^{II}Br_2$) to facilitate the establishment of reaction equilibrium between radical and dormant species, which usually leads to dead chain formation and lowers initiator efficiency at the initial stage of polymerization.

2. Experimental

2.1. Materials

2-Ethylhexyl methacrylate (EHMA, vapor pressure 18 mmHg at 120 °C) (from Aldrich) was purified by passing it through an inhibitor removal column (Aldrich) and dried over calcium hydride for overnight. Ultra filtered water (conductivity <0.055 μS/cm) was boiled and cooled down under a nitrogen blanket. Ethyl 2-bromoisobutyrate (EBiB) as an initiator (Aldrich), 4,4′-dinonyl-2,2′-bipyridyl (dNbpy) as a ligand (Aldrich), CuBr and $CuBr_2$ as catalysts (Aldrich 99.999%) and emulsifiers: polyoxyethylene sorbitan monooleate (Tween 80) (Sigma), polyoxyethylene(20) oleyl ether (Brij 98) (Aldrich), polyoxyethylene(10) oleyl ether (Brij 97) (Aldrich), dodecyltrimethyl ammonium bromide (DTAB) (Aldrich), and myristyltrimethyl ammonium bromide (MTAB) (Aldrich) were used as received without further purification.

2.2. Typical polymerization run

Copper (I) bromide (12.14 mg, 0.0846 mmol), copper (II) bromide (0.99 mg, 0.00445 mmol), and 4,4′-dinonyl-2,2′-bipyridyl (72.8 mg, 0.1781 mmol) were added to a 30 ml flat-bottom reactor (Corning 1340) and then purged with ultra high purity nitrogen (N_2 99.999% purity) for 20 min. EHMA (2 ml, 1.766 g, 8.905 mmol), bubbled with ultra high purity nitrogen for 20 min, was transferred to the reactor with a syringe and the solution was agitated with a stirrer (octagonal 5/8×5/16 in.) at 600–1000 rpm for 20 min at 50 °C to dissolve the copper salts. The catalyst/ligand complex was completely soluble in EHMA. The mixture turned deep brown at the end. A required amount (0.2562 ml, 0.2726 g) of surfactant Tween 80 was added to the solution. The temperature was set to 30 °C. Nitrogen-blanketed water of 18 ml was transferred to the reactor dropwisely under an intense mixing. The mixture turned to pale brown. After 10 min, EBiB of 13.1 μl (0.089 mmol) was added to start polymerization. Samples were taken periodically during the reaction using glass pipettes.

2.3. Conversion

A 200 MHz spectrometer (Bruker, AV200) was used to record ^{1}H NMR spectra. Deuterated chloroform (Cambridge Isotope Library) was used as the solvent. Spectra were obtained using a spectral width of 2604 Hz, an acquisition time of 3.14 s and a pulse delay of 5 s after an accumulation of 16 scans. Deuterated chloroform and magnesium sulfate were added to the samples from the polymerization. The samples were shaken, left for overnight and centrifuged. The aqueous layer was removed using a syringe and the chloroform-rich layer was dried using magnesium sulfate. The concentrations of polymer/monomer mixtures for NMR were about 10% for all the samples. The conversions were calculated from the $–OCH_2–$ peak areas of the monomer at 4.02 and 4.05 ppm and the polymer at 3.82 ppm.

2.4. Molecular weight measurement

Number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution were measured by a size exclusion chromatography system consisting of Waters 717 Plus Autosampler, Waters 600 Controller and Waters 410 Differential Refractometer with three linear columns in series (one Waters Styragel HR 5E and two Shodex KF-804L). Data acquisition and processing was carried out using Millenium 32 software. THF was used as a solvent with a flow rate of 1.0 ml/min. The columns were calibrated against several standard PS samples (Toyosoda): $K_{PS}=1.14\times10^{-4}$ dl/g, $\alpha_{PS}=0.716$. The universal calibration curve was constructed using the poly (EHMA) parameters reported by Hutchinson et al. [19] ($K_{PEHMA}=6.3\times10^{-5}$ dl/g and $\alpha_{PEHMA}=0.707$). Polymer samples were measured after being dried over magnesium sulfate and filtered through 0.2 μm PTFE filter.

2.5. Particle diameter measurement

The particle size distributions were measured by laser light scattering using Mastersizer 2000 (Model APA 2000) with Hydro 2000 accessory (Model AWA 2000). Data acquisition and processing was carried out using Malvern software. The measurement was done after the emulsion was diluted to a desired obscuration by water according to Mastersizer 2000 Catalogue with 1% Tween 80 to avoid surfactant desorption and to stabilize particles.

