

CONTROLLED/"LIVING" RADICAL POLYMERIZATION OF STYRENE IN AN AQUEOUS DISPERSION SYSTEM

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Abstract Atom transfer radical polymerization (ATRP) of styrene catalyzed by cuprous (CuX)/1,10-phenanthroline (Phen) and CuX/CuX₂/Phen was conducted in an aqueous dispersed system. A stable latex was obtained by using ionic surfactant sodium lauryl sulfonate (SLS) or composite surfactants, such as SLS/polyoxyethylene nonyl phenyl ether (OP-10), SLS/hexadecanol and SLS/OP-10/hexadecanol. Among which SLS and SLS/OP-10/hexadecanol systems established better dispersed effect during the polymerization. It was found that Phen was a more suitable ligand than *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) to maintain an appropriate equilibrium of the activator Cu(I) and the deactivator Cu(II) between the organic phase and the water phase. The effect of several initiators (such as EBiB, CCl₄ and 1-PEBr) and the temperature on such a kind of ATRP system was also observed. The number-average molar mass (M_n) of polystyrene (PS) increased with the conversion and the molar mass distribution (M_w/M_n) remained narrow. These experimental data show that the polymerization could be controlled except for the quick increase of monomer conversion and the number-average molar mass of PS in the initial stage of polymerization. Furthermore, the initiator efficiency was found to be low (~57%) in CuX/Phen catalyzed system. To overcome this problem, Cu(II)X₂ (20 mol%–50 mol% based on CuX) was introduced into the polymerization system. In this case, higher initiator efficiency (60%–90%), low M_w/M_n of PS (as low as 1.08) were achieved and the molar masses of the PS fit with the theoretical ones.

Keywords Controlled/"Living" radical polymerization, Polystyrene, Water dispersed polymerization, 1,10-Phenanthroline

INTRODUCTION

The preparation of well-defined polymers with predictable M_n , narrow M_w/M_n and controlled architecture has been a subject of intense interest since living anionic polymerization^[1] and group transfer polymerization^[2] were discovered. The recent progress in controlled or "living" radical polymerization makes it possible to synthesize many kinds of novel polymer materials with complex structure owing to the wider range of monomers available for radical polymerization than for ionic polymerization under less rigorous conditions^[3,4]. Thus, much research effort has been devoted to controlled or "living" radical polymerization in recent years. However, most studies were confined to bulk or solution systems that have many disadvantages such as difficulty in heat transfer, slow polymerization rate, and environment pollution as well as high production cost in solution systems.

It is well known that most industrial processes of polymerization *i.e.* emulsion and suspension polymerization^[5,6], always use water as the dispersing medium. Therefore, a combination of the controlled or "living" radical polymerization with an aqueous dispersion system is able to yield well-defined polymers and copolymers.

During the past several years, many attempts have been made to confirm the feasibility of "living" radical polymerization in an aqueous dispersion system, including atom transfer radical polymerization (ATRP)^[7–14], stable free radical polymerization (SFRP)^[15–18], reversible addition fragment chain transfer radical polymerization (RAFT)^[19–21] and degenerative transfer (DT)^[22–24]. For ATRP systems, much progress has been

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made, a large amount of difficulties and problems still remain to be discovered and resolved. Recently, Matyjaszewski *et al.* reported the extension of ATRP to aqueous emulsion systems to synthesize well-defined polymers composed of butyl methacrylate (BMA), methyl methacrylate (MMA) or butyl acrylate (BA)^[8]. However, even with CuBr/4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) or CuBr/4,4'-di(alkyl)-2,2'-bipyridine (dAbpy) as catalyst, which has a high solubility in the organic phase, the polymerization of styrene in an aqueous dispersion system was still out of control^[8]. In this paper, ATRP of styrene catalyzed with CuX/1,10-phenanthroline (Phen) or CuX/CuX₂/Phen in an aqueous dispersion system is reported. To maintain the "living" character of ATRP in an aqueous dispersion system, several factors have to be considered carefully. First, the choice of the appropriate surfactants is very important. Second, the solubility equilibrium of the catalyst/ligand and the initiator between the organic phase and the aqueous phase is a crucial aspect in determining whether the reaction is under control or not.

