

Emulsion Copolymerization of Styrene and Butyl Acrylate by Reverse Atom Transfer Radical Polymerization

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ABSTRACT: Reverse atom transfer radical copolymerization of styrene (St) and butyl acrylate was carried out in emulsion under normal emulsion conditions, using CuBr_2/bpy complex as catalyst. The effects of surfactant type, initiator type and concentration, and CuBr_2 addition on the system livingness, polymer molecular weight control, and latex stability were examined in detail. It was found that the Polysorbate 80 (Tween 80) and azodiisobutyronitrile gave the best exhibition in this system, polymer samples were got with narrow molecular-weight dispersity ($M_w/M_n = 1.1\text{--}1.2$) and linear relationships of molecular weight versus

monomer conversion, as well as a relatively low polydispersity index (<0.1). Through the GPC and SEM analysis, the polymerization processes under these conditions showed good living/control characteristics relative to the processes under normal emulsion polymerization, although the latex stability was susceptible to the CuBr_2 catalyst. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: atom transfer radical polymerization; emulsion polymerization; copolymerization; gel permeation chromatography; molecular-weight dispersity

INTRODUCTION

Emulsion polymerization was one of the most important methods that produce polymers^{1–3}; with its advantages of low cost, fast polymerization rates, high monomer conversion, and safety, it has been proved a diverse and benign means for the industrial scale polymerization. The use of an environmental friendly solvent (water) instead of organic solvents as the dispersion medium allowed the excellent heat dissipation and could get high weight fractions of polymer, which is not easily accessible in solution or bulk polymerizations.⁴ However, as the free radical chain termination rate was rapid, the structures and constitutes of the polymers can hardly be precisely controlled by traditional emulsion polymerization, so it was radically impossible to improve the capability of the polymers through traditional way. Fortunately, controlled/living radical polymerization (CRP) provided an excellent tool to synthesize polymers with precise controlled structure and narrow molecular-weight dispersity.⁵ In the absence of termination and chain transfer reactions, the combination of CRP with emulsion polymerization has received much attention.^{6,7}

Among the several kinds of CRP, atom transfer radical polymerization (ATRP) has received signifi-

cant attention since its debut in 1995,⁸ due to its excellent controlled/living character. In addition, as its adaptability to most monomers and commercially available initiators, it has emerged as one of the most powerful synthetic techniques for preparation of well-defined polymeric material.⁹ ATRP can be widely conducted in solution, bulk,¹⁰ dispersion,¹¹ and emulsion¹² polymerization systems. Last decade has witnessed the great progress including new initiation-catalyst systems,^{13,14} new monomers,¹⁵ and new routes¹⁶ in conducting ATRP. Considering the success of emulsion in industrial processes, people naturally began to take ATRP into emulsion polymerization. Eslami and Zhu¹⁷ reported the emulsion ATRP of 2-ethylhexyl methacrylate (EHMA) with ethyl 2-bromoisobutyrate as an initiator and copper(I) bromide (CuBr)/4,4'-dinonyl-2,2'-bipyridyl (dNbpy) as a catalyst system. Peng et al.¹⁸ synthesized Poly (*n*-butyl methacrylate)-*b*-polystyrene-*b*-poly (*n*-butyl methacrylate) tri-block copolymers by emulsion ATRP. The polymerization was nearly under control, and the ATRP of styrene (St) from macroinitiators showed linear increases in the number average molecular weight (M_n) with conversion. Eslami and Zhu¹⁹ continued their research of ATRP in emulsion and reported the synthesis of block copolymer of EHMA and methyl methacrylate. The process exhibited living and good control over the polymer molecular weights, and the polymer molecular weights increased linearly with the monomer conversion, with the polydispersity <1.2 . All these research got attractive results, but there was still

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some trickiness hard to treat: besides the low initiator efficiency and monomer conversion, the colloidal stability was a constant problem. Most attempts in emulsion ATRP resulted in final products with relatively large particle size and broad particle size distribution, and the ATRP in microemulsion²⁰ is under poor performance, neither.

