

# Properties of Poly(*n*-butyl methacrylate) Prepared by Reverse Atom Transfer Radical Polymerization in an Aqueous Dispersed System

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**ABSTRACT:** Reverse atom transfer radical polymerization (ATRP) of *n*-butyl methacrylate (BMA) in waterborne media using Cu(II) complexes with azo initiators (i.e., reverse ATRP) was conducted. The influence of several factors, such as surfactant, catalyst, and reaction time, on the stability of the emulsion, the particle size, the morphology of the emulsion particles, and the control of the polymerization

was investigated. The results showed great differences between ATRP and conventional emulsion polymerization, especially the nucleation mechanism and the kinetics. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1542–1547, 2003

**Key words:** atom transfer radical polymerization; emulsion polymerization; morphology; nucleation

## 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).<sup>1</sup> Most of these reactions were performed in bulk or in solution, whereas those in the more challenging heterogeneous systems<sup>2</sup> were less studied. Recently, several reports have addressed emulsion or other aqueous dispersed CRPs by various methods, such as atom transfer radical polymerization (ATRP),<sup>3,4</sup> stable free-radical polymerization (SFRP),<sup>5,6</sup> degenerative transfer polymerization, and reversible addition–fragmentation chain transfer polymerization (RAFT). In these novel heterogeneous systems, colloidal stability is of great importance in addition to control over polymerization. A deeper understanding of both parameters requires much more research in this area.

Of all the types of controlled/living radical polymerization, copper-mediated waterborne ATRP thus far has been the most versatile system. It has been successfully employed for the (co)polymerization of styrene, acrylate, and methacrylates. Most studies focused on the polymerization of BMA.<sup>10–15</sup> The polymerization can start either with an alkyl halide and a

Cu(I) complex<sup>16</sup> or with a conventional radical initiator and a Cu(II) complex.<sup>17</sup> The latter process is called reverse ATRP. This process was applied to an aqueous dispersed system with a high expectation of success for two reasons: first, many water-soluble initiators used in conventional emulsion polymerization could be utilized, and, second, the initial system was easy to handle because Cu(II) species, which are stable in air, were used in place of Cu(I) species. Reverse ATRP has been employed successfully in homogenous<sup>18</sup> and in heterogeneous conditions.<sup>10</sup>

In this article an exploration of reverse ATRP of *n*-butyl methacrylate (BMA) in waterborne media is reported. The reactions were conducted using Cu(II) complexes with azo initiators. The influence of several factors, such as surfactant, catalyst, and reaction time on the stability of the emulsion, the particle size, the morphology of the emulsion particles, and the control of the polymerization was investigated. Efforts were also made to achieve a better understanding of the similarities and differences between ATRP and conventional emulsion polymerization.

## EXPERIMENTAL

### Materials

BMA was dried over CaH<sub>2</sub> and distilled under vacuum (obtained from Tianjin, China). 4,4'-Di(5-nonyl)-2,2'-bipyridine (dNbpy) was obtained from Aldrich Chemical Company and used as received. 2,2'-Bipyridine (bpy) was recrystallized from ketone. Bis(*N,N'*-dimethylaminoethyl)ether (bde) was obtained from Tokyo Kasei Kogyo Company and used as received.

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**TABLE I**  
**Typical Recipes for Polymerization of BMA by Reverse ATRP in Water**

Component		Amount
Monomer	BMA	200
Initiator	AIBN	1 equiv
Catalyst	CuCl <sub>2</sub>	1.5 equiv
Ligand	dNbpy (bpy, bde)	3 equiv (4.5 equiv)
Surfactant	Brij 35 (SDS, OP)	2 wt % vs water
Water		Monomer:water = 15:100 (w/w)

Azodiisobutyronitrile (AIBN) was recrystallized from ethanol. CuCl<sub>2</sub> was purified according to literature (obtained from Shanghai, China).<sup>19</sup> All surfactants—poly[oxyethylene-23]lauryl ether] (Brij 35, Sigma Chemical Company, USA), poly[(oxyethylene)nonyl-phenyl ether] (OP-10, Wuhan, China), and sodium lauryl sulfate (SDS, Guangzhou, China)—were from commercial sources and used as received.

### General procedure of polymerization

Table I lists the typical recipes used for reverse ATRP. Catalyst, monomer, and a magnetic stir bar were added to a 50-mL round-bottom flask. The flask was then sealed with a rubber stopper and deoxygenated by applying vacuum and backfilling with nitrogen. Then the surfactant solution (previously purged with nitrogen) was added via syringe. After an emulsion formed under stirring, the round-bottom flask was placed in an oil bath set at 80°C–85°C. The initiator was finally added, which corresponded to the zero point for the polymerization, and the polymerization was conducted for 10 h.

