

The Research of RATRP of Styrene in the Microemulsion

Haike Feng, Yi Dan

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

Received 9 September 2004; accepted 3 May 2005

DOI 10.1002/app.22384

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this paper, the reverse atom transfer radical polymerization of styrene in microemulsion was studied and some small molecular electrolyte was introduced into the microemulsion to limit the content of transition-metal in the aqueous medium by salt effect and to control the molecular weight well ulteriorly. The polymerization was carried out at 80°C, with a mechanical agitator, using 2,2'-A20-bisbutyro-nitrile (AIBN) as initiator and CuCl₂/bpy as catalyst, under N₂ atmosphere. Effects of the mole ratio of AIBN/CuCl₂/bpy, the kind and content of small molecular electrolyte on the molecular weight of the polymers, and convention of the monomer were investigated through viscosity measurement, gel permeation chromatography, and transmission electronic microscope. The results show that adding CuCl₂/bpy to the reactive system could control the increase of the molecular weight and the conversion effectively. The molecular weight and conversion would de-

crease with the increase of amount of CuCl₂. When the mole ratio of AIBN/CuCl₂/bpy is 1:2:6, the molecular weight is no more than 18×10^4 . Adding NaCl or NaBr could make the molecular weight and conversion decrease too. A linear relationship between the molecular weight and the conversion can be obtained when the amount of NaCl or NaBr reaches 1.0% to water. The distribution index of molecular weight of the system with NaCl is narrower than that of system without NaCl. What's more, latex particles' shape is spherical whose diameter is from 10 to 100 nm. All researches we have laid a foundation for further study. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1093–1099, 2006

Key words: styrene; microemulsion; atom transfer radical polymerization; reverse atom transfer radical polymerization

INTRODUCTION

Since Szwarc first reported on anionic living polymerization and defined the living polymerization as a chain-growth process without chain breaking reactions (transfer and termination), much effort has been made to find a living radical polymerization system^{1–4} and the “living”/controlled radical polymerization has attracted much attention.⁵ Wang and Matyjaszewski, for example, have successfully introduced this method into polymerization chemistry as a novel polymerization.² The “living” polymerization including cationic polymerization, anionic polymerization, radical polymerization, etc. A reactive new method to synthesize well-defined polymers and copolymers is controlled radical polymerization. In this field, several methods and systems, such as infesters, nitroxides, Cobased system, degenerative transfer with alkyl io-

ides, and most recently Ru- and Ni-mediated polymerizations, have been applied to control molecular weights and end functionalities. One of the most successful methods is atom transfer radical polymerization which allows for the polymerization of a wide range of monomers such as styrene, acrylates, and methacrylates including a variety of functional monomers (vide infra). Atom transfer radical polymerization (ATRP) is a new and prospective research of living polymerization. There is a rapid progress in this research area, and several approaches have been reported. In addition to a typical ATRP initiating system using a alkyl halide, R—X, as an initiator and a transition-metal species complexed with suitable ligands as catalyst, a “living”/controlled polymerization is observed using a conventional radical initiator (2,2'-A20-bisbutyro-nitrile; AIBN) and a transition-metal compound at high oxidation state complex with suitable ligands (2,2'-bipyridine, bpy) as a catalyst, the later is called reverse ATRP (RATRP).⁶ The RATRP is controlled easily and the activator is cheaper, it is the main reason why we adopted it. Many researches have been taken on ATRP, but the means are all limited at noumenon polymerization and suspend polymerization, and most of the polymerizations are carried out under obdurate system. There was very little report about ATRP in water system and RATRP in

Correspondence to: Y. Dan (sklpme@scu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20374036.

Contract grant sponsor: Research Foundation of Sichuan Province; contract grant number: 03JY029–054-1.