To the most important, the polymerization conditions of ATRP are so rigorous that even tiny amount of oxygen is not allowable in the reaction process, as the catalyst is in the reductive state. So conducting ATRP in emulsion is a far more complicated work that still needs chemists' further investigation.

Compared with normal ATRP process mentioned above, reverse atom transfer radical polymerization (RATRP) provides an easier initiation process, and the kinetic process of the two ATRP pathway is quite different.²¹ Using conventional radical initiators²² and high-valent transition metal complex, instead of the reduced transition metal complex which may easily be oxidized and hence need rigorous react condition,²³ RATRP is much easy to be industrialized and will get an extensive application in polymer design realm.

Recent years have witnessed a rapid progress in the development of RATRP in emulsion system.²⁴ Zhang et al.²⁵ conducted RATRP of St in emulsion, using Cu(II)/2,2'-bipyridine or Cu(II)/phen complexes as the catalyst, azodiisobutyronitrile (AIBN) or 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50) as the initiator, alcohol polyoxyethylene ether (Brij-98) or alkyl phenol ethoxylates (OP-10) as surfactant. The polymerization process showed living characters and the latex particles obtained from the polymerization were mean and stable when using Brij-98 as the surfactant. However, the monomer conversion remained very low when water-soluble initiator V-50 was used, although many reaction conditions such as temperature and the monomer concentration varied, which is because that the polymerization is conducted in the oil phase while most V-50 is dissolved in the water phase, leading to difficult balance establishment of the activators and the deactivators between the two phases.

As to the relatively stable submicron monomer droplets and the high shearing forces, mini emulsion RATRP proved to be more feasible. Mei and coworkers²⁶ conducted an ATRP with simultaneous reverse and normal initiation process in a miniemulsion system with the use of highly active transition-metal complexes. Simms and Cunningham²⁷ successfully conducted RATRP of *n*-BMA using the cationic surfactant hexadecyl trimethyl ammonium bromide (CTAB) at 90°C with tris[2-di(2-ethylhexyl acrylate) aminoethyl] amine (EHA₆-TREN) as ligand and 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) as thermal initiator, although some phase

separation was observed when the conversion was over 75%, we could not expect more because the amount of CTAB was as low as 1 wt % relative to monomer. Subsequently, Simms and Cunningham²⁸ synthesized poly (butyl methacrylate) in mini emulsion RATRP, a redox pair hydrogen peroxide/ascorbic acid initiation system was used. Although high molecular weight polymers with well controlled degree and narrow molecular-weight dispersity were obtained, the initiation efficiency was rather low, which was possibly due to the termination reactions occurring at the initial stage of polymerization. Min et al.²⁹ successfully prepared a series of butyl acrylate (BA)/St copolymers by ATRP in miniemulsion, using activators generated by electron transfer initiation technique.

RATRP in emulsion still faces some challenge, especially that the colloidal stability and controllability are still not so satisfactory. The selection of appropriate catalyst-ligand system, surfactant, monomer, initiator, and the type of aqueous dispersed media all displayed significant influence on latex stability and level of control over the polymerization.³⁰ Combining the industrially accessible and environmentally friendly emulsion polymerization with the living/controlled RATRP, RATRP in emulsion can be carried out under significantly simple conditions, with the polymer molecular accurately designed, which of course is quite promising to the polymerization industry.

In this article, we novelly conducted the copolymerization of St and BA in emulsion under RATRP conditions, using different initiators and surfactants. The most important point of this work is that we investigated different conditions for the emulsion RATRP process, getting the proper formula and very simple process for this new system. Further more, as far as I am aware, this may be the first example of RATRP in emulsion for a copolymerization system, which can be a great expansion for the application range of RATRP and can make it more feasible in industry, as the researches before were mostly homopolymerization process.