Monomer conversion was measured by gravimetric methods. Molecular weight and polydispersities were determined by gel permeation chromatography (GPC; Wyatt Technology Corp.). The solid recovered by gravimetry was dissolved in THF and passed through a small alumina column to remove the catalyst. After being filtered through a 0.45 μm syringe filter, the obtained colorless solution was injected onto GPC columns at 25°C, the flow phase was THF, and the flow rate was 0.8 mL/mm.

### Particle size and its distribution

Particle size (i.e., particle average diameter) was determined by dynamic light scattering. A polydispersity index value was obtained using a Malvern Autosizer Loc.

### Morphology of emulsion particles

Emulsions particle morphology was observed by transmission electron microscopy using a 100-SX transmission electron microscope. Internal particle morphologies were examined by staining emulsion with phosphotungstic acid aqueous solution.

## RESULTS AND DISCUSSION

### Effect of surfactant

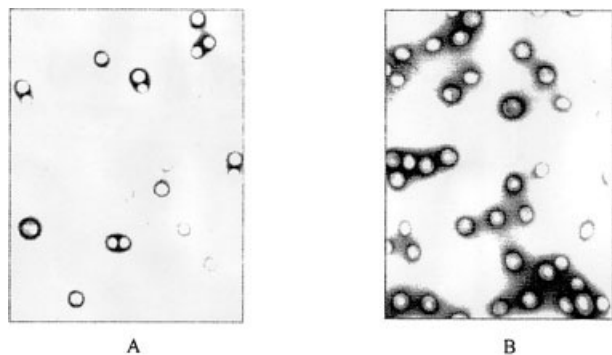
There are two main criteria for a good surfactant in an ATRP system: it should not affect the ATRP activation and deactivation processes, and it must provide a stable emulsion with a minimum amount of coagulum throughout the polymerization. According to the literature, copper-mediated ATRP of BMA in a waterborne system was investigated with various surfactants. The results indicated that polymerization could be successful in both colloidal stability and control of molecular weights and polydispersities by employing a nonionic surfactant, unlike in conventional emulsion polymerization, in which an anionic surfactant is always used. Therefore, to compare a latex's properties by atom transfer and conventional radical polymerization, BMA polymerization was conducted using an anionic surfactant, SDS, and two kinds of nonionic surfactants, Brij 35 and OP-10, which are similar in molecular structure and hydrophilic-lipophilic balance (HLB).

Conventional polymerization of BMA, using either Brij 35 or SDS, produced an excellent, very stable emulsion, no observable coagulum, and particles with smaller diameters, especially with SDS. The final average particle size was around 50 nm. But when using OP-10, no stable emulsion was obtained, and there was phase separation. There were great changes from reverse ATRP. From Table II, it can be seen that using SDS generally led to the formation of high-molecular-

**TABLE II**  
**Polymerization of BMA by Reverse ATRP in Water with Different Surfactants**

Surfactant	Particle size (nm)	Molecular weight ( $M_n$ )	Polydispersity ( $M_w/M_n$ )	Coagulum (%) <sup>a</sup>
Brij 35	114	35,440	1.28	17
SDS	105	272,000	3.8	48

<sup>a</sup> Weight percent of the coagulum versus the solid content at the final conversion.



**Figure 1** TEM micrographs ( $\times 20,000$ ) of emulsion particles: (a) prepared by conventional polymerization; (b) prepared by reverse ATRP.

weight polymers with broad polydispersities, resulting emulsions that were not very stable, and serious coagulation of the polymers during polymerization. We attributed this to the reaction of the Copper(II) chloride with the sulfate anion to form copper(II) sulfate and sodium chloride. Thus, the growing radicals could not be deactivated, as the sulfate group was not capable of being transferred to the growing radicals, and the polymerization would behave as if it were a conventional, redox-initiated radical polymerization. Using OP-10, which is similar to conventional polymerization, may lead to phase separation. It could not provide a stable emulsion, whereas, with the nonionic surfactant Brij 35 (Table II), the resulting colloids were stable, only a small amount of coagulation was observed, and the formed polymer was of low molecular weight and had low polydispersities.