Contract grant sponsor: Talent Foundation of Sichuan Province.

microemulsion. The ATRP in microemulsion using water as medium would be fit for the heat dispersion, and it is an important factor of polymerization. The reaction about ATRP in water system having been reported cannot be well controlled, i.e., the conversion corresponding to start point of the linear curve of molecular versus conversion is too high or the linear relation is not as good as we expected. To solve this problem, we put forward a new approach by introduction of some small molecular electrolyte into the microemulsion to limit the content of transition-metal in the aqueous medium by salt effect, and to control the molecular weight well ulteriorly. In this article, we put our main attention into the research of the RATRP of styrene in microemulsion using AIBN as initiator and CuCl_2/bpy as catalyst. Effects of the mole ratio of AIBN/ CuCl_2/bpy , the kind and content of small molecular electrolyte on the molecular weight of the polymers, and the convention of the monomer will be focused on.

EXPERIMENTAL

Materials

Sodium chloride (analytic reagent grade, A.R), ethanol absolute(A.R), sodium bromide(A.R), *n*-hexanol(A.R), copper(II) chloride dehydrate(A.R), and butyric ketene (A.R) were obtained from Chengdu Kelong Chemical Reagent Factory (Chengdu, China), and were used directly. AIBN (A.R) was obtained from Beijing Chemical Reagent Factory (Beijing, China) and was used directly. Hydroquinone (A.R) was purchased from Chengdu Reagent Factory. Styrene (St) (A.R) was obtained the Tian Jin No.1 Chemical Reagent Factory (Tian Jin, China) and was distilled under reduced pressure prior to use. Sodium lauryl sulfate (SLS) was from Chengdu Kelong Chemical Reagent Factory, and was used after recrystallization using ethanol absolute as solvent. 2,2'-bipyridine(bpy) (A.R) was purchased from Beijing Shiyong Chemical Reagent Factory (Beijing, China), and used directly. Deionized water was used for all experiments.

Preparation of microemulsion of St

Under magnetic agitation, deionized water, SLS, and *n*-hexanol were charged into a beaker successively, and then St was added and mixed completely. The obtained mixture was placed for 18 h and the color of the mixture was observed and noted.

The polymerization of St

The microemulsion of St was prepared as described earlier, in which CuCl_2 was added together with SLS, and bpy and AIBN were first dissolved into St and

then charged in a reactor, which was equipped with a magnetic stirring bar and tightly sealed with a rubber septum. Then the reactor was degassed under vacuum and charged with N_2 (three times). The polymerization was carried out at 80°C for 4 h, and during the process, the sample was quickly taken out into a 25-mL weighing bottle containing certain Hydroquinone for every 30 min. Finally, the obtained polystyrene (PSt) was dried at 80°C for 36 h.

Characterization

The conversion of St

The conversion (C%) of St was measured by gravity method and was calculated by the following equation:

$$C\% = \frac{(W_3 - W_0) - (W_1 - W_0) \times 2\% - (W_2 - W_1) \times N}{(W_2 - W_1) \times M} \times 100\%$$

where W_0 is the weight of empty weighting bottle; W_1 is the weight of weighting bottle in which hydroquinone was added; W_2 is the weight of weighting bottle in which the sample was added; W_3 is the weight of dried weighting bottle; M is the weight percent of monomer to the total weight reactant; and N is the weight percent of the substances including bpy, CuCl_2 , SLS, NaCl/NaBr, and hydroquinone whose weight was not changed after reaction with the total materials. 2% meant the concentration of the hydroquinone solution.

Determination of molecular weight of the obtained PSt

The molecular weight of the obtained PSt was measured by means of viscosity measurement⁷ using Ubbelohde viscometer with 2.3 mL of measuring-ball and 0.35 mm of inner diameter capillary at $(25 \pm 0.5)^\circ\text{C}$. The sample was about 0.1–0.2 g and the solvent was butyric ketene. The molecular weight of the obtained PSt was calculated according to the following equation:

$$[\eta] = kM_\eta^\alpha$$

where $[\eta]$ is intrinsic viscosity (mL/g), M_η is molecular weight, k is 39×10^{-3} (mL/g), and α is 0.58.

