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Atom transfer radical suspension polymerization of methyl methacrylate catalyzed by CuCl/bpy

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Abstract

Atom transfer radical suspension polymerization (suspension ATRP) of methyl methacrylate (MMA) was carried out using 1-chloro-1-phenylethane (1-PECl) as initiator, copper chloride/bipyridine (CuCl/bpy) as catalyst. The polymerization was accomplished with a mechanical agitator under the protection of nitrogen atmosphere. Apart from the dispersing agent (1% PVA), NaCl was also used in the water phase to decrease the diffusion of CuCl/bpy to water and the influence of the concentration of NaCl was investigated. Subsequently, the kinetic behavior of the suspension ATRP of MMA at different temperatures was studied. At 90 and 95 °C, the polymerization showed first order with respect to monomer concentration until high conversion. The molecular weight (M_n) of the polymer increased with monomer conversion. However, at lower temperatures, different levels of autoacceleration was observed. The polymerization deviated from first order with respect to monomer concentration when the conversion was up to some degree. The lower the temperature was, the more the deviation displayed. On comparison with bulk ATRP of MMA, the rate of suspension ATRP was much faster.

Keywords: Methyl methacrylate; Atom transfer radical polymerization; Suspension polymerization

1. Introduction

Since atom transfer radical polymerization (ATRP) was first reported in 1995 [1,2], intensive investigation has been conducted by many researchers. Large effort has been directed toward both better understanding of the reaction mechanism and enlargement of the fields of application. The role of, and the selection criteria for, each component of the polymerization mixture (monomer, initiator, transition metal, ligand, and solvent) also have been investigated in detail [3–10]. Methyl methacrylate (MMA) is a common and important monomer for radical polymerization, so the ATRP of it has been widely studied. However, with respect to the polymerization methodology, most of the ATRP of MMA were conducted in organic solutions [3,4,6,11,12], some was in bulk [13], and some was in emulsion [14]. Only a few reports have been found concerning suspension ATRP. Teyssie and co-workers briefly reported their work on the suspension ATRP of MMA using Ni complex and Pd complex as catalyst. The reaction was carried out in a sealed tube and the polymer with molecular weight distribution index (M_w/M_n) of 1.7 and 1.55 was obtained, respectively, [15,16]. Sawamoto and co-workers reported their work on suspension ATRP of MMA in water/toluene, in water and in alcohols. They used Ru complex as catalyst. The reaction was carried out in a sealed flask with a magnetic stirrer. The reaction was fast and PMMA with $M_w/M_n < 1.4$ was obtained [17].

Our research group used to report our work on suspension ATRP of styrene and MMA. We used CuCl/bipyridine (bpy) as catalyst. The reaction was conducted in an open apparatus with a mechanical agitator under the protection of nitrogen atmosphere. Apart from the dispersing agent (PVA), NaCl was used in the water phase to reduce the diffusion of CuCl/bpy complex to water. The polymer with molecular weight distribution index of 1.63–1.37 was obtained [18,19]. In this present work, we wish to report our further work of the suspension ATRP of MMA using the above catalyst. The main work was targeted on the influence of the concentration of NaCl to the polymerization and the kinetic behavior of the polymerization at different temperatures.

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2. Experimental

2.1. Materials

MMA (AR) was from Tianjin Chemical Co., China and purified by vacuum distillation before use. 1-chloro-1-phenylethane (1-PECl) was prepared from styrene and hydrochloric acid using the method of the Ref. [20]. CuCl was prepared by the reaction of copper chloride and sodium sulfite. Bpy (AR) was from Shanghai Chemical Co., China and used as received. NaCl (AR) and PVA (1788) were provided by the Chemical Plant of Nankai University, China. THF (AR) was also from Tianjin Chemical Co., China and used without further purification. Ethanol was industrial grade.