Figure 1(a,b) shows the particles prepared by conventional polymerization and reverse ATRP, respectively, using the Brij 35 nonionic surfactant. Comparison of the two micrographs led to the following conclusions: (1) the morphology of the particles was spherical. In conventional polymerization the particles were regulated spherical, but with reverse ATRP there was great scaling on the surface, probably caused by the metal complex. The metal chloride  $\text{CuCl}_2$  dissolving in the aqueous phase destroyed the particles. We will discuss the effect of various factors on the morphology of particles in detail in another article. (2) The size of the particles prepared by reverse ATRP was larger than that in conventional polymerization. This probably resulted from the different ionic strengths of

the aqueous phase: when  $\text{CuCl}_2$  dissolves in the aqueous phase, ionic strength may increase, which may change the partitioning of the surfactant and enhance the rate of particle coalescence, leading to a latex with a large average particle size.

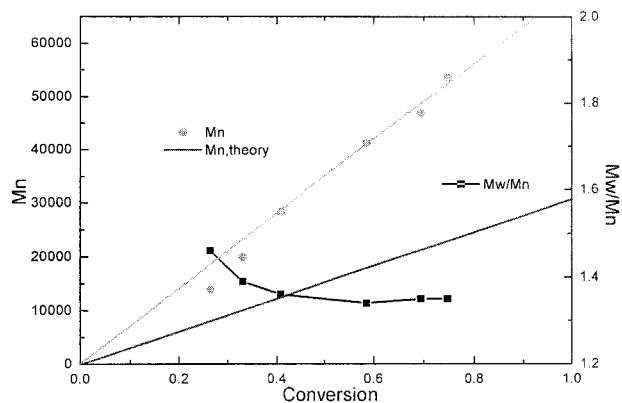
As with conventional polymerization, the final particle size and latex stability were very dependent on the quantity of the surfactant. As has already been seen in Table III, with 0.5 wt % of Brij 35 (vs. water), serious coagulum occurred; with 1% of the surfactant, the latex was much more stable, although some coagulum was still observed on the stir bar and the wall of the reaction flask, about 30% versus the solid content at 85% conversion. When the surfactant was increased to 2%, the emulsion was very stable, nearly no coagulum was observed, and smaller particle diameters were obtained.

#### Effect of catalyst

The key to a controlled radical polymerization is maintaining a fast equilibrium between the growing radicals and the dormant species. The same principle holds for aqueous dispersed systems. Because the polymer chains grow in the organic phase, the first requirement for control over polymerization is having sufficient concentrations of both the activator and the deactivator in the organic phase. Otherwise, either no polymerization or an uncontrolled polymerization would occur. Therefore, the choice of the proper ligand becomes crucial. Several common ATRP ligands, including bipyridyl and terpyridyl derivatives and aliphatic and picolyl amines, were examined for the polymerization of BMA in the aqueous dispersed media.<sup>16</sup> It was found that not every ligand that worked in bulk or solution ATRP continued to be successful in waterborne systems. Only those ligands that display sufficient hydrophobicity can bring at least some activator and deactivator into the organic phase and therefore maintain a fast equilibrium between the growing radicals and the dormant species. Ligands that form water-soluble complexes with copper halide are not effective because of a failure in establishing atom transfer equilibrium in the polymerization loci. In this study three kinds of ligands, dNbpy,<sup>20,21</sup> bpy,<sup>22</sup> and bde,<sup>23</sup> which had been successfully used by some researchers in aqueous dispersed systems, were mea-

**TABLE III**  
Polymerization of BMA by Reverse ATRP in Water with Different Amounts of Brij 35

Brij35 vs. water	Particle size (nm)	Molecular weight ( $M_n$ )	Polydispersity ( $M_w/M_n$ )	Coagulum (%)
1.0%	128.4	38,900	1.314	29
1.5%	119.9	35,800	1.263	22
2.0%	108.7	35,600	1.254	16

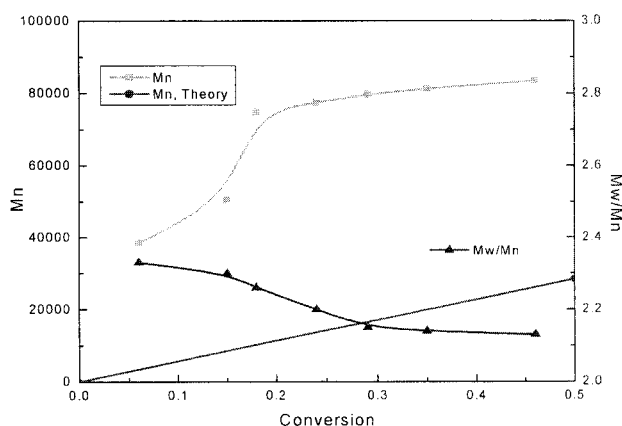


**Figure 2** Figure Dependence of molecular weight and dispersity on conversion for emulsion polymerization of *n*-butyl methacrylate by reverse ATRP using dNbpy as ligand.