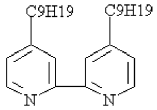
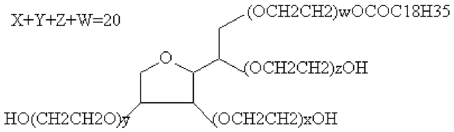
3. Results and discussion

3.1. Effect of surfactant type

Table 1 gives the chemical structures of the monomer, initiator, catalysts, ligand, and surfactants used in this work. Latex stability is one of the major challenges in emulsion ATRP the selection of surfactant is crucial. A suitable surfactant should be able to stabilize latex but does not react with other species in the medium. In this work, we evaluated three nonionic and two cationic surfactants. The cationic surfactants are alkyl trimethyl ammonium bromide. Table 2 summarizes the polymerization results with various types of surfactants. The coagulum percentage is an indicator of latex stability. It is the weight of coagulum collected after passing an emulsion sample through 200-mesh stainless steel filter over the weight of the total monomer initially charged. Fig. 1 shows the kinetic data of these runs ((a): M_n versus x; (b): x versus t; (c): $\ln([M]_0/[M])$ versus t; (d): GPC curves). The ATRP of EHMA appeared to be very fast with most of the runs completed within 3 h. The high polymerization rates agreed with those in the conventional free radical polymerization of EHMA, which is one of the fastest methacrylate monomers [20]. The basic experimental conditions of these runs were: EHMA: 1.766 g (8.905 mmol), surfactant: 0.21 mmol, $[EHMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[DNbpy]_0=100/1/0.95/0.05/2$, EHMA/water: 10/90 (v/v), and temperature: 30 °C. The surfactant/monomer molar ratio was fixed to 2.4% (mol/mol).

In Run S1 with dodecyl trimethyl ammonium bromide (DTAB), the system livingness and the control of polymer molecular weight were good. Poly(EHMA) molecular weight increased linearly with conversion. The agreement of experimental M_n data with the theoretical line in Fig. 1(a) indicated a good initiator efficiency. The polydispersities were about 1.1. The $\ln([M]_0/[M])$ versus time, shown in Fig. 1(c), also showed a linear relationship. However, this batch was coagulated shortly after the start of polymerization, suggesting poor performance of the surfactant in stabilizing latex. In Run S2, myristyl trimethyl ammonium bromide (MTAB) was used as the surfactant. The latex stability was

Table 1
Chemical structures of monomer, initiator, catalysts, ligand, and surfactants used in this study

Chemical		Structure
Monomer	2-Ethylhexyl methacrylate	$CH_2{=}C(CH_3)COOCH_2CH(C_2H_5)CH_2CH_2CH_2CH_3$
Initiator	Ethyl 2-bromoisobutyrate	$(CH_3)_2CBrCOOC_2H_5$
Catalyst	Copper bromide, copper dibromide	CuBr, $CuBr_2$
Ligand	4,4′-dinonyl-2,2′-bipyridyl	
Surfactant	Polyoxyethylene(10) oleyl ether (Brij 97)	$C_{18}H_{35}(OCH_2CH_2)_{10}OH$
	Polyoxyethylene(20) oleyl ether (Brij 98)	$C_{18}H_{35}(OCH_2CH_2)_{20}OH$
	Dodecyltrimethylammonium bromide (DTAB)	$C_{12}H_{25}N(CH_3)_3Br$
	Myristytrimethylammonium bromide (MTAB)	$C_{14}H_{29}N(CH_3)_3Br$
	Polyoxyethylene sorbitan monooleate (Tween 80)	

good with only 1% coagulum. The molecular weight increased linearly with conversion, so did the $\ln([M]_0/[M])$ with time. Unfortunately, the polymer samples had very broad molecular weight distributions with a polydispersity of 2.59 at the conversion 99.6% (Table 2). The GPC curves showed a big tail of ultra high molecular weight chains. These two cationic surfactants (DTAB and MTAB) appeared to be not suitable for the emulsion ATRP of EHMA. Interactions between the cationic surfactants and other reactant species were not clear.

Polyoxyethylene (10) oleyl ether (Brij 97, $C_{18}H_{35}(OCH_2CH_2)_{10}OH$), gave a good linearity of molecular weight versus conversion (Fig. 1(a)), and a good linearity of $\ln([M]_0/[M])$ versus time. The polydispersity was 1.24 at the conversion of 87.5% (Table 2). However, the surfactant did not stabilize the system and the latex particles were coagulated after 2 h from the start of polymerization. Brij 97 has a hydrophile–lyophile balance (HLB) value of 12.4. HLB is an index that gives an estimate of hydrophile portion of a surfactant. It is zero for a non-hydrophile and 20 for a completely hydrophile surfactant. For an ethoxylated alcohol like Brij 97, it is calculated simply as the ethoxylate weight percentage divided by 5. Polyoxyethylene (20) oleyl ether (Brij 98, $C_{18}H_{35}(OCH_2CH_2)_{20}OH$), has a longer polyoxyethylene block and a HLB value of 15.3. Brij 98 is a popular surfactant for emulsion ATRP. In the emulsion ATRP of EHMA, it gave a good latex stability with 3.5% coagulum. The polymerization system was living and the polymer molecular weight development was well controlled. Among the surfactants investigated in this work, Tween 80 (HLB = 15.0) gave the best performance. It gave good system livingness, good control over poly(EHMA) molecular weight, and a negligible amount of coagulum. Fig. 1(d) shows the GPC curves of four poly(EHMA) samples produced with Tween 80 as the surfactant. The low molecular weight peak was from Tween 80. The poly (EHMA) molecular weight peak gradually moved to the left side as the polymerization proceeded.