The polydispersity index (PI) of St was measured on a Waters 150C gel permeation chromatography (GPC) equipped with styragel columns and adjusted using values of K and a with THF as solvent at 25°C .

TABLE I
Composition of Microemulsion

| No. | St (g) | <i>n</i> -hexanol (g) | SLS (g) | H ₂ O (g) | Phenomenon of system |
|-----|--------|-----------------------|---------|----------------------|--|
| 1 | 1.56 | 1.10 | 2.73 | 25.72 | White and viscous |
| 2 | 1.00 | 1.26 | 2.00 | 23.60 | White and viscous |
| 3 | 0.80 | 0.80 | 2.00 | 40.00 | Superstratum was white; substrate was translucence and awry |
| 4 | 2.50 | 0.50 | 1.00 | 25.00 | Translucence and azury; no delamination |
| 5 | 2.50 | 0.50 | 0.80 | 25.00 | Translucence and azury but there was some monomer on the surface |

RESULTS AND DISCUSSION

Confection of microemulsion

To get a good composition of microemulsion, we first took some experiments on the confection of microemulsion. The recipes and phenomenon of the system are shown in Table I. It can be seen that the mixture with different composition have different phenomenon. In NO.1, the mass ratio of St:*n*-hexanol:SLS:H₂O is 1.56:1.10:2.73:25.72 and there is excessive amount of SLS, which cannot dissolve well into the water. So it is not a stabilization system. NO.2 and NO.3 have the same problem as NO.1. NO.5 is deficient in amount of SLS and so the monomer (St) cannot disperse well into the water; therefore, it is not a stabilization system too. In NO.4, the mass ratio of St:*n*-hexanol:SLS:H₂O is 5:1:2:50, the solution is translucence, zury, and not delaminate, so it is a better recipe of the microemulsion of St and the researches of the article is based on this recipe.

Polymerization of St

We tried to introduce the "living" character by the way of adding AIBN/CuCl₂/bpy in the microemulsion, thereby setting a reversible balance between a conventional radical initiator (AIBN) and a catalyst composing by CuCl₂ and bpy. To test the assume, we have done many experiments according to different mole ratio of AIBN/CuCl₂/bpy, since the ratio is a key factor affecting the "living"/controlled radical polymerization. The reaction would be well controlled if the molecular weight of the obtained polymer increases with increasing convention linearly. In the reaction for all system the mole ratio of AIBN/CuCl₂/bpy was different, while the other reactants such as St, H₂O, SLS, *n*-hexanol were all in the same amount. Figure 1 shows the relationship between convention and time of samples with different mole ratio of AIBN/CuCl₂/bpy. It can be seen that there are same trend of increase of convention with the time for all systems, i.e., with increase of time, the convention increases fast initially and then becomes constant. It can also be seen from the Figure 1 that there are some differences between every curve, i.e., with the increase of content of CuCl₂ and bpy in the reaction, the time corresponding to the jumping of different curve is

different, and the extent of increase of convention for different system is also different. Furthermore, the time appearing flat at curve is different for different mole ratio of AIBN/CuCl₂/bpy and it is reached earlier if the content of CuCl₂ and bpy in the reactant is less. The relation between molecule weight and conversion is shown in Figure 2, and the curves are different for different mole ratio of AIBN/CuCl₂/bpy. When there are no CuCl₂/bpy, the molecular weight initially increases, becomes a plat, and decreases at last. When the amount of CuCl₂/bpy increases, the molecular weight increases rapidly and then comes to a constant. When the mole ratio of AIBN/CuCl₂/bpy is 1:3:6, the molecular weight of the obtained polymer increases with increasing conversion of monomer, the molecular weight increase fast in lower convention, and then become moderate in higher convention, but the final convention is not more than 30% and the molecular weight is lower than 3.5×10^4 . When the mole ratio of AIBN/CuCl₂/bpy is 1:2:6, the molecular weight of the obtained polymer increases with increasing conversion of monomer linearly except the