EXPERIMENTAL

Materials

After being washed by 5% aqueous sodium hydroxide solution and deionized water thrice, and dried by anhydrous Na₂SO₄ and CaH₂, *n*-BA (A.R.), and St (A.R.) were distilled under reduced pressure to remove the inhibitor, and then stored under nitrogen atmosphere at -15°C for use. Four kinds of initiators including potassium persulfate (KPS, A.R.), 2,2'-Azobisisobutyronitrile (AIBN, Tianjin Guangfu Chemical, A.R.), 2,2'-azobis (2-methylpropionamide) dihydrochloride (V-50, Wako, Japan), and 2,2'-azobis

[2-(2-imidazolin-2-yl) propane]dihydrochloride (VA-044, Wako, Japan) were all used as received. Copper bromide (CuBr_2 , A. R. Sinopharm Chemical Reagent) and 2,2'-bipyridine (bpy, A. R. Aladdin Chemistry) were used as received without further purification. Sodium dodecyl sulfate (SDS, A.R.), nonyl phenol poly ethyleneoxy ether (OP-10) and polyoxyethylene sorbitan monooleate (Tween 80) were both produced by Tianjin Bodi Chemical and were used as received. Deionized water was used throughout this experiment.

Polymerization

The polymerization was conducted in a 100 mL three-neck flask. Catalyst, ligand, surfactant, and initiator ($[\text{initiator}]/[\text{catalyst}]/[\text{ligand}]/[\text{monomers}] = 2/1.5/3/200$; surfactant was 2 wt % vs. water) along with St, *n*-BA, and deionized water (monomers : water = 15 : 100, w/w) were added one by one to the flask, followed by purging with pure nitrogen for 5–10 min. After a homogeneous mixture through ultrasonication, the flask was immersed in an oil bath held at the desired temperature (80°C), purged by pure nitrogen to get rid of oxygen, and stirred by a polytetrafluoroethylene muddler. At certain time intervals, samples were withdrawn from the flask for further characterization.

Characterization

Monomer conversion was determined by gravimetric method. The relative molecular weight and molecular-weight dispersity were measured by gel permeation chromatography (GPC), on a system equipped with a SHIMADZU (LC-10ADVP) pump and a RID-10A detector. THF was used as an eluant with a flow rate of 1 mL/min. The temperature of the column oven was 40°C. Monodisperse polystyrene standards were used to generate the calibration curve. Twenty microliters of each sample was injected into the column after passing through a 0.2 μm filtration membrane. Particle size and its distribution were measured by laser light scattering using Malvern Instruments Zetasizer Nano ZS-90. SEM analysis was carried out by JSM6700F Field emission scanning electron microscope, after the emulsion was diluted 20 times.

RESULTS AND DISCUSSION

Effect of ligand

To make the polymerization process under good control, the active and dormant species must be dissolved in the organic phase where the polymerization happens. The major function of the ligand is to establish the concentration equilibrium of metal

complex between water and oil phases. Obviously, not every ligand that works well in the bulk or solution ATRP is suitable in aqueous dispersed system, especially in emulsion polymerization system. It is very important to choose appropriate ligand in emulsion because only a few hydrophobic enough ligand are high efficient.³¹ However, some long substituted ligand are hard to obtain, and often with high prices. Here, we chose a correspondingly low-cost ligand of bpy to conduct polymerization. Meanwhile, the molecular structure of bpy is very similar to St, so there should be of higher concentration of bpy that can exist in the oil phase, which, as a result, makes it possible to establish good equilibrium between the activators and the deactivators in emulsion RATRP of St and *n*-BA. The results showed good performance of bpy in this RATRP emulsion system.

Effect of surfactant

Another crucial factor affecting RATRP in emulsion can be surfactant. Besides assuring colloidal stability of the latex particles, the surfactant also plays an important role in retaining the catalyst complex in the oil phase, as the reaction takes place in the monomers droplets. A good surfactant for a controlled ATRP in emulsion should at least meet the following criteria¹¹: (i) provide a stable dispersed system throughout the polymerization and (ii) do not interfere with the equilibrium between the radicals and the dormant species.