EXPERIMENTAL

Materials

Styrene (St, CP, Shanghai No.1 Chemical Reagent Plant) was distilled twice in the presence of CaH₂ under vacuum before use. Cuprous bromide (CuBr) and cuprous chloride (CuCl) (CP, Shanghai No.1 Chemical Reagent Plant) were purified according to Ref [25] and cupric bromide (CuBr₂) (CP, Shanghai No.1 Chemical Reagent Plant) was used without purification. *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (98%, Air Production Co.) was used as received and Phen (AR, Shanghai No.3 Chemical Reagent Plant) was recrystallized with acetone. Ethyl 2-bromoisobutyrate (EBiB) was prepared according to Refs. [26, 27] and distilled twice under reduced pressure. Carbon tetrachloride (CCl₄) (AR, Shanghai No.1 Chemical Reagent Plant) was distilled twice. 1-Bromoethyl benzene (1-PEBr) (97%, Acros) was used as received. Sodium lauryl sulfonate (SLS), polyoxyethylene nonyl phenyl ether (OP-10) and hexadecanol were commercial products and used as received. Deionized water was purged with nitrogen for 30 min just before use.

Typical Recipe and Polymerization Procedure

The typical recipes for ATRP of styrene in an aqueous dispersion system are listed in Table 1. The formulation was changed only when we investigated the influence of the initiator, the catalyst and the surfactants on the polymerization.

The polymerization was performed in a 30 mL flask equipped with a magnetic stirrer bar. A typical procedure of aqueous dispersion polymerization was as follows: First, the surfactants and the catalyst/ligand were added to the dried reactor, followed by three cycles of degassing and replacing with N₂. Then the monomer, initiator and deionized water were added sequentially to the reactor through a degassed syringe. Finally, the reactor was immersed in an heated oil bath to begin the polymerization at the desired temperature and an aliquot portion of the reactant was drawn out from the reactor at a definite interval of time by a degassed syringe.

Characterization

The monomer conversion was measured gravimetrically. The obtained polymers were dried at 60 °C in an vacuum oven to constant weight. The conversion was calculated from the percentage of the recovered polymers.

The polymers recovered for determining number-average molar masses and molar mass distributions were dissolved in THF and passed through a small alumina column to remove the catalyst. Then after being filtered through a 0.2 μm membrane filter, the filtrate was injected into a GPC equipped with Waters 510 HPLC pump and Waters 410 differential refractometer. THF was used as the eluant at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration.

RESULTS AND DISCUSSION

Aqueous Dispersion Polymerization of Styrene with CuBr/Phen as Catalyst

Generally, ATRP employs transition metals as catalysts such as Cu^[28, 29], Fe^[30], Re^[31], Ru^[32] and Pd^[33], which may react with the ionic surfactant, affecting the stability of the latex. Matyjaszewski *et al.*^[8] reported that the

ionic surfactant sodium dodecyl sulfate (SDS) was not appropriate for the emulsion ATRP of BMA and the polymers had much higher molar masses than the calculated ones and broad molar mass distributions indicating an uncontrolled polymerization system. They concluded that SDS reacted with Cu(II) to generate copper(II) sulfate, which was an inefficient deactivator, and the polymerization would behave as if it was a conventional redox initiated radical polymerization. Therefore, in most reported aqueous emulsion systems^[8-14], nonionic surfactants such as poly(ethylene glycol) (PEG), poly(oxyethylene oleyl ether) (Brij98) and OP-10, were widely used. Primarily, the polymerization of styrene in water dispersion system with nonionic surfactant OP-10 was examined. Unfortunately, when the polymerization temperature was over 80 °C, the latex was unstable. On lowering the temperature to 60 °C, the latex became stable, but the polymerization was uncontrollable ($M_w/M_n > 2$) (Table 1, entry 7). In this case, it was difficult to establish the fast equilibrium between the growing species and the dormant species. In order to obtain stable latex at higher temperature (80 °C), we attempted for the first time to use the composite surfactants of sodium lauryl sulfonate (SLS) and OP-10, but the result was still not ideal (Table 1 entry 5). However, when using SLS/OP-10/hexadecanol as composite surfactant (Table 1 entry 1, 2 and 3) or only SLS (Table 1 entry 4) as surfactant, a stable latex was obtained and the polymerization was controllable at 80 °C or 90 °C. These experimental results show that the electric charge and the chemical structure of surfactants play an important role in control over the polymerization by influencing the solubility equilibrium of Cu(I)/Phen and Cu(II)/Phen.