2.2. Suspension ATRP of MMA

To a 100 ml three-necked round-bottom flask, 40 ml 1% PVA aqueous solution with a certain amount NaCl was added. The solution was cycled by vacuum and nitrogen for three times in a salt-ice bath. To a 100 ml four-necked round-bottom flask, the monomer, catalyst, ligand and initiator were added. After the mixture was cycled by vacuum and nitrogen for three times in a salt-ice bath, the above aqueous solution was transferred to this four-necked flask through a rubber tube. Then a condenser, an agitator, and a thermometer were quickly installed to the flask under the protection of nitrogen. The flask was then placed in a preheated oil bath of a desired temperature. The reaction was proceeded under constant agitation and the protection of nitrogen purge. After a given time, the reaction was stopped by cold water cooling and the content in the flask was poured into 300 ml ethanol and stirred. After filtration the solid product was washed with water to remove the dispersing agent, NaCl and the catalyst residue. Then it was vacuum dried and weighed. For GPC measurement, some amount of polymer was dissolved in THF and precipitated by ethanol to further remove the residual catalyst.

2.3. Bulk ATRP of MMA

To a 50 ml two-necked round-bottom flask, the monomer, catalyst, ligand and initiator were added and a magnetic bar was introduced. The mixture was cycled between vacuum and nitrogen for three times in a salt-ice bath. Then the flask was placed in an oil bath of 85 °C. When the reaction finished, THF was added into the flask to dissolve the polymer and then precipitated by ethanol. After filtration, washing, and drying, the polymer was weighted. For GPC measurement, some amount of polymer was dissolved in THF and precipitated by ethanol to further remove the residual catalyst.

2.4. Characterization

The monomer conversion was calculated from the weight of recovered polymer. Molecular weight (M_n) and molecular weight distribution were analyzed by Waters 208 gel permeation chromatography instrument. Samples were run in THF at 25 °C, with a flow rate of 1.0 ml/min. Polystyrene standards were used for calibration. The M_n of PMMA was then calibrated using its K, α value according to the following equation:

$$\lg M_B = 1/(\alpha_B + 1) \times \lg(K_A/K_B \times M_A^{\alpha_A+1})$$

where A and B represent PS and PMMA, respectively.

3. Results and discussion

3.1. Influence of the concentration of NaCl to the suspension ATRP of MMA

In our previous work of suspension ATRP using CuCl/bpy as catalyst, we discovered that CuCl/bpy complex was somewhat hydrophilic and they could partially diffuse into the water phase. We employed the method of adding NaCl to the dispersion medium, PVA solution, to restrain the diffusion of the catalyst complex into water and the results showed that this was effective [18,19]. In this present work, the influence of the concentration of NaCl to the polymerization of MMA was further investigated and the results were showed in Table 1. We can see that without NaCl, the monomer conversion was low, the molecular weight of the polymer was very high, and the initiator efficiency was very low ($f = 0.002$). These indicate that a large amount of initiator had lost their initiation ability. However, the molecular weight distribution was reasonable narrow ($M_w/M_n = 1.50$), meaning that the polymerization in the oil phase was basically in a controlled fashion. This result indicate that in this experiment not only a large part of catalyst complex entered the water phase, but a certain amount of initiator also left the oil phase and entered the water phase. Considering that the initiator, 1-PECl, was hydrophobic and the probability of the diffusion of itself

Table 1
Influence of the concentration of NaCl to the suspension ATRP of MMA

NaCl (%)	Conv. (%)	M_n th	M_n GPC	M_w/M_n	f
0	12.39	2464	1,319,945	1.50	0.002
5	18.59	3739	876,444	1.51	0.004
10	48.11	9595	595,547	1.52	0.016
15	53.32	10,618	303,371	1.50	0.035
20	59.93	11,893	216,368	1.49	0.055
25	53.18	10,303	177,394	1.49	0.058
30	29.89	5833	159,567	1.48	0.037

$[\text{MMA}]_0 = 9.36$ M, $[\text{1-PECl}]_0 = 0.047$ M, $[\text{CuCl}]_0 = 0.047$ M, $[\text{bpy}]_0 = 0.14$ M, water phase: 1% PVA, O/W = 1/4, $T = 85$ °C, $t = 120$ min.

into the water phase was very few, we suppose that they would have entered the water by the carrying of catalyst complex. This is most probably occurred via the following mechanism: after the catalyst complex at reduction state caught the halogen atom of the initiator, the catalyst complex at oxidation state didn't divorce from the active radical center freely, they most probably still remained in a complexing state:

$$\text{R–Cl} + \text{Cu}^{\text{I}}/\text{bpy} \rightleftharpoons \text{R}^{\cdot}\cdots\text{Cl}\cdots\text{Cu}^{\text{II}}/\text{bpy}$$