Herein, an ionic surfactant of SDS and two kinds of common nonionic surfactants, OP-10 and Tween 80, were investigated in RATRP of St and *n*-BA. Table I illustrates the polymerization results with different types of surfactants and initiators. The coagulum percentage was used as the 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. The results clearly showed that there was no polymer obtained when the anionic surfactant SDS and water soluble initiators were used. Although the conversion was high when AIBN was used, the stability was poor, with the coagulum much to 79.3%. This may be because that the ionic surfactant could poison the catalyst,^{6,7} and inhibit the Cu^{2+} being reduced to Cu^+ , leading the RATRP process could not be initiated. The absence of color change during the polymerization can prove the above conclusion. Furthermore, SDS can hardly hold the latex stability in this system, as the latex particles were coagulated after 2 h from the start of polymerization, and the system may even exhibit visible phase separation after static placement. Hence anionic surfactant SDS appeared to be

TABLE I
Results of Emulsion RATRP of Styrene and *n*-Butyl Acrylate Using Different Surfactants and Initiators

Entry	Surfactant	Initiator	Time (h)	Conversion (%)	M_n	M_w/M_n	Coagulum (%)
1	SDS	KPS	8	No polymer	27,000	3.8	79.3
2		V-50	8	No polymer			
3		VA-044	8	No polymer			
4	OP-10	AIBN	8	84.5	36,500	1.216	65.9
5		KPS	8	No polymer			
6		V-50	8	4.6			
7		VA-044	8	5.7			
8		AIBN	2	35.3			
9			4	55.6			
10			6	72.8			
11			8	89.2			
12	Tween 80	KPS	8	No polymer	14,000	1.324	0
13		V-50	8	5.1			
14		VA-044	8	6.3			
15		AIBN	2	36.3			
16			4	63.7			
17			8	83.2			
18			12	88.6			
				26,200	1.276	0	
				32,700	1.213	5.3	
				35,400	1.221	8.7	

St: 4.0 g, BA: 5.0 g, surfactant: 1.2 g. [monomers]/[initiator]/[CuBr₂]/[bpy] = 200/2/1.5/3, monomers/water: 15/100(v/v), and temperature: 80°C.

not suitable for the RATRP of St and BA. Contrary to the anionic surfactant, the two nonionic surfactants exhibited good performance in this system when the hydrophobic initiator AIBN was used. The color of polymerization systems changed from the initial light green to dark brown and finally returned to light green at the end of the reaction, indicating that the balance between the activators and the deactivators has been established.

Figure 1 shows the polymerization process when OP-10 or Tween 80 was used. The M_n increased linearly with the monomer conversion, and the molecular-weight dispersity (M_w/M_n) remained low (1.1–1.3). Figure 2 shows the kinetic plots of $\ln([M_0]/[M])$ versus reaction time for RATRP of St and BA in emulsion copolymerization, the trends are almost linear. All these characteristics proved controlled/living properties of the polymerization.

Further more, the linear relationship when Tween 80 was used is better than that when OP-10 was used, which may be caused by the different molecular structures between Tween 80 and OP-10. The unsaturated C=C in the molecule of Tween 80 may exhibit better emulsification effect in the system of St and BA. Meanwhile, the unsaturated C=C of Tween 80 molecule may copolymerize with St and BA at the water/oil interface, which made the molecular-weight dispersity a little broader when using Tween 80 as the surfactant (Table I).

Compared Tween 80 with OP-10, it was found that both Tween 80 and OP-10 gave a better performance in system livingness, control over polymer molecular weight (Fig. 1). However, there was much residue left when OP-10 was used as the emulsifier

and the latex was not very stable in the end, with a relatively high coagulum ratio of 65.9% (Table I). Thus, the Tween 80 can provide favorable stability property, and the polydispersity index (PDI) of the polymer when Tween 80 was used were relatively higher than that of OP-10, but were still very low (<1.4). So the subsequent experiments compromised by using Tween 80 as the surfactant.