Brij 98 and Tween 80 were also evaluated with the cationic surfactant DTAB as a cosurfactant. With the pair of Brij 98—DTAB, the batch started to coagulate after the polymerization proceeded for 1 h. The coagulum in the final

Table 2
Results of the emulsion ATRP of 2-ethylhexyl methacrylate—the effects of surfactant type on control of molecular weight and latex stability

Run	Surfactant type	Surfactant[a] (g)	Time (min)	Conv. (%)	$M_{n,GPC}$ (g/mol)	$M_{n,theor}$ (g/mol)	PDI_{GPC}	Particle size (nm)	Coagulum[b] (%)
S1	DTAB	0.0649	180	99.0	24,400	19,600	1.08	611	95.0
S2	MTAB	0.0709	180	99.6	25,120	19,720	2.59	625	1.0
S3	Brij 97 (HLB = 12.4)[c]	0.1494	180	87.5	20,100	19,680	1.24	304	82.0
S4	Brij 98 (HLB = 15.3)	0.2423	180	95.3	23,700	18,870	1.11	761	3.5
S5	Tween 80 (HLB = 15)	0.2726	180	96.9	24,360	19,190	1.16	365	0.0
S6	Brij 98 + DTAB	0.1211 + 0.0325	120	98.3	24,560	19,460	1.24	647	63.0
S7	Tween 80 + DTAB	0.1381 + 0.0325	180	86.8	21,230	17,186	1.09	549	47.0

EHMA: 1.766 g (8.905 mmol), surfactant: 0.21 mmol, $[EHMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[DNbpy]_0 = 100/1/0.95/0.05/2$, EHMA/water: 10/90 (v/v), temperature: 30 °C.

[a] A fixed surfactant/monomer ratio: 2.4% (mol/mol).

[b] The weight of coagulum relative to the weight of monomer initially charged.

[c] Hydrophile–lyophile balance value.