Table 1. ATRP of St catalyzed by CuX/Phen in an aqueous dispersion system^a

Entry	<i>T</i> (°C)	Surfactant	CuX/Ligand/Initiator	Conv. (%)	$M_{n, th}^b$	$M_{n, GPC}$	M_w/M_n	f^c (%)
1	90	SLS/OP-10/ hexadecanol	CuBr/Phen/EBiB	100	12130	22600	1.48	54
2	80	SLS/OP-10/ hexadecanol	CuBr/Phen/EBiB	69	15400	29300	1.61	53
				79	17600	33000	1.54	53
				88	19250	36000	1.47	53
				100	22000	38600	1.39	57
3	80	SLS/OP-10/ hexadecanol	CuBr/Phen/EBiB	92	38270	75200	1.59	51
4	80	SLS	CuBr/Phen/EBiB	98	22000	39600	1.43	56
5	80	SLS/OP-10	CuBr/Phen/EBiB	97	22000	49200	2.16	45
6	80	SLS/hexadecanol	CuBr/Phen/EBiB	98	22000	35700	1.76	62
7	60	OP-10	CuBr/Phen/EBiB	63	13860	70400	2.07	20
8	60	SLS/OP-10/ hexadecanol	CuBr/Phen/EBiB	100	22000	44500	2.43	49
9	80	SLS/OP-10/ hexadecanol	CuCl/Phen/ CCl ₄	40	8800	42200	1.70	21
				81	16850	82500	2.13	20
10	80	SLS/OP-10/ hexadecanol	CuBr/Phen/1-PEBr	96	21120	75400	2.46	28
11	80	SLS/OP-10/ hexadecanol	CuCl/Phen/1-PEBr	100	22000	116800	2.43	19
12	80	SLS/OP-10/ hexadecanol	CuBr/PMDETA/EBiB	100	22000	87900	3.03	25

Formulation:

^a St/CuX/Phen/EBiB (1-PEBr) = 211/1/3/1 (molar ratio) (entry 3: St/CuBr/Phen/EBiB = 400/1/3/1, entry 9: St/CuCl/Phen/CCl₄ = 211/1/3/0.5, entry 12: CuBr/PMDETA = 1/1); Deionized water: 10 mL. SLS/OP-10 composite surfactants: SLS, 2.5 wt% (to water), OP-10, 2 wt% (to water); SLS/OP-10/hexadecanol composite surfactants: SLS, 2.5 (wt%, to water), OP-10, 2 wt% (to water), hexadecanol, 0.5 wt%–1 wt% (to water); SLS/hexadecanol composite surfactants: SLS, 2.5 wt% (to water), hexadecanol, 0.5 wt% (to water); SLS surfactant: 5 wt% (to water). OP-10 surfactant: 5 wt% (to water). St: 18 wt% (to water) (entry 9: 30%); Total reaction time (*t*) = 300 min (except entry 1 *t* = 315 min when Conv.% = 100%).

^b $M_{n, th}$: in case of EBiB and 1-PEBr, $M_{n, th} = M_{St} \times \text{Conv.}\% \times [M]_0/[I]_0$; in case of CCl₄, $M_{n, th} = M_{St} \times \text{Conv.}\% \times [M]_0/2[I]_0$

^c $f = M_{n, th}/M_{n, GPC}$

According to results^[8, 13] reported by our group and other researchers, there must be an appropriate partition ratio of the catalyst (both the activator Cu(I)/L and the deactivator Cu(II)/L) in the organic phase to maintain the living character of the polymerization. Otherwise, polymerization becomes uncontrollable or gives no polymer. Therefore, the selection of appropriate ligand is a key factor in determining whether the reaction is controlled or uncontrolled. Table 1 shows that Phen is much better than PMDETA for ATRP of St in an aqueous dispersion system, as in the latter case, the M_w/M_n of PS is as high as 3.03 and its M_n is much higher than the calculated one. These experimental data could be attributed to the higher water solubility of Cu(II)/PMDETA than that of Cu(II)/Phen.