Effect of initiators

Along with the ligand and surfactants, different kinds of initiators in emulsion RATRP exhibited

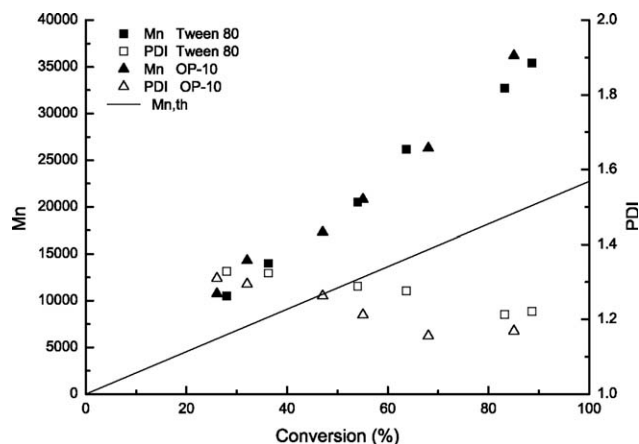


Figure 1 Evolution of molecular weight and polydispersity versus conversion for RATRP of St and BA in an emulsion copolymerization. [monomers]₀/[bpy]₀/[CuBr₂]₀/[AIBN]₀ = 200/3/1.5/2; OP-10 or Tween 80 = 2.0 wt % to water; [St]₀/[BA]₀ = 1/1; 15% solid content based on 100% conversion; 80°C. $M_{n,th} = ([M]_0 \times \text{conv.} \times M_0) / (2 \times f \times [AIBN]_0)$, assuming the initiation efficiency of AIBN.

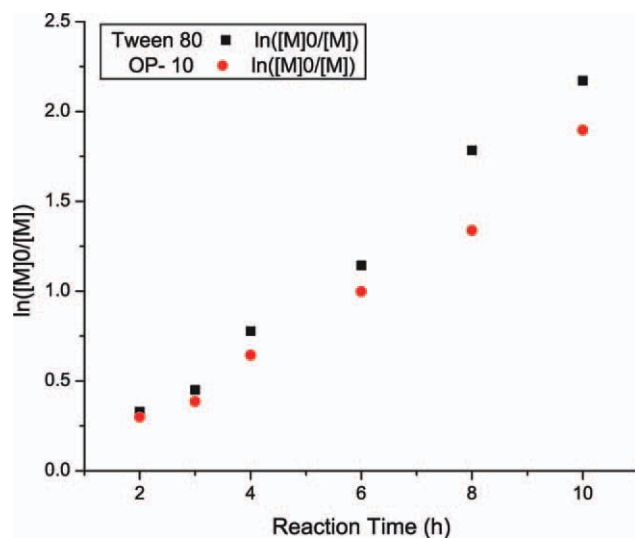


Figure 2 Evolution of $\ln([M]_0/[M])$ versus reaction time for RATRP of St and BA in an emulsion copolymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

diverse capability. Emulsion RATRP of *n*-butyl methacrylate²² has been carried out successfully by using the two widely used water-soluble initiators V-50 and VA-044. However, the two azo initiators exhibited inefficiently when they were used in this St and BA emulsion RATRP copolymerization system, no matter under what kind of reaction conditions. As is shown in Table I, there was only little polymer left after a long reaction time (>8 h), the conversion was even not reach 10%. Even more, the stability of the emulsion system was too bad that all the outcomes became layered soon. It was also very poor when the KPS was used. We reckon that the water soluble initiators are not suitable for this system, as they are generally soluble in water so that the radical mediators cannot diffuse immediately from the monomer droplets where most of the monomers exit into the growing particles (the polymerization loci), thus it is very difficult to establish the balance of the activators and the deactivators between the oil and water phases. Furthermore, the small part of the initiator in the oil phase tended to move to the interface because of its hydrophilicity so that the polymerization initiated by the initiators would diffuse into water. As a result, the polymerization may terminate easily. To the contrary, the