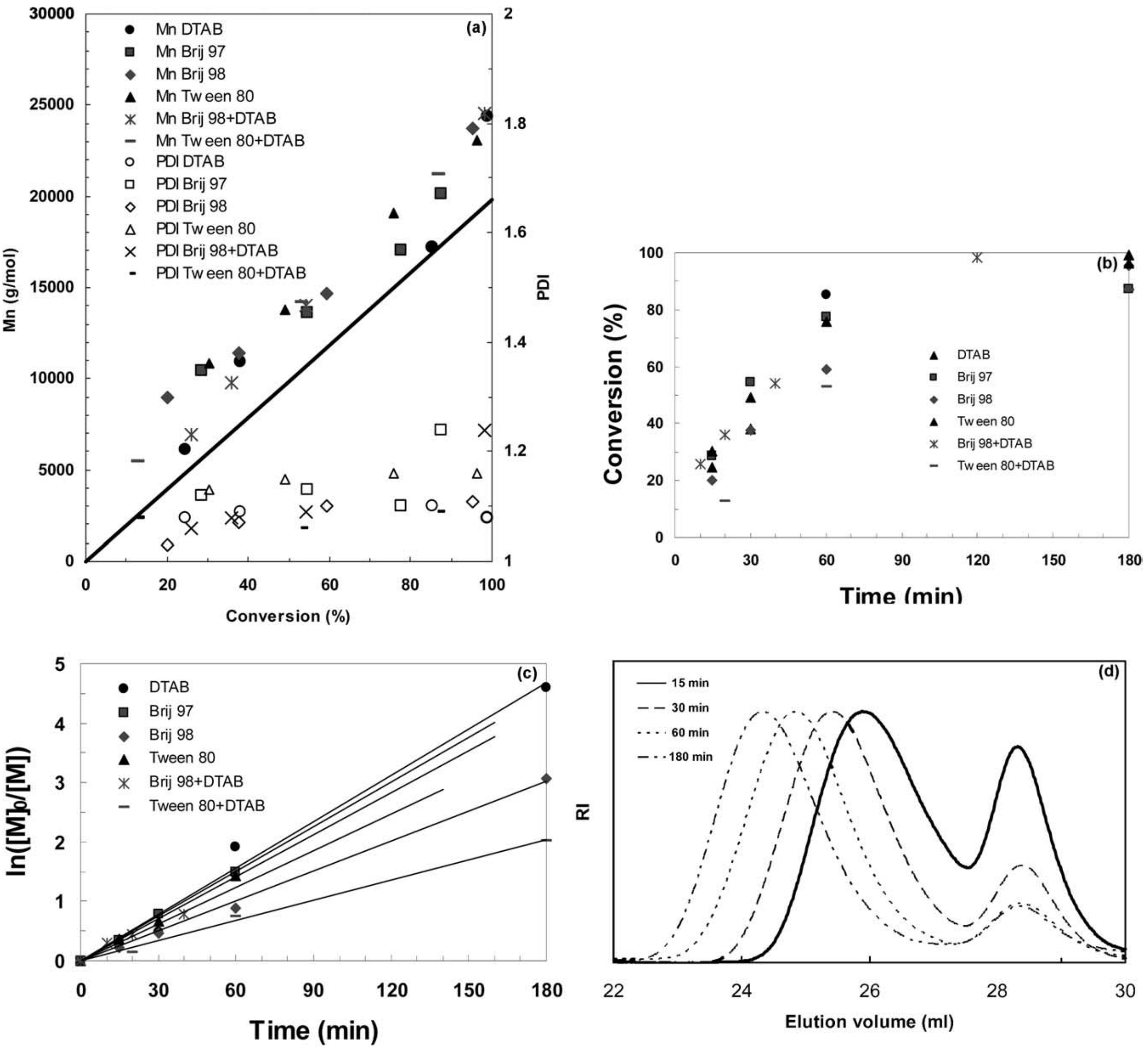


Fig. 1. (a) Molecular weight (solid symbols) and polydispersity (empty symbols) versus conversion, (b) conversion versus time, and (c) $\ln([M]_0/[M])$ versus time data for the emulsion ATRP of EHMA with various types of surfactants. The experimental conditions are: temperature: 30 °C, EHMA: 1.766 g (8.905 mmol), surfactant: 0.21 mmol, EHMA/water: 10/90 (v/v), a fixed surfactant/monomer: 2.4% (mol/mol), $[\mathrm{EHMA}]_0/[\mathrm{EBiB}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr}_2]_0/[\mathrm{DNbpy}]_0 = 100/1/0.95/0.05/2$. (d) GPC curve of the poly(EHMA) samples produced with Tween 80 as the surfactant.

sample was about 63%. With the pair of Tween 80—DTAB, the batch coagulated after 2 h with about 47% coagulum in the final sample.

In general, the system livingness and the polymer molecular weight control with all the five types of surfactants and their combinations, except for MTAB, were good. The molecular weight increased linearly with conversion and the experimental M_n data were close to their theoretical values (Fig. 1(a)). The effect of surfactant type on polymerization rate was minor (Fig. 1(b)). The $\ln([M]_0/[M])$ versus time curves were also linear (Fig. 1(c)). The polydispersity values were in the range of 1.09–1.25. Even with some highly coagulated systems, the system livingness and the molecular weight control were still good. The challenge was the latex stability. It was observed that even the least stable batches, with a severe coagulation in 30 min, gave molecular weights close to the theoretical line (e.g. DTAB). It may be because the capture of radicals by monomer droplets resulted in polymerization similar to bulk operation. The most stable systems, namely the runs with Brij 98 and Tween 80, had more pronounced deviation from theoretical line at the early stage.

3.2. *Effects of temperature*

Fig. 2 shows the kinetic data of the emulsion ATRP of

EHMA with Brij 98 as the surfactant at three temperatures (30, 50, 70 °C). The other experimental conditions were the same as in Fig. 1. The molecular weight versus conversion data appeared to be closer to the theoretical line at higher temperatures (Fig. 2(a)). At 50 and 70 °C, the experimental points almost coincided with the theoretical line, suggesting the initiator efficiencies close to unity. The effect of temperature on the polymerization rate was also significant. It took 3 h to complete the reaction at 30 °C while it needed only 1 h for the same conversion at 70 °C. The ln($[M]_0/[M]$) versus time curves remained to be linear (Fig. 2(c)). The challenge was still the latex stability. Table 3 summarized the data. The stability became worse at higher temperatures. It could be attributed to higher solubilities of the surfactant in the organic phase at higher temperatures, as observed by Qiu et al. [7].

Fig. 3 shows the effect of temperature on the emulsion ATRP of EHMA with Tween 80 as the surfactant. Its effect on the molecular weight versus conversion profile was minimal (Fig. 3(a)). The data points were almost on the same line and were close to their corresponding theoretical values. However, the higher temperature samples had lower polydispersities of about 1.1. Its effect on the polymerization rate was similar to that with Brij 98 (Fig. 3(b) and (c)). Increasing temperature expectedly shortened the polymerization time. The problem was again its effect on the latex stability. The coagulum amount was 12% at 50 °C and 10% at 70 °C (Table 3). In comparison, the samples with Brij 98 had 21% coagulum at 50 °C and 54% at 70 °C. Tween 80 may also have higher solubilities in the organic phase at higher temperatures.

We also tried a run at 0 °C and found the system had very high viscosity. The system started to coagulate soon after the start of polymerization. The final product had 95% coagulum. Mixing was a big problem due to a very high viscosity of the emulsion. The conversion data of this batch were very scattered. The operation window with temperature in the emulsion ATRP of EHMA appeared to be narrow with an optimal temperature at about 30 °C.

3.3. Effect of reactant concentrations

We also examined the operation windows of the concentrations of $CuBr_2$ and EBiB, as well as Tween 80. The data were summarized in Table 4. It appeared that an adequate surfactant amount was critical in the emulsion ATRP of EHMA. We reduced Tween 80 amount from 15.4 to 12.3% (w/w based on monomer). The coagulum increased from almost none to 61%. The kinetic data were also very scattered and were difficult to get a good reproducibility. As long as the Tween 80 amount was over the critical level, a further increase in the Tween 80 amount did not make any significant changes in the latex stability, and the relationship of molecular weight versus conversion and that of conversion versus time, as shown in Fig. 4. The effect of Tween 80 amount on particle size was evident from Table 4 with a diameter of 468 nm at 12.3% Tween 80 reduced to 253 nm at 21.6% Tween 80.