Three kinds of initiator *i.e.* 1-PEBr, CCl_4 and EBiB for such an ATRP system were studied further and the results are also listed in Table 1. It is clear that EBiB shows excellent initiator efficiency, while both CCl_4 (Table 1 entry 9) and 1-PEBr (Table 1 entry 10 and 11) lead to loss of control over the polymerization. The reason for these behaviors might be complicated, but it may be responsible for the decomposition rate and the hydrolysis stability of the initiator in an aqueous dispersion system.

Figure 1 shows the polymerization kinetics of styrene with CuBr/Phen as catalyst and EBiB as initiator. The rate of polymerization of St at 80 °C is very fast at the initial stage of the reaction and conversion reaches over 60% within 50 min. A nonlinear plot of $\ln[M]_0/[M]$ versus reaction time was observed, indicating that some contribution of termination may come into effect. These experimental results may be related to the diffusion of the deactivator Cu(II)/L generated by the reaction between the activator Cu(I)/Phen and EBiB from the organic phase to water phase, leading to the shortage of deactivator Cu(II)/L in the organic phase at the beginning of polymerization. Until the solubility equilibrium of Cu(II)/Phen between the organic phase and the aqueous phase was established, the polymerization would be under better control. In this case, a very quick polymerization rate in the early stage of the reaction and a nonlinear relationship between $\ln[M]_0/[M]$ and reaction time could be expected. Figure 2 shows the dependence of M_n and M_w/M_n of the produced PS on the conversion of monomer. It indicates that M_n increases with the increase of monomer conversion and M_w/M_n gradually becomes narrow during the course of polymerization. However, the molar masses of PS measured by GPC deviate from the theoretical values ($M_{n,th}$), indicating low initiator efficiency ($\sim 57\%$).

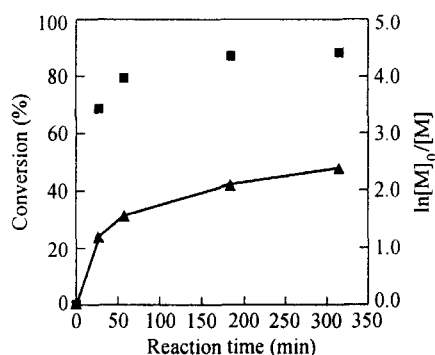


Fig. 1 Polymerization kinetics of St catalyzed and initiated by CuBr/Phen/EBiB in an aqueous dispersion system
Conditions were the same as in Table 1 entry 2.
(▲) $\ln[M]_0/[M]$; (■) Conversion

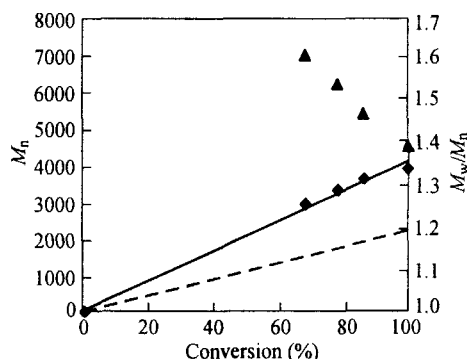


Fig. 2 Dependence of M_n and M_w/M_n on monomer conversion for ATRP of St catalyzed and initiated by CuBr/Phen/EBiB in an aqueous dispersion system
Conditions were the same as in Fig. 1.
(◆) M_n , GPC; (▲) M_w/M_n ; (---) $M_{n,th}$

Aqueous Dispersion Polymerization of Styrene with CuBr/CuBr/Phen as Catalyst

The peculiar mechanism of ATRP based on a fast equilibrium between the growing species and the dormant species, and the heterogeneous nature of the aqueous dispersion system makes it very difficult to perform the emulsion ATRP. For the CuBr/Phen catalyst system, in the initial stage of polymerization, due to the migration of

Cu(II)/Phen, there is not enough deactivator Cu(II)/Phen to control the reaction in the organic phase, leading to poor control over the polymerization.