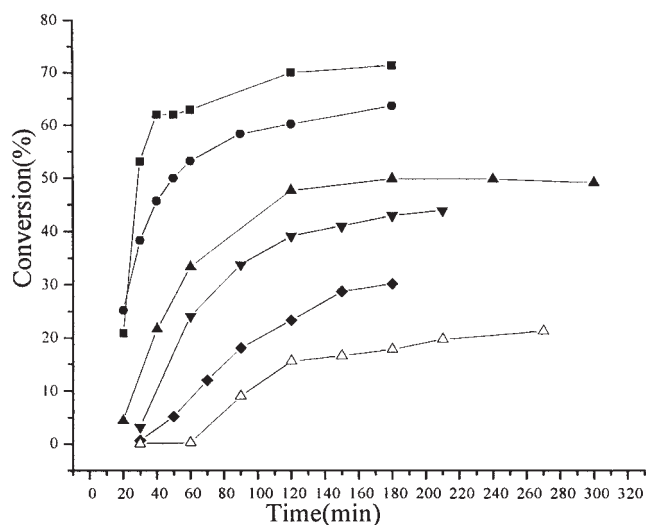


Figure 1 Conversion versus time with different mole ratio of AIBN/CuCl₂/bpy. (■) AIBN/CuCl₂/bpy(mole ratio) = 1:0:0; (▲) AIBN/CuCl₂/bpy(mole ratio) = 1:2:6; (◆) AIBN/CuCl₂/bpy(mole ratio) = 1:3:6; (●) AIBN/CuCl₂/bpy(mole ratio) = 1:1:2; (▼) AIBN/CuCl₂/bpy(mole ratio) = 1:2.5:6; (△) AIBN/CuCl₂/bpy(mole ratio) = 1:9:6.

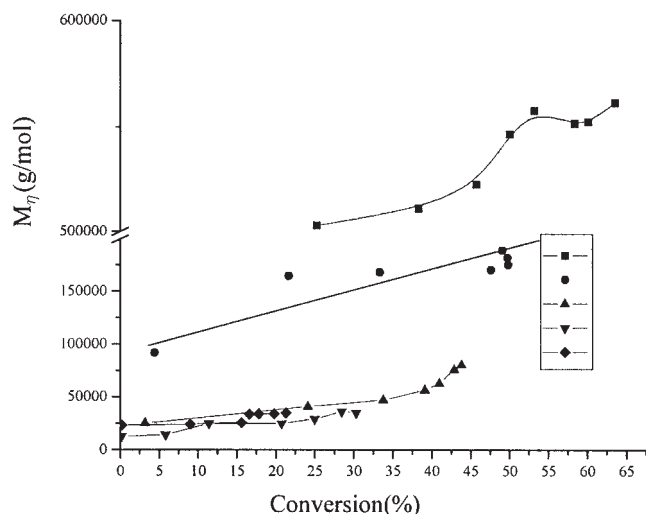


Figure 2 Molecular weight (M_n) versus conversion with different mole ratio of AIBN/CuCl₂/bpy. (■) AIBN/CuCl₂/bpy(mole ratio) = 1:1:2; (▲) AIBN/CuCl₂/bpy(mole ratio) = 1:2.5:6; (◆) AIBN/CuCl₂/bpy(mole ratio) = 1:9:6; (●) AIBN/CuCl₂/bpy(mole ratio) = 1:2:6; (▼) AIBN/CuCl₂/bpy(mole ratio) = 1:3:6.

beginning part, and the final molecular weight is about 18×10^4 , indicating that the reaction is controlled in a certain extent. From the observation of the reaction, it can also be seen that when the mole ratio of AIBN/CuCl₂/bpy is 1:2:6 and the temperature of the polymerization is 80°C, the color of the solution is first blue, then turns into gray, and lastly becomes red-brown, the reasons maybe that some part of radical is dissolved into water and complexed compound between a transition-metal species and suitable ligands is formed.