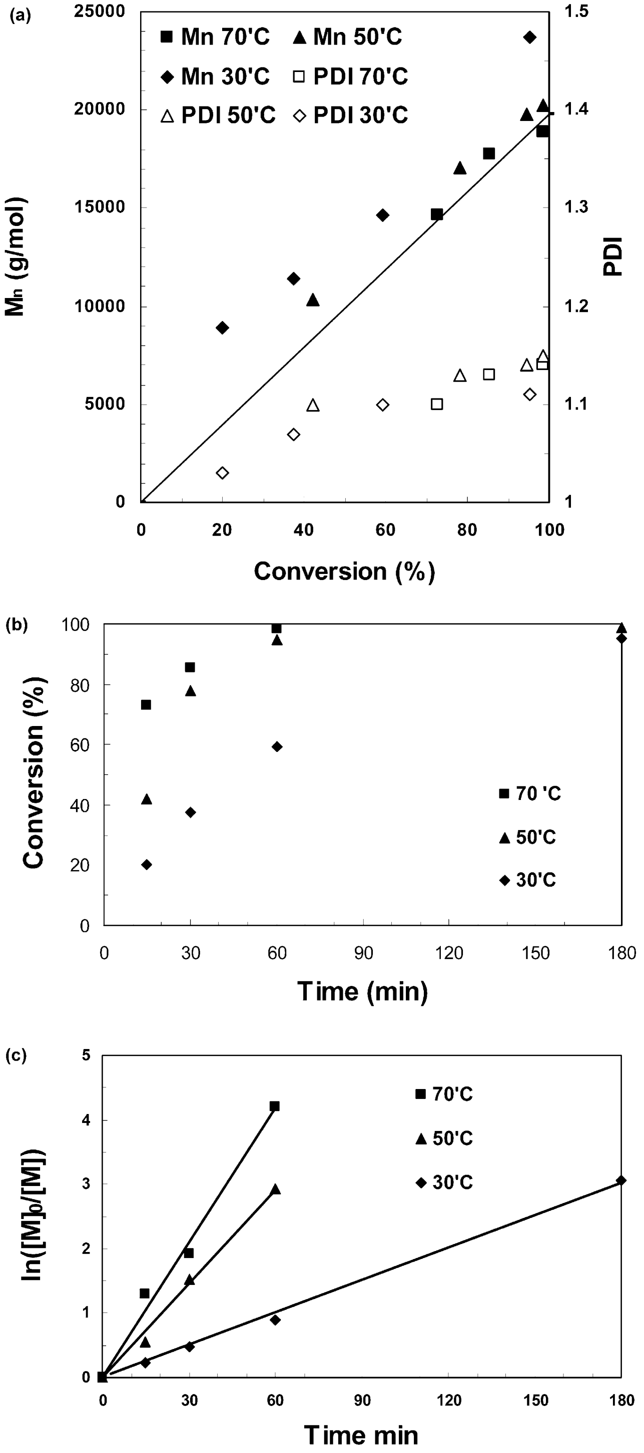


Fig. 2. (a) Molecular weight and polydispersity versus conversion, (b) conversion versus time, and (c) ln($[M]_0/[M]$) versus time for the emulsion ATRP of EHMA with Brij 98 as the surfactant at three temperatures 30, 50, and 70 °C. Brij 98/EHMA = 13.5% (w/w). The other experimental conditions are the same as in Fig. 1.

The latex stability is a real problem in controlled/living radical polymerizations. Most experimental emulsion

Table 3
Results of the emulsion ATRP of 2-ethylhexyl methacrylate—the effect of temperature on control of polymer molecular weight and latex stability

Run	Temperature (°C)	Time (min)	Conv. (%)	$M_{n,GPC}$ (g/mol)	$M_{n,theor}$ (g/mol)	PDI_{GPC}	Particle size (nm)	Coagulum (%)
TB1[a]	30	180	95.3	23,700	18,870	1.11	761	3.5
TB2	50	60	94.6	19,810	18,730	1.14	536	21.4
TB3	70	60	98.5	18,920	19,500	1.12	701	54
TT1[b]	0	180	80.5	21,000	15,940	1.1	1044	95
TT2	30	180	96.9	24,360	19,190	1.16	365	0.0
TT3	50	60	93.7	21,880	18,550	1.09	713	12
TT4	70	60	97.9	22,870	19,380	1.08	882	10

EHMA: 1.766 g (8.905 mmol), $[EHMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[DNbpy]_0 = 100/1/0.95/0.05/2$, EHMA/water: 10/90 (v/v).

[a] TB: Brij 98/EHMA = 13.7% (w/w).

[b] TT: Tween 80/EHMA = 15.4% (w/w).

ATRP systems reported in the literature used large amounts of surfactants. Different from conventional free radical polymerization, polymer chains are very short at the early stage of polymerization in ATRP. The particles are, therefore, not stable and require a large amount of surfactant to stabilize. With the increase of polymer molecular weight, the particles become more stable. A practical approach to reduce the weight percent of surfactant relative to final product is to add more monomer after the nucleation stage to prepare high molecular weight and high solid content products. This will be reported in a future paper.

