

## RAFT polymerization of acrylamide manipulated with trithiocarbonates in poly(ethylene glycol) solution

Yulin Zhang, Lei Ye, Yongfu Diao, Weiwei Lei, LinYing Shi, Rong Ran

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, China

Correspondence to: R. Ran (E-mail: ranrong@scu.edu.cn)

**ABSTRACT:** The reversible addition fragmentation chain transfer (RAFT) polymerization of acrylamide (AM) in aqueous two-phase system was successfully carried out in polyethylene glycol (PEG) aqueous solution. Because of phase transition involved in the polymerization process, the  $\ln([M]_0/[M])$ -time plots were indicated in two-stages significantly. Both the initial homogeneous polymerization and the subsequent heterogeneous polymerization were under good control. The effects of various synthesis parameters such as polymerization temperature, concentration of CTA, and initiator on RAFT polymerization behaviors have been investigated. Furthermore, the evolution process of the droplet morphologies after separation was examined by transmission electron microscope. The results showed that the nuclei were formed throughout the whole heterogeneous polymerization and stable sphere particles with an average size of about 1  $\mu\text{m}$  were produced finally. More importantly, it was also found that the viscosity played a significant role in the stabilization of the dispersion of polymer particles. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43000.

**KEYWORDS:** Acrylamide; aqueous two-phase; RAFT polymerization

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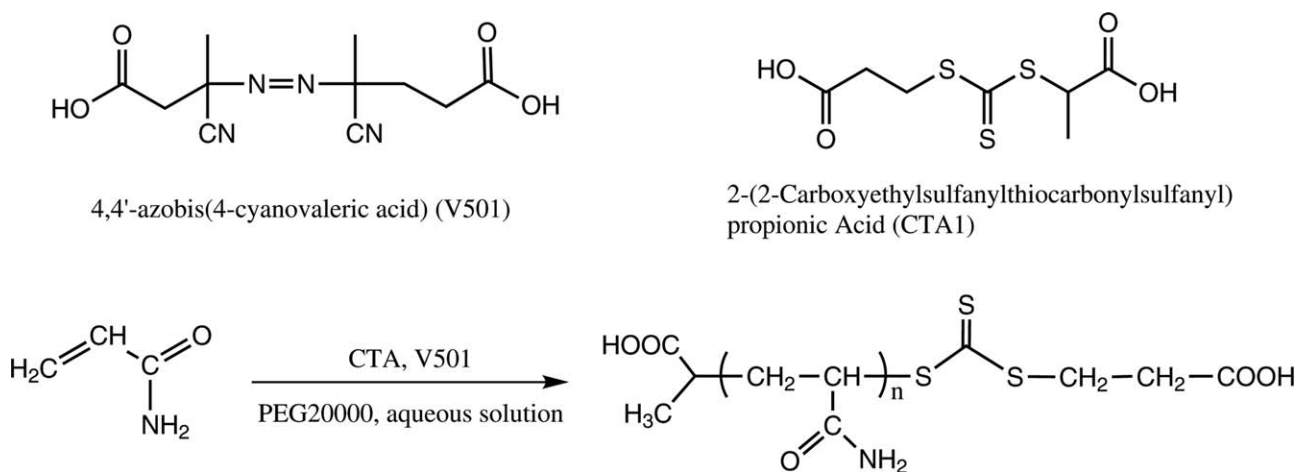
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### INTRODUCTION

Reversible addition fragmentation chain transfer polymerization (RAFT), has shown as a powerful technique for synthesis polymers with predefined molecular weights, narrow molecular weights distributions, and well-defined architectures.<sup>1–6</sup> It has attracted great interest of researchers for its mild reaction conditions and application to a wide range of monomers such as acrylamide (AM), styrene (St), and methacrylate (MMA). Polyacrylamide (PAM) is one of the most important water-soluble polymers and has widely been applied in waste-water treatment, paper making, printing, and oil recovery industries. The first report on RAFT polymerization of AM was proposed by McCormick group. They successfully synthesized PAM with narrow molecular distribution by RAFT polymerization in aqueous solution (Scheme 1). Then a number of researches on RAFT polymerization of AM in homogeneous system such as aqueous and the organic solvent dimethyl sulfoxide (DMSO),<sup>7–12</sup> and in heterogeneous system such as inverse emulsion<sup>13</sup> and inverse miniemulsion,<sup>14–16</sup> have been very well documented. However, all of these implement methods have some problems. For instance, the high reaction heat of solution polymerization for AM as well as high viscosities at high conversion leads to many problems such as difficult heat transfer, non-uniform mixing, and organic solvent in inverse heterogeneous system may cause

environment pollution. While, another kind of polymerization method called “aqueous two-phase” polymerization may be a promising method to solve these problems.<sup>17</sup>