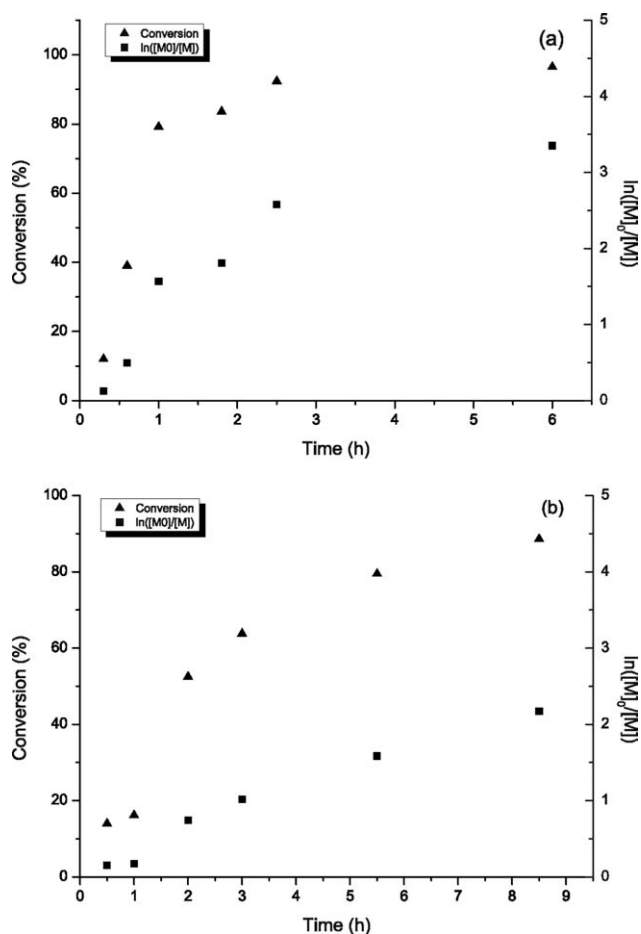


Figure 3 (a) Dependence of monomer conversion and $\ln([M]_0/[M])$ on the polymerization time without catalyst/ligand system, respectively. (b) Dependence of monomer conversion and $\ln([M]_0/[M])$ on the polymerization time with catalyst/ligand system, respectively.

hydrophobic initiators can avoid these matters. All the experiments initiated by AIBN showed good initiate efficiency, and the polymerization was well controlled.

As is shown in Figure 1, the experimental values of molecular weight were much higher than the theoretical ones when AIBN is used as initiator. This phenomenon illustrates that the initiator efficiency of AIBN here is relatively low, which may be caused by the presence of CuBr_2 . This is a troublesome of RATRP, the ions of catalyst existing in the reaction system threaten the initiators, and the initiator efficiency in RATRP system is generally very low.

TABLE II
Results of Emulsion Copolymerization of Styrene and *n*-Butyl Acrylate Using Tween 80 as Surfactant

Reaction time (h)	0.3	0.6	1.0	1.8	2.5	6.0
Monomer conversion (%)	12.2	39.5	79.2	83.6	92.4	96.5
M_n	16,100	16,630	17,350	17,600	18,100	18,200
M_w/M_n	1.93	2.23	2.41	2.63	2.72	2.81

St: 4.0 g, BA: 5.0 g, surfactant: 1.2 g. [monomers]/[initiator] = 200/2, monomers/water: 15/100 (v/v), temperature: 80°C.