$CuBr_2$ is often added to an ATRP system to facilitate the establishment of the radical/dormant species equilibrium. In most of our experimental runs, we added 5% $CuBr_2$. It was found that the addition of $CuBr_2$ was essential for narrow molecular weight distributions. Without $CuBr_2$, the system yielded an average particle diameter of 717 nm and 4.5% coagulum. With 5% $CuBr_2$, the diameter was 318 nm and the coagulum amount became negligible. However, further increasing the $CuBr_2$ amount to 10% resulted in severe coagulation with 95% coagulum. This batch started to coagulate shortly after the start of polymerization. The $CuBr_2$ addition also significantly affected the kinetic behavior. Increasing $CuBr_2$ amount reduced the polymerization rate, but resulted in a better control over the molecular weight development. Fig. 5 shows the molecular weight versus conversion data. The samples without $CuBr_2$ had the molecular weight data points far away from the theoretical line and the polydispersity values of 1.25. In comparison, the samples with 10% $CuBr_2$ had their molecular weights very close to the theoretical values and polydispersities below 1.1. It becomes clear that the amount of $CuBr_2$ in the emulsion ATRP needs to be optimized considering its combined effects on the control of polymer molecular weight and the latex stability.

The effects of initiator concentration on an emulsion

Table 4
Results of the emulsion ATRP of 2-ethylhexyl methacrylate—the effect of Tween 80, $CuBr_2$ and EBiB concentrations on control of polymer molecular weight and latex stability

Run	Tween 80 (g/g EHMA)[a]	Time (min)	Conv. (%)	$M_{n,GPC}$ (g/mol)	$M_{n,theor}$ (g/mol)	PDI_{GPC}	Particle size (nm)	Coagulum (%)
CT1	0.123	180	98.5	25,690	19,500	1.15	560	61
CT2	0.154	180	96.9	24,360	19,190	1.16	365	0.0
CT3	0.185	180	95.3	24,670	18,870	1.12	359	1.0
CT4	0.216	180	94.0	25,240	18,610	1.19	347	0.0
Run	$CuBr_2$ (g/g Cat)[b]	Time (min)	Conv. (%)	$M_{n,GPC}$ (g/mol)	$M_{n,theor}$ (g/mol)	PDI_{GPC}	$D(50)$ (nm)	Coagulum (%)
CC1	0.0	180	96.0	23,730	19,000	1.26	1064	4.5
CC2	0.05	180	96.9	24,360	19,190	1.16	365	0.0
CC3	0.10	180	93.6	20,680	19,000	1.19	333	95.0
Run	EHMA/EBiB (mol/mol)[c]	Time (min)	Conv. (%)	$M_{n,GPC}$ (g/mol)	$M_{n,theor}$ (g/mol)	PDI_{GPC}	$D(50)$ (nm)	Coagulum (%)
CI1	100	180	96.9	24,360	19,190	1.16	365	0.0
CI2	200	180	92.1	35,330	36,470	1.17	409	3.5
CI3	300	180	86.0	51,040	51,080	1.19	348	2.5

EHMA: 1.766 g (8.905 mmol), EHMA/water: 10/90(v/v), temperature: 30 °C.

[a] Tween 80 (g) varied. $[EHMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[DNbpy]_0 = 100/1/0.95/0.05/2$.

[b] $CuBr_2/(CuBr + CuBr_2)$ (g/g) varied, $[EHMA]_0/[EBiB]_0/([CuBr]_0 + [CuBr_2]_0)/[DNbpy]_0 = 100/1/1/2$.

[c] [EBiB] varied. $[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[DNbpy]_0 = 1/0.95/0.05/2$.