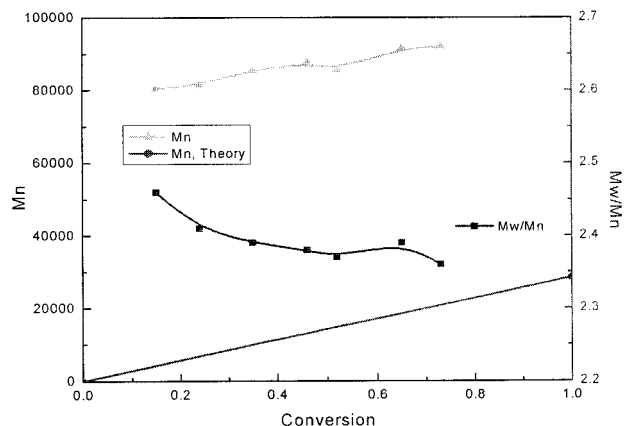
sured by reverse ATRP in aqueous dispersed system under conditions described in Table I.

Figure 2 shows the molecular weight and polydispersities of the polyBMA with conversion using dNbpy as the ligand. Two important features of controlled radical polymerization were observed in the typical reverse ATRP in the aqueous dispersed system. The first was a linear increase of molecular weight with monomer conversion, indicating that the number of chains was constant; in other words, chain transfer reactions were negligible, and the molecular weight corresponded with what was predicted by theory. The second feature was the low polydispersities of the polymer chains, meaning nearly all chains started to grow simultaneously.

Figure 3 shows the polymerization of *n*-BMA using bpy as the ligand. It can be seen that when the conversion was less than 25%, the polymerization was controlled, and the molecular weight of the poly-(BMA) increased linearly with conversion, but it did not correspond with predicted values. Polydispersities



**Figure 3** Figure Dependence of molecular weight and dispersity on conversion for emulsion polymerization of *n*-butyl methacrylate by reverse ATRP using bpy as ligand.



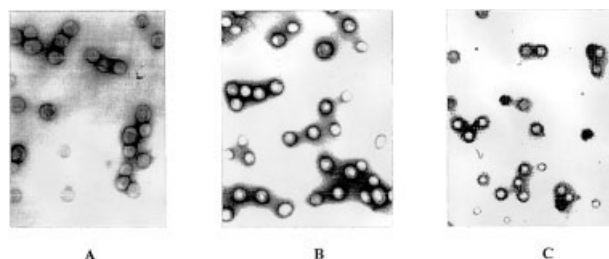
**Figure 4** Dependence of molecular weight and dispersity on conversion for emulsion polymerization of *n*-butyl methacrylate by reverse ATRP using bde as ligand.

decreased with increasing conversion, but with broad molecular weight distributions. When the conversion was greater than 25%, the molecular weight and the polydispersities did not change any more with increasing conversion, behaving like conventional radical polymerization.

Figure 4 shows the polymerization of BMA using bde as the ligand. From this figure it can be seen that the molecular weight did not increase linearly with conversion—it deviated greatly from the theoretical value, and the polydispersities were broader. The features of controlled radical polymerization were not observed clearly.

Figure 5(a–c) shows the particles prepared using, respectively, dNbpy, bpy, and bde as the ligand. A comparison of the three micrographs led to the following conclusions: the morphology of all the particles was a spherical structure, with scaling on the surface; the sizes of the particles were similar, containing some coagulum, especially the bpy and bde. So, considering both the controllability of the polymerization and the stability of the particles, dNbpy was the best of the three for polymerization.

The effect of the amount of the metal complex is shown in Table IV. The particle size was quite sensitive to the amount of the metal complex. The variation



**Figure 5** TEM micrographs ( $\times 20,000$ ) of emulsion particles prepared by different ligands: (a) dNbpy, (b) bpy, (c) bde.