The results also show that the molecular weight of the obtained polymer does not increase with increase of conversion of monomer linearly at the beginning part. The main reason is that the decomposing of radical initiator is very fast, while the transition-metal compound complex with ligands needs some time, which is not fit for setting a dynamic equilibration between the propagating radicals and the dormant species, and the reaction cannot be controlled well.

Affect of CuX₂ and bpy

The reaction can be controlled in some degree when the mole ratio of AIBN/CuCl₂/bpy was 1:2:6. We set up system 1, system 2, and system 3 to confirm the function of CuCl₂ or bpy in the polymerization, respectively (Table II). System 1 was the system of traditional microemulsion,⁸ system 2 was the system in which CuCl₂ was added based on system 1, and system 3 was the system in which bpy was added based on system 1. Figure 3 shows the correlation between conversion and time of these systems. It can be seen

TABLE II
Composition of System 1, System 2, and System 3

| Material | System 1 | System 2 | System 3 |
|-------------------|----------|----------|----------|
| St | ✓ | ✓ | ✓ |
| H ₂ O | ✓ | ✓ | ✓ |
| SDS | ✓ | ✓ | ✓ |
| AIBN | ✓ | ✓ | ✓ |
| RON | ✓ | ✓ | ✓ |
| CuCl ₂ | — | ✓ | — |
| bpy | — | — | ✓ |

✓ indicates that the substance existed in the system; — indicates that the substance did not exist in the system.

from the Figure 3 that the conversion of monomer in system 2 is lower but that in system 3 is higher than that in system 1. From Figure 3, it can also be seen that the curve of system 2 is similar to that of system 1, whereas the curve of system 3 is different. In the curve of system 3, the conversion increasing with the increase of time is slower compared with system 1. Figure 4 shows the correlation between molecular weight and conversion. It can be seen that, for these three systems, there are no good linear relation between molecular weight and conversion, which means that the reaction are all not controlled when bpy and/or CuCl₂ do not exist in the system. The reaction can be controlled only when bpy and CuCl₂ existed in the system together just like we have discussed in the part of "polymerization of St."

Effect of small molecular electrolyte

Effect of NaCl

As we know, ATRP is based on a dynamic equilibration between the propagating radicals and the dor-

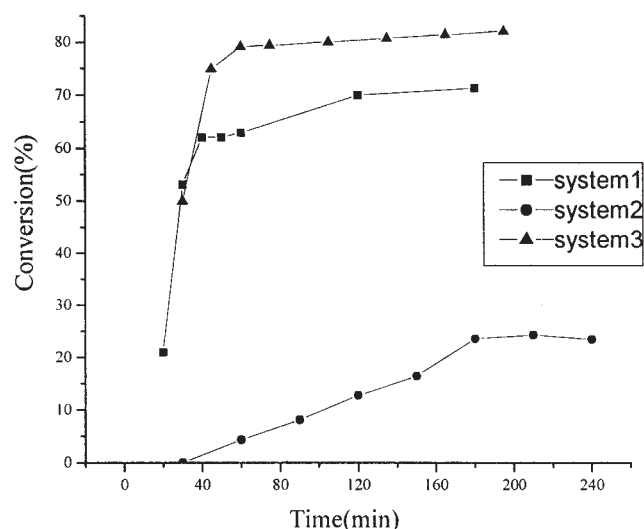


Figure 3 Conversion versus time of system 1, system2, and system3.