The so called “aqueous two-phase” system was proposed by Mario, when they obtained a stable water by water dispersion by mixing polyoxyethylene (PEO), poly (2-vinyl pyridine chloride) (PVCP), and their copolymer in aqueous solution.<sup>18</sup> Subsequently, Hosoda *et al.*<sup>19</sup> first carried out free radical polymerization of sodium acrylate (SA) in “aqueous two-phase” system. Hu *et al.*<sup>20</sup> studied polymerization of AM in aqueous PEG solution based on the phase diagram of PAM–PEG–water. They found that the aqueous PEG solution is the continuous phase, and the PAM is the dispersed phase, respectively. These polymerization implement approaches were previously treated as a “water in water” emulsion polymerization or aqueous dispersion polymerization. Recently, the polymerization of AM in aqueous PEG solution was investigated systematically on phase diagram, polymerization kinetics, and dispersed droplets as well as the viscosity of polymerization product by Shan *et al.*<sup>21–28</sup> They suggested that these processes are different from emulsion polymerization or aqueous dispersion polymerization, and could be named as “aqueous two-phase polymerization,” because the polymerization may take place at the same time in two aqueous phases in the presence of PEG.<sup>22</sup>



**Scheme 1.** “Aqueous two-phase” RAFT polymerization of AM.

Compared with conventional polymerization implement methods, aqueous two-phase polymerization is a new and green approach to prepare water-soluble polymer, and has received great attention in the recent years.<sup>29–42</sup> However, this polymerization system has been ignored in RAFT polymerization. As far as we know, RAFT polymerization in “aqueous two-phase” system has not been investigated by now. Therefore, the exploration of performing RAFT polymerization in “two-phase” system may provide a new approach to synthesize predefined molecular weights and structure water soluble polymers. In this work, the RAFT aqueous two-phase polymerization of AM has been carried out in PEG aqueous solution. An azo initiator, azobis-(4-cyanopentanoic acid) (V-501) was used to avoid the accelerating effect which was existing in persulfate initiated polymerization. The “living/controlled” characters of the polymerization was examined, meanwhile the effects of polymerization temperature, concentration of AM, initiator, and RAFT agent on polymerization behaviors were investigated. In order to get a further inspection into the polymerization, transmission electron microscopy (TEM) was employed to observe the evolution process of the product droplet morphologies in aqueous two-phase system.

## EXPERIMENTAL

### Materials

AM (>98 wt %, Bodi chemical Co. Ltd.) was recrystallized from acetone. V-501, (>98%, Sigma Aldrich) was used as initiator and used as received. PEG20000 ( $M_n > 17,000$  g/mol, Kermal Chemical Reagent Co. Ltd.) was used without further purification. 2-(2-Carboxyethylsulfanylthiocarbonylsulfanyl) propionic acid (CTA, Figure 1) was used as chain transfer agent and synthesized according to the literature.<sup>43</sup>  $^1\text{H}$  NMR ( $d_6$ -DMSO, d, ppm): 1.52 (d,  $\text{CH}_3-\text{CH}$ ), 2.69 (t,  $-\text{CH}_2-\text{COOH}$ ), 3.55 (t,  $-\text{CH}_2-\text{S}-$ ), 4.70 (q,  $-\text{S}-\text{CH}-\text{CH}_3$  (COOH)), 12.82 (s,  $-\text{COOH}$ ). IR ( $\text{cm}^{-1}$ ): 1410 ( $\text{CH}_2-\text{S}$ , s), 1200 ( $\text{C}=\text{S}$ , s), 650 ( $\text{S}-\text{CH}$ , w).

### RAFT Polymerization of AM in Aqueous Two-Phase System

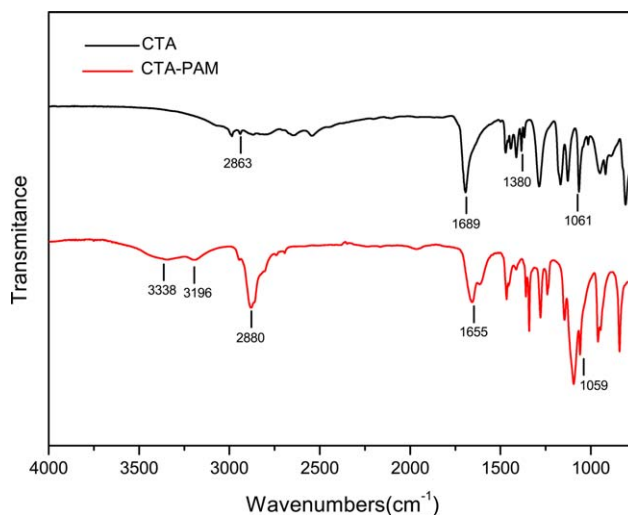
The RAFT two-phase polymerization of AM was carried out as follows. Briefly, 15 g of PEG20000, 6 g of AM, certain amount

of CTA, and 74 mL water were added to a 250 mL glass jacket reactor with a four-necked cover equipped with a motor-driven Teflon stirrer, reflux condenser, nitrogen inlet tube, thermometer, and sampling tube. Then the reaction mixture was heated to 35°C and purged with  $\text{N}_2$  for 1 h. Thereafter, the reaction mixture was heated to certain temperature, and the 4 g aqueous initiator V-501 solution was injected to start the polymerization. The polymerization was carried out under the protection of  $\text{N}_2$  throughout its course with stirring speed at 100 rpm. The detailed formulation and temperature are shown in Table I.