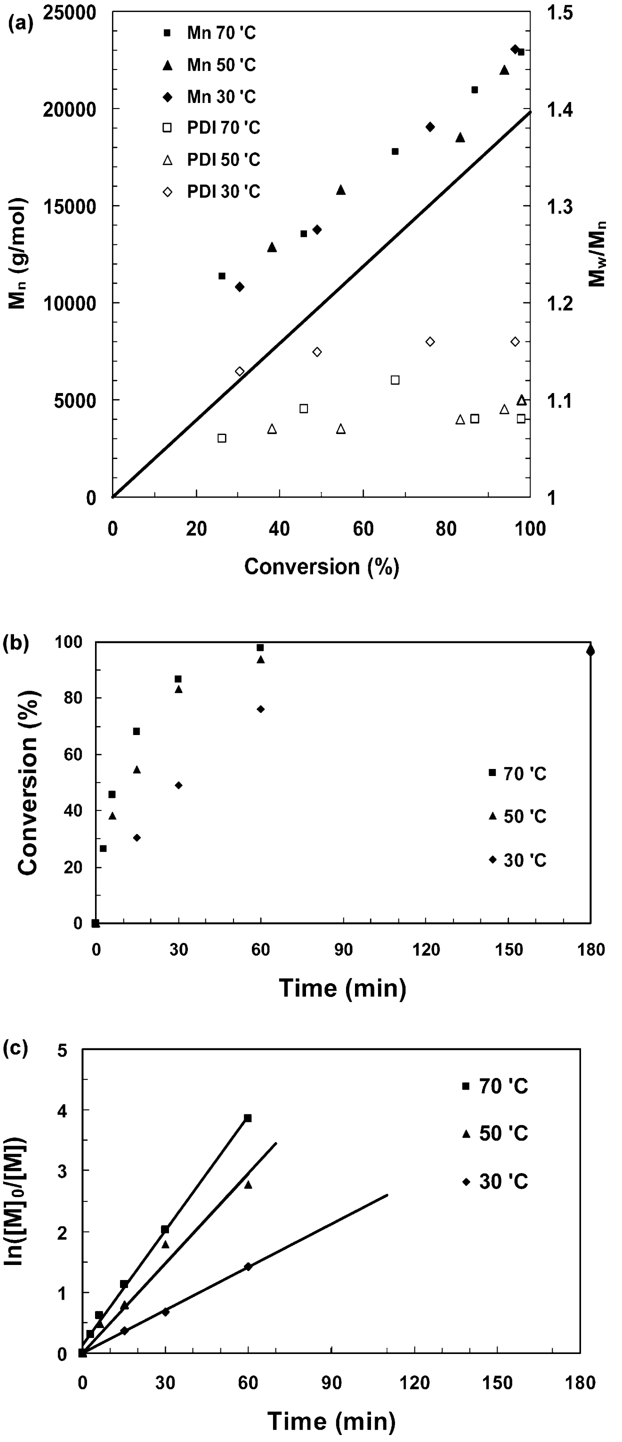


Fig. 3. (a) Molecular weight and polydispersity versus conversion, (b) conversion versus time, and (c) ln($[M]_0/[M]$) versus time for the emulsion ATRP of EHMA with Tween 80 as the surfactant at four temperatures 0, 30, 50, and 70 °C. Tween 80/EHMA = 15.4% (w/w). The other experimental conditions are the same as in Fig. 1.

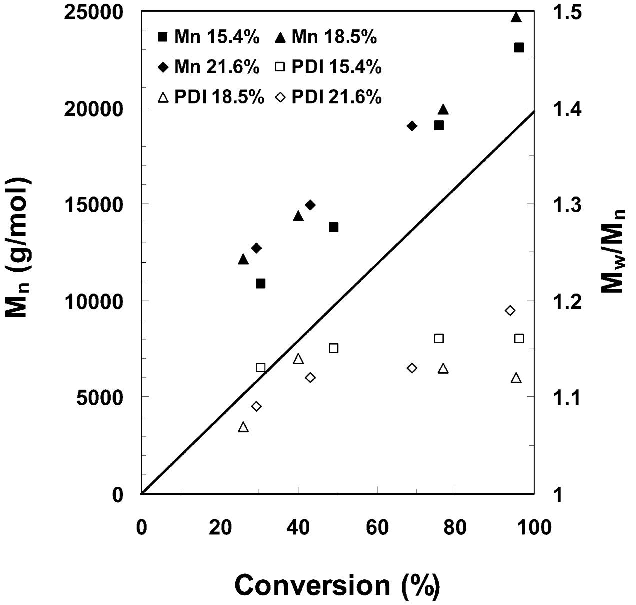


Fig. 4. Molecular weight and polydispersity versus conversion for the emulsion ATRP of EHMA at 30 °C, with three Tween 80 concentration levels. The other experimental conditions are the same as in Fig. 1.

ATRP are very complicated through partitioning between aqueous/organic phases, particle nucleation, and equilibrium of radical/dormant species. Increasing EBiB accelerated the rate of polymerization. All the runs with the different EBiB levels showed a good latex stability with negligible coagulum amounts (Table 4). The effect of initiator concentration on the particle size in the studied range was not conclusive. The particle diameter was in the range of 350–400 nm. The experimental molecular weight versus conversion data were in a good agreement with the

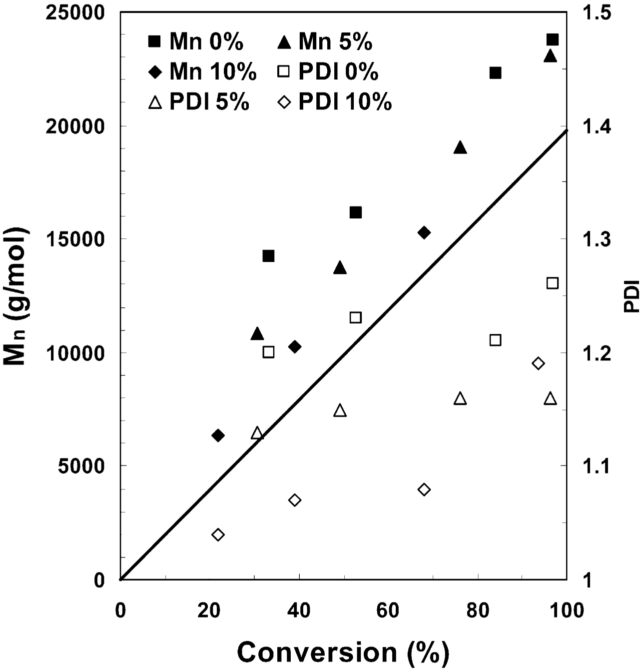


Fig. 5. Molecular weight and polydispersity versus conversion for the emulsion ATRP of EHMA at 30 °C, with three $CuBr_2$ concentration levels of $[CuBr_2]/([CuBr]+[CuBr_2])$ (mol/mol), $[EHMA]_0/[EBiB]_0/([CuBr]_0+[CuBr_2]_0)/[DNbpy]_0 = 100/1/1/2$. The other experimental conditions are the same as in Fig. 1.