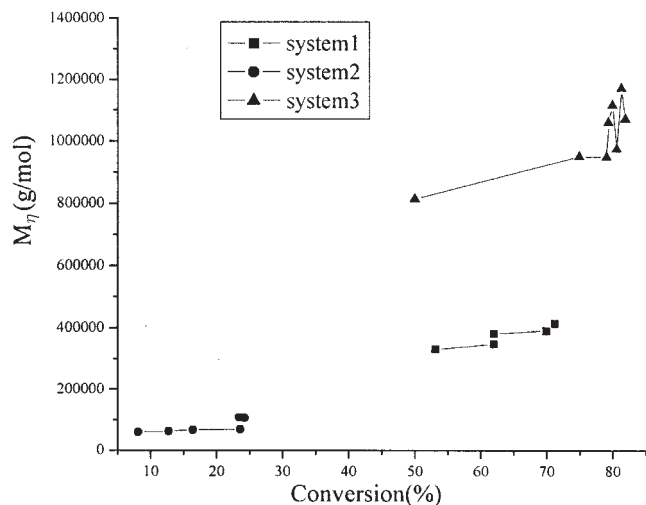
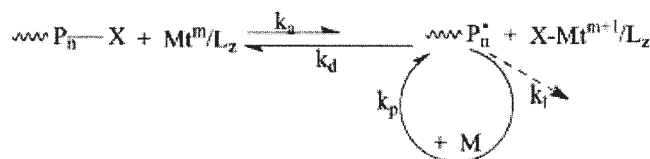


Figure 4 Molecular weight (M_n) versus conversion of system 1, system2, and system3.

mant species, which is established through the reversible transition-metal-catalyzed cleavage of the covalent carbon-halogen bond in the dormant species (Scheme 1).^{1,2} Metal salt can easily dissolve into water, but bpy cannot, and so there is a hindrance in the set up of the balance. We attempted to add some small molecular electrolyte in the microemulsion to control the amount of CuCl_2 dissolved into the water. It would be fit for the set up of balance if the effect of salt works well. When the amount of NaCl to water is from 0.5 to 1.5% (showed in Table III) and the mole ratio of AIBN/ CuCl_2 /bpy is 1:1:2, the relations of conversion versus time and molecular weight versus conversion are expressed in Figure 5 and Figure 6 respectively. Figure 5 shows that there are similar curves when the amount of NaCl to water is different, but the final conversion decreases with the increase of the amount of NaCl. From Figure 6, we can see that when the amount of NaCl to water is 0.5%, the molecular weight increases rapidly and then become a plat, and when the amount of NaCl to water was 1.5%, the molecular weight increases to a stable point and never increases with the increasing conversion. There is a good linear relation between molecular weight of the obtained polymer and conversion of monomer when NaCl to water was 1.0%, and the final molecular



Scheme 1 Atom transfer radical polymerization (ATRP) (M: monomer, Mt: metal).

TABLE III
Proportion of NaCl and NaBr to Water in Different System

| System | NaCl (%) | NaBr (%) |
|--------|----------|----------|
| 4 | 0.5 | — |
| 5 | 1.0 | — |
| 6 | 1.5 | — |
| 7 | — | 1.0 |

— indicates that the substance did not exist in the system.

weight of the polymer is not more than 10×10^4 . The result indicates that the reaction is controlled well.

Furthermore, we measured the PI of the polymer by GPC. The result shows that the molecular weight distribution of the polymer got from the system in which the mole ratio of AIBN/ CuCl_2 /bpy was 1:2:6 with NaCl to water was 1.0% was narrower than that from the system with no NaCl.

Effect of NaBr

The reaction can be controlled well if there was small molecular electrolyte in the microemulsion, so we try to test if it can work well too when NaCl was replaced by NaBr and CuCl_2 was replaced CuBr_2 , where the mole ratio of AIBN/ CuBr_2 /bpy is 1:1:2. Figure 7 shows the relationship between conversion and time and Figure 8 shows the relationship between molecular weight of polymer and conversion. It can be seen from Figure 7 that the conversion of two systems have the same increasing trend with increase of time, but the corresponding conversion in system with NaBr is higher than that in system with NaCl. From Figure 8,