Therefore, in order to get better control over the water dispersion polymerization of styrene, additional CuBr₂ (20 mol%–50 mol% based on CuBr) was introduced into the polymerization system. Table 2 lists the results of ATRP of St with CuBr/CuBr₂/Phen/EBiB as catalyst and initiator. The molar mass of PS increases with the increase of conversion resulting in a relatively narrow M_w/M_n (1.37–1.08) and a higher initiator efficiency (60%–90%) (see Table 2 entry 1). It is clear that much better results of controlled polymerization are achieved with CuBr/CuBr₂/Phen as catalyst. Table 2 also shows that with increasing amount of CuBr₂ from 20% (entry 5) and 30% (entry 3) to 50% (entry 1 and entry 2), the controllability over the polymerization is improved further, which is consistent with the role of CuBr₂ as a deactivator. It is of interest to find that at the same composition of CuBr/CuBr₂/EBiB (1/0.5/1, molar ratio), the final conversion of St increases with the decrease of temperature, *i.e.* from 83% (80 °C, $t = 225$ min, Table 2 entry 1) to 90% (70 °C, $t = 200$ min, Table 2 entry 6), although the distribution of molar mass is nearly same (1.13–1.17). The high conversion of monomer with decreasing amount of CuBr₂ at 80 °C, and the broad M_w/M_n were observed (see entry 3 and 4). Such experimental behaviors should be expected. In addition, the influence of surfactant concentration on polymerization was investigated as well. With increasing concentration of the surfactant SLS from 5% (entry 1 and 3) to 7.5% (entry 2 and 4), the molar masses of PS tested by GPC came closer to the calculated ones, indicating that the amount of the surfactant really plays an important part in controlling the polymerization of styrene.

Table 2. ATRP of St in water dispersion system with CuBr/CuBr₂/Phen^a as catalyst and EBiB as initiator

Entry	<i>T</i> (°C)	SLS (wt%, to water)	CuBr/CuBr ₂ /EBiB (molar ratio)	Conv. (%)	$M_{n, th}$	$M_{n, GPC}$	M_w/M_n	<i>f</i> (%)
1	80	5	1/0.5/1	20	4288	7230	1.35	60
				40	8362	11400	1.20	74
				58	12435	15100	1.17	83
				68	14597	17900	1.08	82
				83	18000	22100	1.17	82
2	80	7.5	1/0.5/1	92	15550	17300	1.16	90
3	80	5	2/0.6/1	100	24400	35100	1.28	70
4	80	7.5	2/0.6/1	100	24400	29100	1.25	84
5	70	5	1/0.2/1	91	19734	26200	1.37	75
6	70	5	1/0.5/1	90	18737	24700	1.13	76

^a CuBr/Phen = 1/3, CuBr₂/Phen = 1/3 (molar ratio); Water: 10 mL; St: 18 wt% (to water)

Total reaction time = 200 min (except entry 1 $t = 225$ min when Conv.% = 83, entry 5 $t = 165$ min)

Figure 3 shows the GPC traces of portions of PS samples removed periodically from the reactant during the polymerization. The peaks at low molar mass (ca. 200–400), which are present in each sample, are ascribed to the surfactant SLS and they become smaller as the polymerization proceeds.

The dependences of molar masses and molar mass distributions on monomer conversion shown in Fig. 3 are plotted in Fig. 4. Figure 4 indicates that M_n of PS increases linearly with increasing St conversion, and fits the calculated one. The M_w/M_n becomes narrow with increasing monomer conversion (1.08–1.35) in the course of polymerization.

Figure 5 shows the kinetics of ATRP of St catalyzed and initiated by CuBr/CuBr₂/Phen/EBiB in an aqueous dispersion system at 70 °C and 80 °C, with 20% and 50% CuBr₂ (mol%, based on CuBr), respectively. In the presence of CuBr₂, a linear relationship was observed in both cases, indicating the living nature of polymerization. The polymerization rate at 70 °C with 20% CuBr₂ is slightly faster than that at 80 °C with 50% CuBr₂, as discussed before.