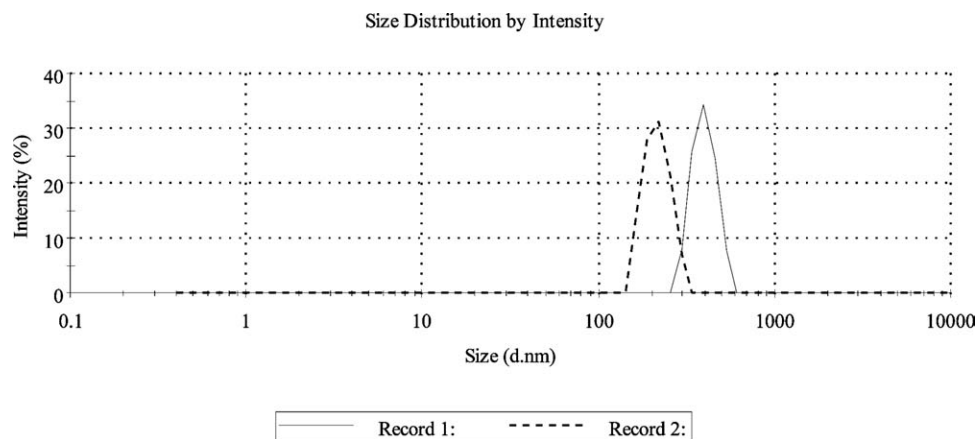


Figure 4 Size distribution by intensity of the latex prepared with (Record 2) and without (Record 1) catalyst/ligand system, respectively. The entry is the same as in Figure 1.

Normal emulsion copolymerization of St and BA

A contrast experiment was taken to verify that the catalyst CuBr_2 indeed acted on the control of the polymerization. As is shown in Figure 3(b), at the beginning of the polymerization, M_n reached a high scalar in a short time, indicating that the polymerization was not being controlled at this moment, and the process was not the first-order kinetics at this process. It was due to the long-time establishment of the balance between the activators and the deactivators, which can take 30–60 min, and the change of color certified this deduction. After the balance was

established, the M_n increases with the monomer conversion and they are in a linear relationship on the whole, indicating that the number of chains is constant, and the value of $M_{n,\text{GPC}}$ is primarily consistent with the corresponding theoretical number average molecular weight ($M_{n,\text{th}}$). In the whole polymerization process, PDI is generally lower than 1.3, meaning high initiating efficiency and nearly all the chains begin to grow simultaneously. The plot of $\ln([M]_0/[M])$ verse reaction time is almost linear [Fig. 3(b)], indicating that the radical polymerization follows first order kinetics. All these are the most important features of living radical polymerization.