Because of the hydrophilicity of the Cu^{II}/bpy, some of the radical and the catalyst complex entered into the water phase together in the form of $\text{R}^{\cdot}\cdots\text{Cl}\cdots\text{Cu}^{\text{II}}$/bpy without adding to any monomer or adding to only a few amount of monomer. In the water phase, although there still exist the above activation–deactivation equilibrium, the radical couldn't add to the monomer because the lack of monomer in the water phase. Accordingly, only the radicals in the oil phase can propagate when they were activated. This can account for the sharp deviation of determined M_n to theoretical M_n and hence the low initiator efficiency was observed. Because of the redox reaction of CuCl still exist in the oil phase, the radical was in the state of activation and deactivation equilibrium (like the above equation). Thus the termination and transfer reaction were inhibited, and the polymer with reasonably narrow molecular weight distribution was obtained.

When NaCl was added into the water phase, the polymerization rate became faster, and the initiator efficiency became higher. This indicates that the salt effect of NaCl and the common ion effect of Cl reduced the diffusion of the catalyst complex to the water phase, and the concentration of radical in the oil phase increased. From Table 1, we can also see that the reaction rate and the initiator efficiency increased with the increase of the concentration of NaCl until it reached 25%, indicating that the effective radical (including both in active and domain state) was increased with the increase of NaCl. From the conversion and the determined M_n, the concentration of the effective radical was calculated and plotted in Fig. 1. We can clearly see the increase of radical concentration with the increase of NaCl. However, when it reached 27%, both the reaction rate and the initiator efficiency slowed down. This means too much NaCl imparted some negative effect to the polymerization. In addition, when the concentration of NaCl was over 25%, the dispersing agent, PVA, partly separated out from water phase, and the dispersion effect was weakened. So we chose 20% as the concentration of NaCl in the subsequent study. From Table 1 we can see that the molecular weight distribution of the polymer not changed a lot with the addition of NaCl. This means that the addition of NaCl mainly improved the initiator efficiency, not improved the control level of the polymerization.

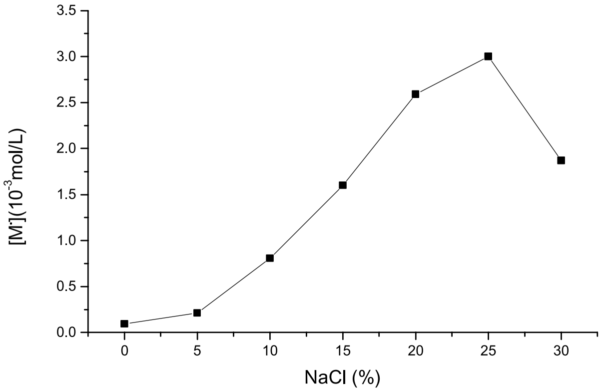

Fig. 1. Variation of the radical concentration in the oil phase with the concentration of NaCl in water phase.

3.2. Kinetic study of the suspension ATRP of MMA catalyzed by CuCl/bpy

In this section, the suspension ATRP of MMA was conducted at 75, 80, 85, 90 and 95 °C, and the kinetic behavior was examined. As well known, the radical polymerization rate can be expressed in the following equation:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{P}^{\cdot}][\mathrm{M}] \tag{1}$$

by integration of Eq. (1), the kinetic equation was obtained as:

$$\ln[\mathrm{M}]_0/[\mathrm{M}] = k_\mathrm{p}^{\mathrm{app}}t \tag{2}$$

where

$$k_\mathrm{p}^{\mathrm{app}} = k_\mathrm{p}[\mathrm{P}^{\cdot}] \tag{3}$$

From Eq. (2), we can obtain $k_\mathrm{p}^{\mathrm{app}}$ from the plot of $\ln[\mathrm{M}]_0/[\mathrm{M}]$ versus time, and then the concentration of living radical $[\mathrm{P}^{\cdot}]$ can be calculated from Eq. (3).