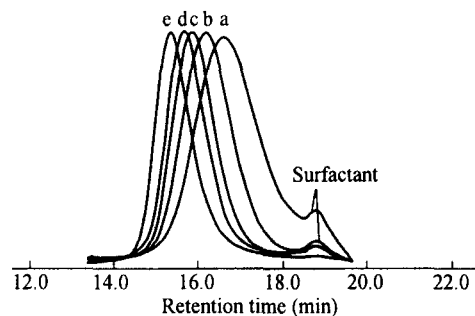


Fig. 3 GPC traces of obtained polymers as a function of conversion for ATRP of St in an aqueous dispersed system

Conditions were the same as in Table 2 entry 1.

a) Conv. = 20%, $M_n = 7230$, $M_w/M_n = 1.35$

b) Conv. = 40%, $M_n = 11400$, $M_w/M_n = 1.20$

c) Conv. = 58%, $M_n = 15100$, $M_w/M_n = 1.17$

d) Conv. = 68%, $M_n = 17900$, $M_w/M_n = 1.08$

e) Conv. = 83%, $M_n = 22100$, $M_w/M_n = 1.17$

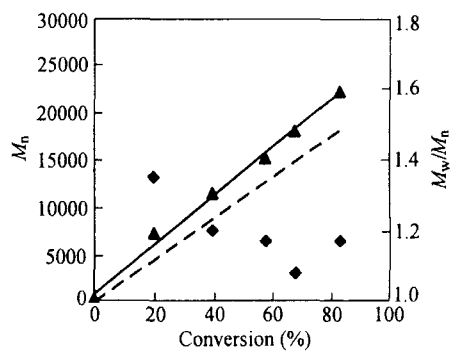


Fig. 4 Dependence of M_n and M_w/M_n on monomer conversion for ATRP of St in an aqueous dispersion system.

Conditions were the same as in Table 2 entry 1.

($\blacktriangle$) M_n , SEC; ($\blacklozenge$) M_w/M_n ; (---) $M_{n,th}$

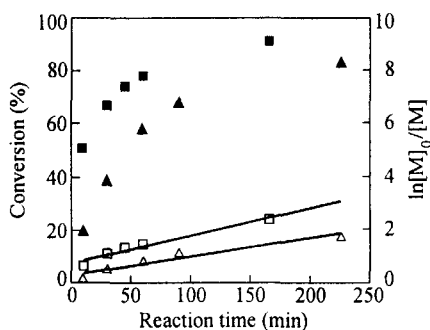


Fig. 5 Polymerization kinetics of St catalyzed and initiated by CuBr/CuBr₂/Phen/EBiB in an aqueous dispersion system

Conditions: ($\blacksquare$), ($\square$) were the same as in Table 2 entry 5; ($\blacktriangle$), ($\triangle$) were the same as in Table 2, entry 1; ($\blacksquare$) Conversion (70°C), ($\square$) $\ln[M]_0/[M]$ (70°C),

($\blacktriangle$) Conversion (80°C), ($\triangle$) $\ln[M]_0/[M]$ (80°C)

CONCLUSION

ATRP of styrene employing Phen as ligand was successfully applied to the aqueous dispersion system by using ionic surfactant SLS and composite surfactants SLS/OP-10/hexadecanol, respectively. When using CuBr/Phen as catalyst, low initiator efficiency (50 mol%), higher number-average molar masses of PS than calculated ones and broad molar mass distributions (> 1.39) were observed. This was due to the inevitable process of solubility equilibrium of Cu(II)/L between the water phase and the organic phase at the beginning of the polymerization. However, on introducing CuBr₂ (20 mol%–50 mol% based on CuBr) into the catalyst system, excellent results were achieved. In this case, the molar masses of PS measured fit well with the calculated ones and higher initiator efficiency (60%–90%) as well as low molar mass distribution (1.08–1.35) were reached. The linear plots of $\ln[M]_0/[M]$ versus reaction time were observed for ATRP of St at 70°C or 80°C in water dispersion system catalyzed and initiated by CuBr/CuBr₂/Phen/EBiB.