TABLE IV  
Polymerization of BMA by Reverse ATRP in Water with Different Amounts of  $\text{CuCl}_2/\text{dNbpy}$

$\text{CuCl}_2/2\text{dNbpy}$ vs. AIBN	Particle size (nm)	Molecular weight ( $M_n$ )	Polydispersity ( $M_w/M_n$ )	Coagulum (%)
1.0 equiv	109.5	38,900	1.318	13
1.5 equiv	116.3	35,100	1.263	18

in particle diameters with the amount of the catalyst was more pronounced at lower levels of the surfactant. This probably resulted from the different ionic strengths of the aqueous phase. With more  $\text{CuCl}_2$  dissolved in the aqueous phase, the increasing ionic strength may change the partitioning of the surfactant and enhance the rate of particle coalescence, leading to a latex with a larger average particle size, which also explain why the particle size prepared by reverse ATRP was larger than that of conventional polymerization under nearly the same conditions.

#### Effect of reaction time

We attempted to follow the particle growth with respect to monomer conversion by measuring the particle size with light scattering. The measured particle size progressively decreased until 15%–45% conversion, and it stayed nearly constant after 45% conversion; the amount of coagulum increased with conversion (Fig. 6). Similar phenomena were observed in conventional emulsion polymerization: the measured particle size progressively decreased with conversion. This particular evolution pattern may be attributed to the nucleation mechanism. For conventional polymerization it was caused by the monomer droplet nucleation mechanism—the density of the polymer was bigger than that of the monomer, and so volume shrinkage may have led to decreasing particle size with conversion. For reverse ATRP this may arise from using a large amount of surfactant at elevated

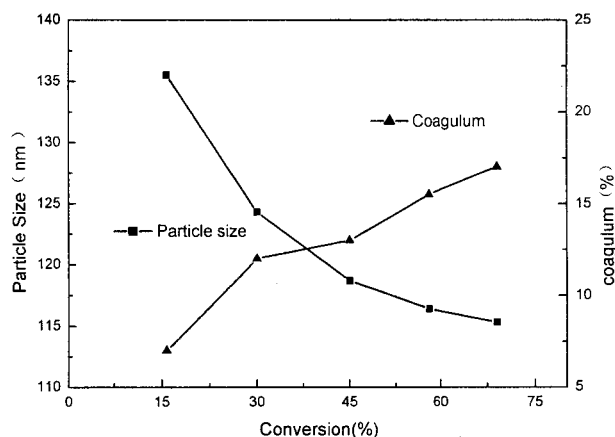


Figure 6 Particle size evolution for reverse ATRP of BMA using Brij 35 as nonionic surfactant.

temperatures or may be the result of the interference in the measurements from the free monomer droplets (low conversion), as well as the remaining monomer inside the particle (after 45% conversion, monomer particles are swollen). To study the nucleation mechanism, additional work is necessary.

Figure 7(a–e) shows the morphology of the particles obtained with conversion. From Figure 7 it can be seen that with increasing conversion, the phenomenon of scaling on a particle's surface was more serious, whereas the size of the particles decreased with increasing conversion.

#### CONCLUSIONS

In this work reverse ATRP of *n*-butyl methacrylate was successfully carried out in an aqueous dispersed system. Several surfactants were screened, and Brij 35 gave the best results in both molecular control and colloidal stability. Similar to conventional polymerization, the final particle size and the latex stability were very dependent on the amount of the surfactant. With an increasing amount of surfactant, the final particle size decreased, the latex stability increased, but the average particle size was bigger than that of the conventional polymerization, and there was great scaling on particle surfaces, which was caused by metal chloride. The choice of a proper ligand was important to the molecular control and colloidal stability. Of the three ligands studied, dNbpy gave the best results. The particle size was quite sensitive to the amount of metal complex—more  $\text{CuCl}_2$  led to a latex with a larger average particle size. Particle growth with respect to the monomer conversion also was studied. With increasing conversion, the particle size decreased, and the amount of coagulum increased. In addition, the phenomena of scaling on a particle's

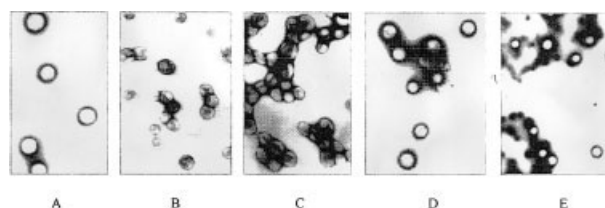


Figure 7 TEM micrographs ( $\times 20,000$ ) of emulsion particles with different reaction times: (a) 2 h, (b) 4 h, (c) 6 h, (d) 8 h, (e) 10 h.

surface was more serious. As a result, there were great differences between ATRP and conventional emulsion polymerization, especially the nucleation mechanism and the kinetics.

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