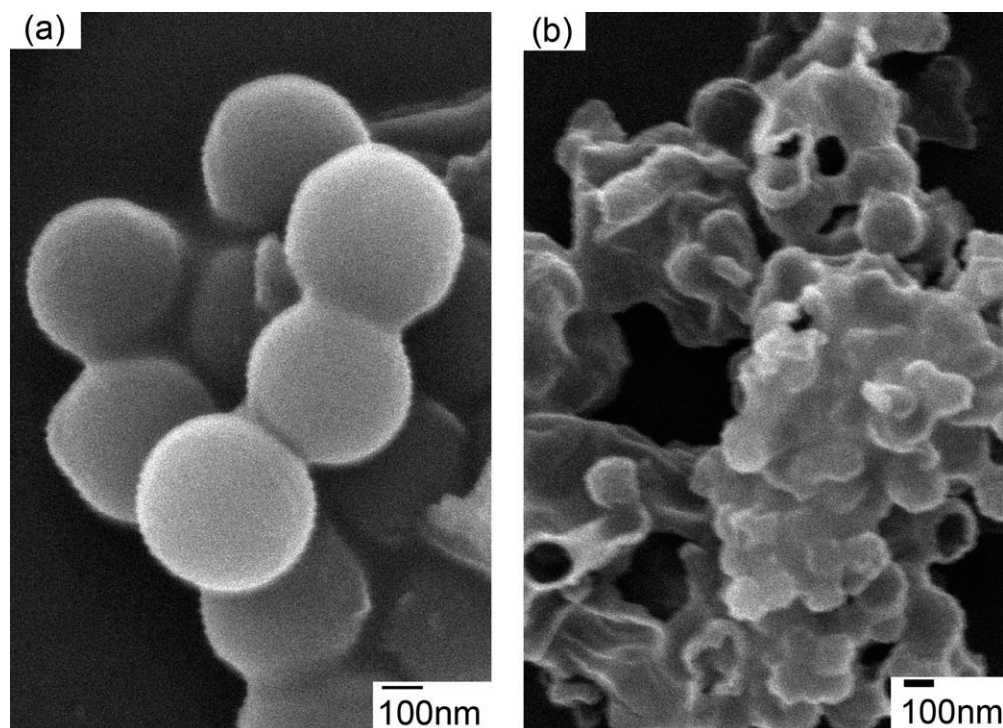


Figure 5 (a) Scanning electron microscopic images of the latex prepared without catalyst/ligand system respectively. (b) Scanning electron microscopic images of the latex prepared with catalyst/ligand system, respectively.

Table II shows the normal emulsion copolymerization results. However, the samples without CuBr_2 had the experimental molecular weight far away from the theoretical line, there was no linear relationship between $\ln([M]_0/[M])$ and time, and the molecular-weight dispersity were broad, as is shown in Figure 3(a). It is obvious that this polymerization was not under control, which in fact proceeded as the conventional radical polymerization. So the catalyst is essential for this controlled polymerization process.

Figure 4 shows the size distribution by intensity when the reaction was carried out with (Record 2) and without (Record 1) the catalyst system, respectively. The polymer particles getting from the process without catalyst had a wide PDI of 0.461, with an average size of 417.5 nm, while the latex produced by the RATRP method exhibited a relatively low PDI of 0.184, with an average particle size of 218.1 nm, much smaller than the former. All those characteristics proved the effect of the catalyst system. As the controlled/living character of RATRP process, the particle size of the polymers was relatively more uniform than those getting from normal emulsion process. This may be caused by the existence of copper ions, which affect the emulsifying capacity of surfactants. Furthermore, the catalyst system could inhibit the diffusion of monomers through droplets, as the catalyst system is hydrophilic; they soluble in the water phase and make the penetration resistance of monomers larger, so the polymer particles could not grow much larger once the droplets have been shaped.

Figure 5 shows the scanning electron microscopic images of the latex prepared by normal emulsion polymerization (a) and by RATRP emulsion system (b). Both the structures of the latexes in the two systems are global, especially those getting from normal emulsion polymerization, while the shape of the latexes in the RATRP emulsion system is relatively not so regular. This may be caused by the presence of CuBr_2 , which can affect the potential of the latex, and thus the performance of the surfactant in this system is changed. Consequently the CuBr_2 remaining in the emulsion is undoubtedly a challenge to the latex stability.

CONCLUSIONS

RATRP of St and BA in emulsion was carried out using the catalyst system of CuBr_2/bpy . Different surfactants and initiators were used. The kinetic result and particle size distribution of the polymerization indicated the controlled/living characteristics of the reaction when Tween 80 or OP-10 was used as surfactant and AIBN as initiator, polymers with relatively low polydispersity ($M_w/M_n < 1.3$) were got, and there's a linear correlation of molecular weights with monomer conversion. While the process was not controllable when using the water-solu-

ble initiators were. Tween 80 was more suitable for this system than OP-10 as its better performance at the latex stability. Compared with normal emulsion polymerization, GPC results furthermore proved the controlled effect of the catalyst system, and SEM analysis illustrated the negative effect of the catalyst on the stabilization of the system.

This work was taken under normal emulsion conditions, which will undoubtedly promote the practical applications of ATRP in emulsion. The extension of this method to other monomers and environment friendly ligand is fertile for further study.

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