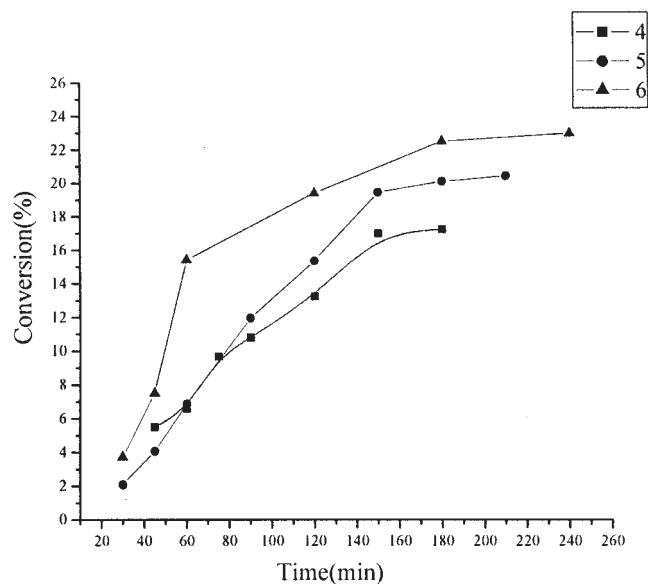


Figure 5 Conversion versus time with different amount of NaCl. (■) 0.5% NaCl; (●) 1.0% NaCl; (▲) 1.5% NaCl.

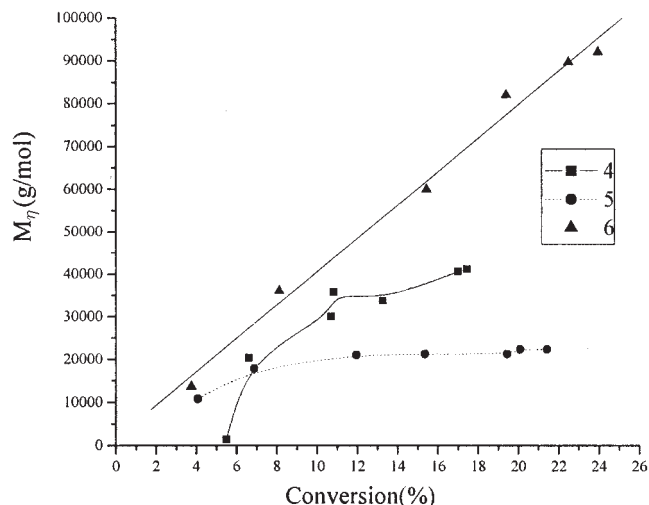


Figure 6 Molecular weight (M) versus conversion with different amount of NaCl. (■) 0.5% NaCl; (●) 1.0% NaCl; (▲) 1.5% NaCl.

it can be indicated that, when NaCl was replaced by NaBr, there is also a good linear relation between molecular weight and conversion. From Figure 8, we can also see that the effect of NaCl on the molecular weight is greater than that of NaBr and, at the same convention, the molecular weight of the polymer obtained from the system with NaCl is smaller than that from the system with NaBr. The result shows that the system with AIBN/CuBr₂/bpy just like the system with AIBN/CuCl₂/bpy is an efficient initiator system of “living”/controlled radical polymerization.

Morphology of PSt latex particles

Figure 9 shows the picture of PSt latex particles by TEM, and we can see that the latex particles are round.

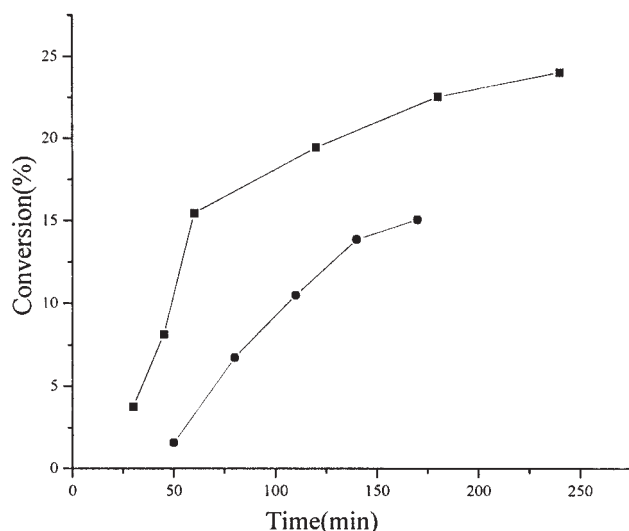


Figure 7 Conversion versus time with 1.0% NaCl (■) and 1.0% NaBr (●).