Fig. 2 shows the variation of conversion with time at different temperatures. One can see that the conversion

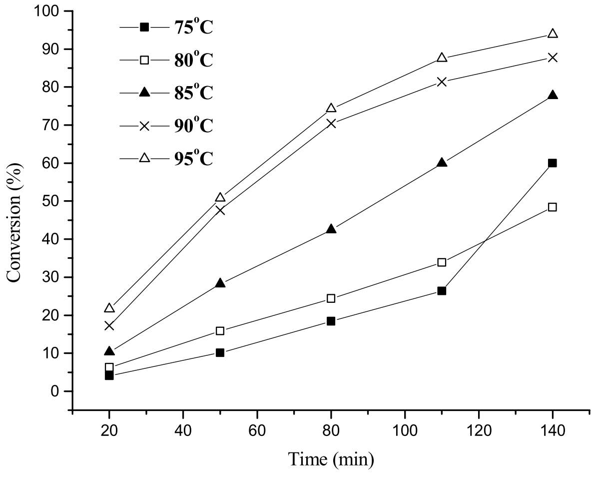

Fig. 2. Variation of conversion with time at different temperatures. $[\mathrm{MMA}]_0 = 9.36$ M, $[\text{1-PECl}]_0 = 0.047$ M, $[\mathrm{CuCl}]_0 = 0.047$ M, $[\mathrm{bpy}]_0 = 0.14$ M, water phase: 1% PVA, 20% NaCl, O/W = 1/4.

increased with time at every temperature. However, different levels of autoacceleration appeared when the temperature was at 75, 80 and 85 °C, and these phenomena became more evident with the decrease of the temperature. Fig. 3 shows the plots of $\ln[M]_0/[M]$ versus time. We can clearly observe that $\ln[M]_0/[M]$ deviated from linear relationship with reaction time when it reached 110 min at 75, 80 and 85 °C. All of these results indicate that the suspension ATRP of MMA deviated from first order with respect to monomer concentration when the conversion was up to some degree at lower temperatures. The low the temperature was, the more the deviation displayed. At 75 °C, the autoacceleration appeared evidently when the conversion was over 25% (see Figs. 2 and 3). As we know, suspension polymerization is a kind of bulk polymerization of small unit. The viscosity of the polymerization unit would increase with the conversion. The above results showed that the viscosity also influenced the polymerization via ATRP. We suppose that the viscosity decreased the deactivation rate of the radical and increased the propagation time of the active radical, so more monomers added to the active radical at every activation step, and hence the rate of polymerization increased.

Fig. 4 shows the variation of the molecular weight (M_n) with monomer conversion. Because the initiator efficiency was low (see Table 2), the curves did not run through the origin. However, with the exception of at 75 °C, the molecular weight increased almost linearly with monomer conversion at other temperatures, indicating that the polymerization was basically in a controlled fashion. At 75 °C, M_n increased with conversion when it was below 25%. However, M_n deviated heavily when the conversion was over 25%. This means that the polymerization had lost its control ability when marked autoacceleration behaved.

Table 2 shows the initiator efficiency and molecular weight distributions at different temperatures when the polymerization time was 110 min. We can observe that the initiator efficiency increased with the increase of temperature. This is probably because that the increase of temperature accelerated the activation speed of the initiator, as well as the propagation speed of the monomer. So the initiator converted to monomer radical and subsequently to chain radical rapidly. As far as they converted to chain radical ($RM_x\cdot\cdot\cdot Cl\cdot\cdot\cdot Cu^{II}/bpy$), they would remain in the oil phase because of the hydrophobicity of $RM_x^{\cdot}$ and they would eventually grow up to macromolecules. The molecular weight distribution was reasonably narrow. However, it displayed a trend of becoming broader with the polymerization temperature, indicating that the chain termination and chain transfer rate increased with the temperature.