theoretical values, particularly at high conversions. The data points at low conversions for $[M]_0/[I]_0=200$ and 300 were somewhat higher than the predicted values, as shown in Fig. 6. However, the polydispersities were all about 1.2. The ratio of $[M]_0/[I]_0$ determined the molecular weight of the final product. Compared to other ATRP techniques, emulsion ATRP has an advantage in preparing high molecular weight samples with high monomer conversions.

There are many fundamental aspects of the emulsion ATRP remaining to be understood. The polymerization mechanism is complicated by the solubility and partitioning of various species in aqueous and organic phases. For example, EBiB is an organic-soluble initiator and the polymerization becomes possible in the monomer droplets, referred to as microsuspension [5]. The significance of micellar nucleation relative to microsuspension depends on the partitioning of EBiB molecules, initiation and propagation rates in the aqueous and organic phases. Coullerez et al. [21] found that the ATRP rate of methoxy-capped oligoethylene glycol methacrylate in an aqueous media is two-to-three orders of magnitude higher than in bulk. If this is also true with EHMA, most polyEHMA oligomers would be generated in the aqueous phase even with a very small initiator concentration. These oligomeric chains enter micelles and nucleate polymer particles. The organic phase acts as a reservoir for the initiator molecules in the aqueous phase that are rapidly consumed by the fast propagation. This mechanism also explains the jump of the experimental molecular weight at zero conversion in the emulsion ATRP system.

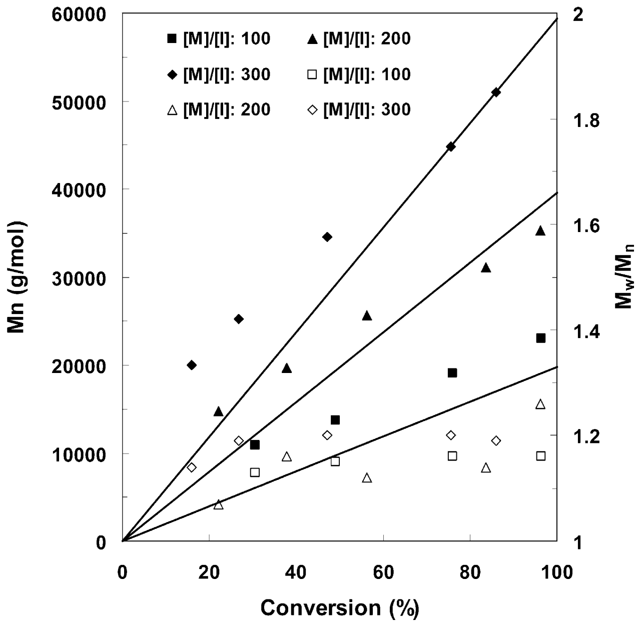


Fig. 6. Molecular weight and polydispersity versus conversion for the emulsion ATRP of EHMA at 30 °C, with three EBiB concentration levels of [EHMA]/[EBiB] (mol/mol), $[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[DNbpy]_0=1/0.95/0.05/2$. The other experimental conditions are the same as in Fig. 1.

4. Conclusions

The emulsion atom transfer radical polymerization (ATRP) of 2-ethylhexyl methacrylate (EHMA) was carried out using the catalyst system of $CuBr/CuBr_2$/4,4′-dinonyl-2,2′-bipyridyl (dNbpy) and the initiator ethyl 2-bromoisobutyrate (EBiB). The effects of surfactant type, polymerization temperature, and reactant concentration on the control of poly(EHMA) molecular weight and the stability of polymer latex were investigated. Five surfactants (DTAB, MTAB, Brij 97, Brij 98, and Tween 80) and their combinations were examined. The system livingness (evident from the linearity of M_n versus x curves and that of $\ln([M]_0/[M])$ versus t) and the control of molecular weight (evident from the linearity of M_n versus x curves and low polydispersity values) were very good, except for the runs with MTAB. The M_n data points were close to their corresponding theoretical values with high initiator efficiencies. The latex stability was a challenge. Brij 98 and Tween 80 at 30 °C gave the best results of latex stability. However, their operation windows were narrow. Increasing temperature to 50 and 70 °C significantly increased the coagulum amount. There also existed a critical surfactant concentration below, which the system resulted in severe coagulation (15.4% Tween 80). It was also found that an addition of $CuBr_2$ helped to improve the control of poly(EHMA) molecular weight, but an excess amount of $CuBr_2$ had a negative effect on the latex stability. The $[M]_0/[I]_0$ ratio was found to be an effective parameter in designing the molecular weight of the final poly(EHMA) products. The polymerization runs with $[M]_0/[I]_0$ up to 300 still produced poly(EHMA) samples with molecular weights close to the theoretical values.

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