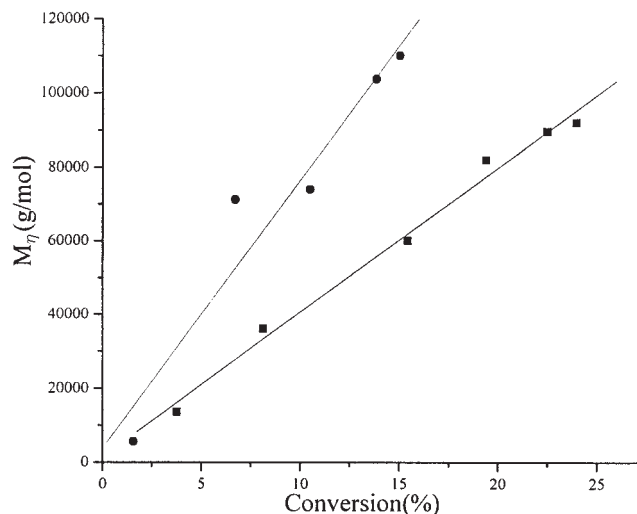


Figure 8 Molecular weight (M) versus time with 1.0% NaCl (■) and 1.0% NaBr (●).

The maximal latex particle is about 100 nm and the minimal latex particle is about 10 nm, which shows that the polymer particles with regular shape and microsize can be obtained by the RATRP in microemulsion.

CONCLUSIONS

1. The introduction of initiator system of AIBN/CuCl₂/bpy in the microemulsion can realize the controlling of polymerization to a certain extent.
2. The introduction of small molecular electrolyte in the microemulsion with initiator system of

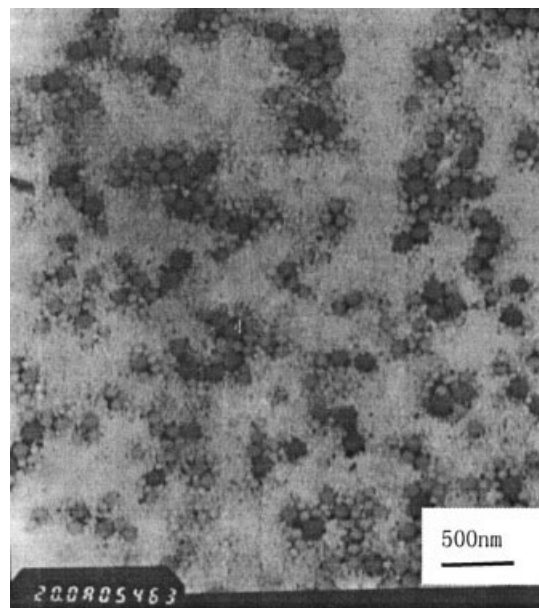


Figure 9 The picture of PSt latex particles by TEM.

AIBN/CuCl₂/bpy can make the polymerization control better, which provides a new method for realizing the "living"/controlled radical polymerization in microemulsion.

References

1. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
2. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
3. Xia, J.; Matyjaszewski, K. *Macromolecules* 1997, 30, 7697.
4. Matyjaszewski, K.; Wang, J. S. *Macromolecules* 1998, 31, 1527.
5. Szwarc, M. *Nature* 1956, 178, 1168.
6. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7572.
7. Editor Group of Chemical College of Sichuan University. *Experiments in Polymer Chemistry and Physics*; Sichuan University Press: Chengdu, China, 1998; p 34.
8. Soffer, J. O.; Bone, T. *Polym Sci* 1980, 18, 2641.