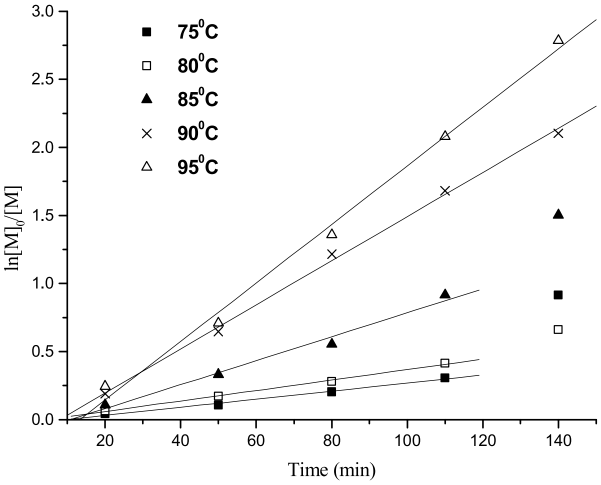

Fig. 3. Plot of $\ln[M]_0/[M]$ versus time at different temperatures. $[MMA]_0 = 9.36$ M, $[1\text{-PECl}]_0 = 0.047$ M, $[CuCl]_0 = 0.047$ M, $[bpy]_0 = 0.14$ M, water phase: 1% PVA, 20% NaCl, O/W = 1/4.

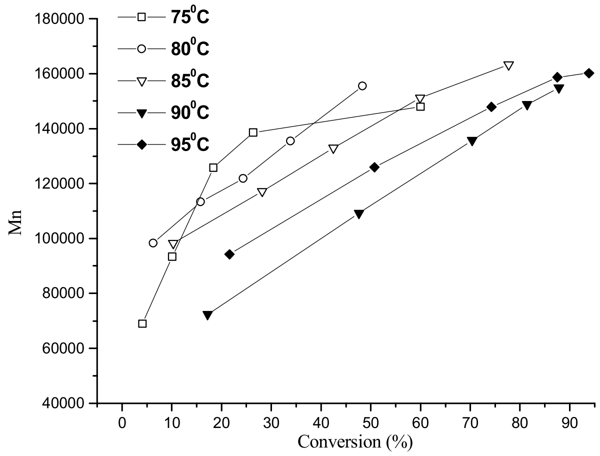

Fig. 4. Variation of the molecular weight with monomer conversion. $[MMA]_0 = 9.36$ M, $[1\text{-PECl}]_0 = 0.047$ M, $[CuCl]_0 = 0.047$ M, $[bpy]_0 = 0.14$ M water phase: 1% PVA, 20% NaCl, O/W = 1/4.

From the linear part of the plot of $\ln[M]_0/[M]$ versus time in Fig. 3, k_p^{app} at different temperatures was obtained, and the active radical concentration($[P^{\cdot}]$) was calculated by Eq. (3) using k_p from the reference [21]. They are summarized in Table 3. We can see that the active radical concentration increased with temperature, corresponding to the high initiator efficiency and the fast reaction rate at higher temperatures.

Fig. 5 is the plot of $\ln k_p^{app}$ versus $1/T$ according to the Arrhenius equation. From the slope, the apparent activation energy (E_a) was calculated as 117.5 kJ/mol. The apparent

Table 2
Molecular weight distribution and initiator efficiency at different temperatures

T (°C)	Conv. (%)	M_n GPC	M_w/M_n	f
75	26.38	138,565	1.26	0.038
80	33.86	115,531	1.26	0.058
85	59.60	151,174	1.50	0.078
90	81.39	138,829	1.59	0.118
95	87.50	131,826	1.69	0.133

$[MMA]_0 = 9.36$ M, $[1\text{-PECl}]_0 = 0.047$ M, $[CuCl]_0 = 0.047$ M, $[bpy]_0 = 0.14$ M, water phase: 1% PVA, 20% NaCl, O/W = 1/4, $t = 110$ min.

Table 3
k_p^{app} and the radial concentration at different temperatures

T (°C)	75	80	85	90	95
[P$^\cdot$] (mol/l)	4.17×10^{-8}	4.95×10^{-8}	9.87×10^{-8}	1.69×10^{-7}	2.08×10^{-7}
k_p^{app} (min^{-1})	0.0028	0.0037	0.0082	0.0156	0.0215

$[MMA]_0 = 9.36$ M, $[1\text{-PECl}]_0 = 0.047$ M, $[CuCl]_0 = 0.047$ M, $[bpy]_0 = 0.14$ M, water phase: 1% PVA, 20% NaCl, O/W = 1/4.

activation energy of ATRP should include the activation energy (E_{act}) that is needed for the activation of the dormant species, and the activation energy of chain propagation (E_p). However, in this suspension system, it also should include the contribution of the increase of initiator efficiency with temperature. So we could not get the E_{act} simply by the subtraction of E_a and E_p. Nevertheless, from the high value of the apparent activation energy and the low value of E_p (22.2 kJ/mol from Ref. [21]), we can propose that the activation energy of the dormant species is quite high and the increase of temperature would increase the activation rate of the dormant species as well as the propagation rate of the active radical. So the reaction rate increased.