REFERENCES

- 1 Swzarc, M., *Nature (London)*, 1956, 178: 1168
- 2 Sogah, D.Y. and Webster, O.W., *Macromolecules*, 1986, 19: 1775
- 3 Matyjaszewski, K., Ed., *Controlled Radical Polymerization*, ACS Symp. Ser., American Chemical Society: Washington, DC, 1998, 685: 483
- 4 Matyjaszewski, K., Ed., *Controlled/Living Polymerization*, Progress in ATRP, NMP, and RAFT, ACS Symp. Ser., 2000, 768: 484
- 5 Lovell, P.A. and El-Aasser, M.S., "Emulsion Polymerization and Emulsion Polymers", John Wiley and Sons, New York, 1997, P.510
- 6 Gibert, R.G., "Emulsion Polymerization: A Mechanistic Approach", Academic Press, New York, 1995, P.1
- 7 Makino, T., Tokunaga, E. and Hogen-Esch, T.E., *ACS Polym. Prepr.*, 1998, 39(1): 288
- 8 Gaynor, S.G., Qiu, J. and Matyjaszewski, K., *Macromolecules*, 1998, 31: 5951
- 9 Qiu, J., Gaynor, S.G. and Matyjaszewski, K., *Macromolecules*, 1999, 32: 2872
- 10 Qiu, J., Pintauer, T., Gaynor, S.G., Matyjaszewski, K., Charleux, B. and Varion, J.P., *Macromolecules*, 2000, 33: 7310
- 11 Chambard, G., de Man, P. and Klumaperman, B., *Macromol. Symp.*, 2000, 150: 45
- 12 Matyjaszewski, K., Qiu, J., Tskarevsky, N.V. and Charleux, B., *J. Polym. Sci., Part A: Polym. Chem.*, 2000, 38: 4724
- 13 Wan, X.L. and Ying, S.K., *J. Appl. Polym. Sci.*, 2000, 75: 802
- 14 Matyjaszewski, K., Shipp, D.A. and Qiu, J., *Macromolecules*, 2000, 33: 2296
- 15 Bon, S.A.F., Bosveld, M., Klumperman, B., German, A.L., *Macromolecules*, 1997, 30: 324
- 16 Marestin, C., Noel, C., Guyot, A. and Claverie, J., *Macromolecules*, 1998, 31: 4041
- 17 Prodpran, E.D. and El-Aasser, M.S., *Macromol. Symp.*, 2000, 155: 1
- 18 Macleod, P.J., Barber, R., Odell, P.G., Keoshkerian, B. and Georges, M.K., *Macrol. Symp.*, 2000, 155: 31
- 19 Uzulia, I., Kanagasabapathy, J. and Claverie, J., *Macromolecules*, 2000, 150: 133
- 20 Charmot, D., Corpart, P., Adam, H., Zard, S.Z., Biadatti, T. and Bouhadir, G., *Macromolecules*, 2000, 150: 23
- 21 Moad, G., Chiefari, J., Chong, B.Y.K., Mayadunne, R.T.A., Postma, A., Rizzardo, E. and Thang, S.H., *Polym. Int.*, 2000, 49: 993
- 22 Lansalot, M., Farcet, C., Charleux, B. and Vairon, J.P., *Macromolecules*, 1999, 32: 7354
- 23 Butte, A., Storti, G. and Morvidelli, M., *Macromolecules*, 2000, 33: 3485
- 24 Farcet, C., Lansalot, M., Charlexu, B. and Pirri, R. *Macromol. Rapid Commun.*, 2000, 21: 921
- 25 Keller, R.N. and Wycoff, H.D., *Inorg. Synth.*, 1946, 2: 1
- 26 Volhardt, J., *Ann.*, 1887, 242: 161
- 27 Aunvers, K. and Bernhardt, R., *Ber.*, 1891, 24: 2220
- 28 Wang, J.S. and Matyjaszewski, K., *J. Am. Chem. Soc.*, 1995, 117: 5614
- 29 Wang, J.S. and Matyjaszewski, K., *Macromolecules*, 1995, 28: 7901
- 30 Ando, T., Kamigaito, M. and Sawamoto, M., *Macromolecules*, 1997, 30: 4507
- 31 Kotani, Y., Kamigaito, Y. and Sawamoto, M., *Macromolecules*, 1999, 32: 2420
- 32 Ando, T. and Kato, M., *Macromolecules*, 1996, 29: 1070
- 33 Lecomte, P., Drapier, I. and Dubios, P., *Macromolecules*, 1997, 30: 7631