3.3. Bulk ATRP of MMA

In order to compare suspension ATRP with bulk ATRP, the bulk polymerization of MMA was carried out at the same catalyst system at 85 °C. Fig. 6 shows the relationship of monomer conversion and ln$[M]_0/[M]$ with time. For comparison, the result of the suspension ATRP of MMA at 85 °C was also included in Fig. 6. We can see that the bulk ATRP of MMA also showed autoacceleration, and it behaved more evident than suspension ATRP. It only showed linear relationship of ln$[M]_0/[M]$ with time at the conversion below 12.5%, whereas for suspension ATRP the linear relationship was up to 30% (see Fig. 6). We contribute this difference to the small polymerization unit of suspension ATRP. The heat of the polymerization was easily to be conducted by water, so the affect of the heat accumulation was avoid. From Fig. 6 we also can observe that the rate of suspension ATRP is much faster than that of bulk ATRP. According to the slope of the linear part of ln$[M]_0/[M]$ curve and the k_p of MMA at 85 °C (1384.1 l S/mol)[21], the living radical concentration of the bulk polymerization was calculated as 1.44×10^{-8} mol/l, much lower than that of suspension ATRP at the same temperature(9.87×10^{-8} mol/l, see Table 3). We had observed this phenomena in the study of the suspension ATRP of styrene [18]. Armes and co-workers had investigated aqueous solution ATRP catalyzed by CuCl/bpy. He also discovered the fast polymerization rate in water and suggested that water has the promotion effect to ATRP [22–24]. The above result is another proof of the promotion effect of water.

Fig. 7 shows the variation of the molecular weight and molecular weight distribution with conversion of bulk ATRP. M_n increased almost linearly with conversion when it was below 12.5%. However, after this point, M_n deviated heavily, indicate that when the autoacceleration behaved, some chain transfer or termination occurred. From Fig. 7 we also can see that the molecular weight distribution index also increased when the autoacceleration began, further indicating the poor control at this stage. For comparison, Fig. 8 gives the variation of M_n and M_w/M_n with conversion of suspension ATRP. M_n increased almost linearly with conversion and M_w/M_n not changed a lot with the conversion. This indicate that the control of the polymerization was improved in suspension ATRP because the acceleration was more moderate than that in bulk.

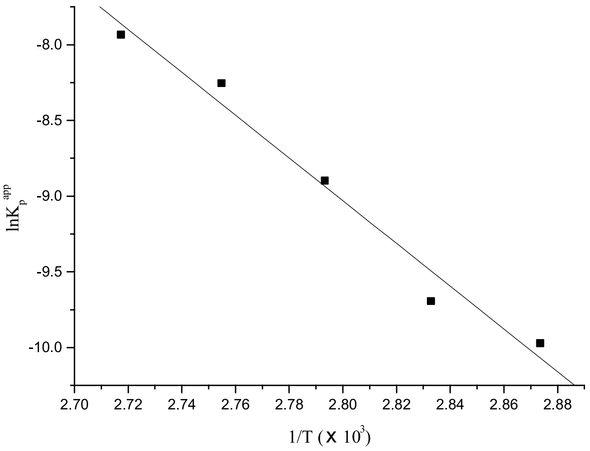

Fig. 5. Plot of lnk_p^{app} versus $1/T$. $[MMA]_0 = 9.36$ M, $[1\text{-PECl}]_0 = 0.047$ M, $[CuCl]_0 = 0.047$ M, $[bpy]_0 = 0.14$ M, water phase: 1% PVA, 20% NaCl, O/W = 1/4.

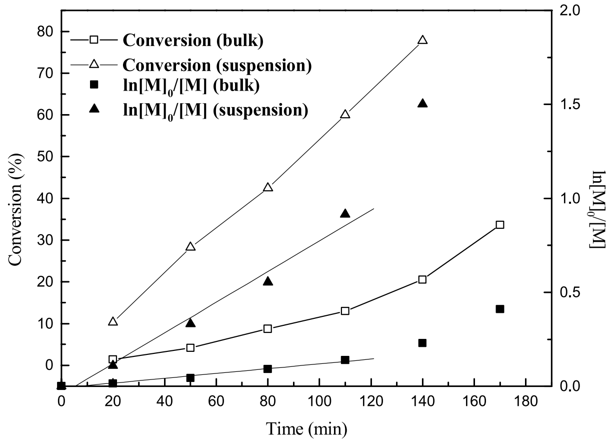

Fig. 6. Kinetic plot of bulk and suspension ATRP of MMA at 85 °C $[MMA]_0 = 9.36$ M, $[1\text{-PECl}]_0 = 0.047$ M, $[CuCl]_0 = 0.047$ M, $[bpy]_0 = 0.14$ M, for suspension: water phase: 1% PVA, 20% NaCl, O/W = 1/4.

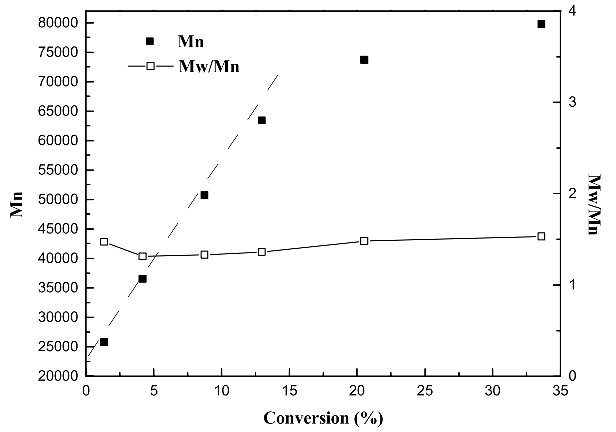

Fig. 7. Variation of M_n and M_w/M_n with conversion of bulk ATRP of MMA $[MMA]_0 = 9.36$ M, $[1\text{-PECl}]_0 = 0.047$ M, $[CuCl]_0 = 0.047$ M, $[bpy]_0 = 0.14$ M.

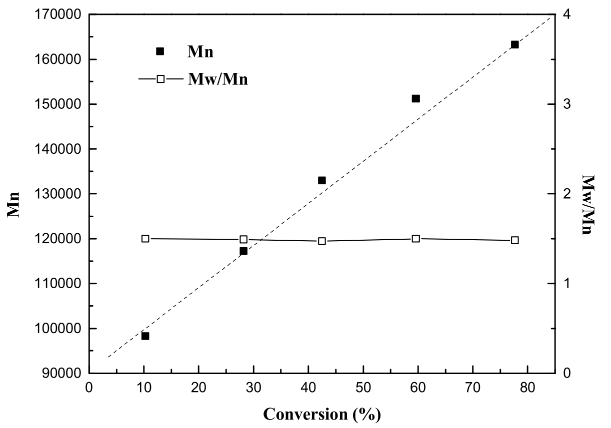

Fig. 8. Variation of M_n and M_w/M_n with conversion of suspension ATRP of MMA at 85 $[MMA]_0 = 9.36$ M, $[1\text{-PECl}]_0 = 0.047$ M, $[CuCl]_0 = 0.047$ M, $[bpy]_0 = 0.14$ M water phase: 1% PVA, 20% NaCl, O/W = 1/4.

4. Conclusions

Suspension ATRP of MMA was conducted in aqueous medium catalyzed by CuCl/bpy. Adding NaCl to the water phase can decrease the diffusion of the catalyst to water and hence improve the initiator efficiency. Kinetic study showed that at lower temperatures (≤85 °C), the autoacceleration which was characterized by the fast increase of conversion was observed. Higher temperature (≥90 °C) was beneficial to the control of the polymerization. The rate of suspension ATRP was much faster than that of bulk ATRP, indicating that water displayed some promoting effect.

Acknowledgements

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