### Characterization

**FT-IR Characterizations.** The Fourier transform infrared (FT-IR) attenuated total reflection (ATR) absorption spectra of the samples were recorded using a Nicolet FT-IR 6700 spectrometer (Thermo Fisher Scientific, United States).

**Conversion Measurement.** The monomer conversion was determined similarly with the literature.<sup>26</sup> Certain amount of reaction mixture was withdrawn in a regular time interval and cooled down immediately to stop the reaction to measure the



**Figure 1.** FTIR spectra of CTA and CPAM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** RAFT Polymerization of AM in PEG Aqueous Solution

Run	Temp. (°C)	[AM]/[CTA]/[I]	Time (min) <sup>a</sup>	$M_{n,th}$	$R_p^b \times 10^{-5}$ mol·(L s) <sup>-1</sup>	Conv. <sup>c</sup> (%)	$R_p^d \times 10^{-5}$ mol·(L s) <sup>-1</sup>	Conv. <sup>e</sup> (%)	$M_{n,GPC}$	PDI
1	70	600/0/1	<10	-	-	-	41.7	100	75,200	9.25
2	70	600/2/1	15, 25	20,787	28.4	34.9	9.1	96.4	26,200	2.62
3	70	600/3/1	30, 60	13,197	14.3	41.6	7.7	91.1	15,300	2.33
4	70	600/4/1	120, 140	9,487	11.6	47.8	4.1	86.6	10,800	1.93
5	70	600/3/1.25	15, 30	13,254	22.5	36.6	9.5	91.5	13,600	2.45
6	70	600/3/0.5	60, 90	12,572	9.9	41.4	4.0	86.7	12,800	2.3
7	60	600/3/1	180, 210	12,984	4.1	42.3	1.9	89.6	14,200	2.19
8	65	600/3/1	60, 90	13,084	10	44.1	4.7	90.3	14,900	2.33
9	75	600/3/1	15, 35	12,522	26.6	41	10.2	86.3	12,900	2.5
10	70	600/3/0.75	45, 70	12,773	12.6	41.5	5.8	88.3	13,200	2.31

<sup>a</sup>The time when polymerization solution turns turbid in the experiment and the polymerization time corresponding to the turning point in the curve of  $\ln([M]_0/[M]) - t$ .

<sup>b</sup> $R_p$  before the turning point.

<sup>c</sup>The monomer conversion corresponding to turning point obtained from the curve of  $\ln([M]_0/[M]) - t$ .

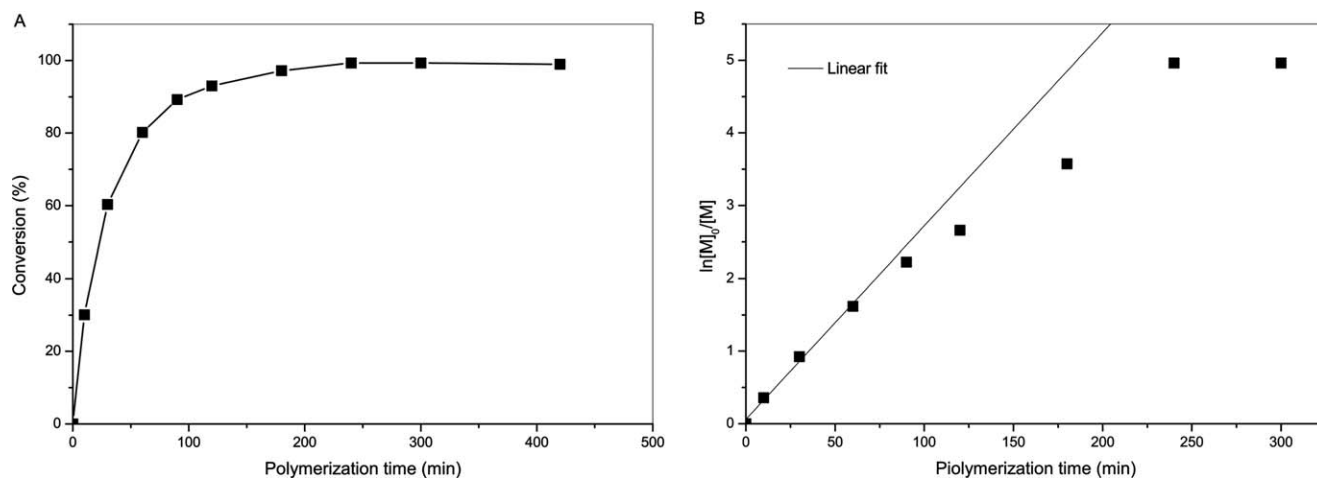
<sup>d</sup> $R_p$  after the turning point.

<sup>e</sup>The monomer conversion after 20 h.

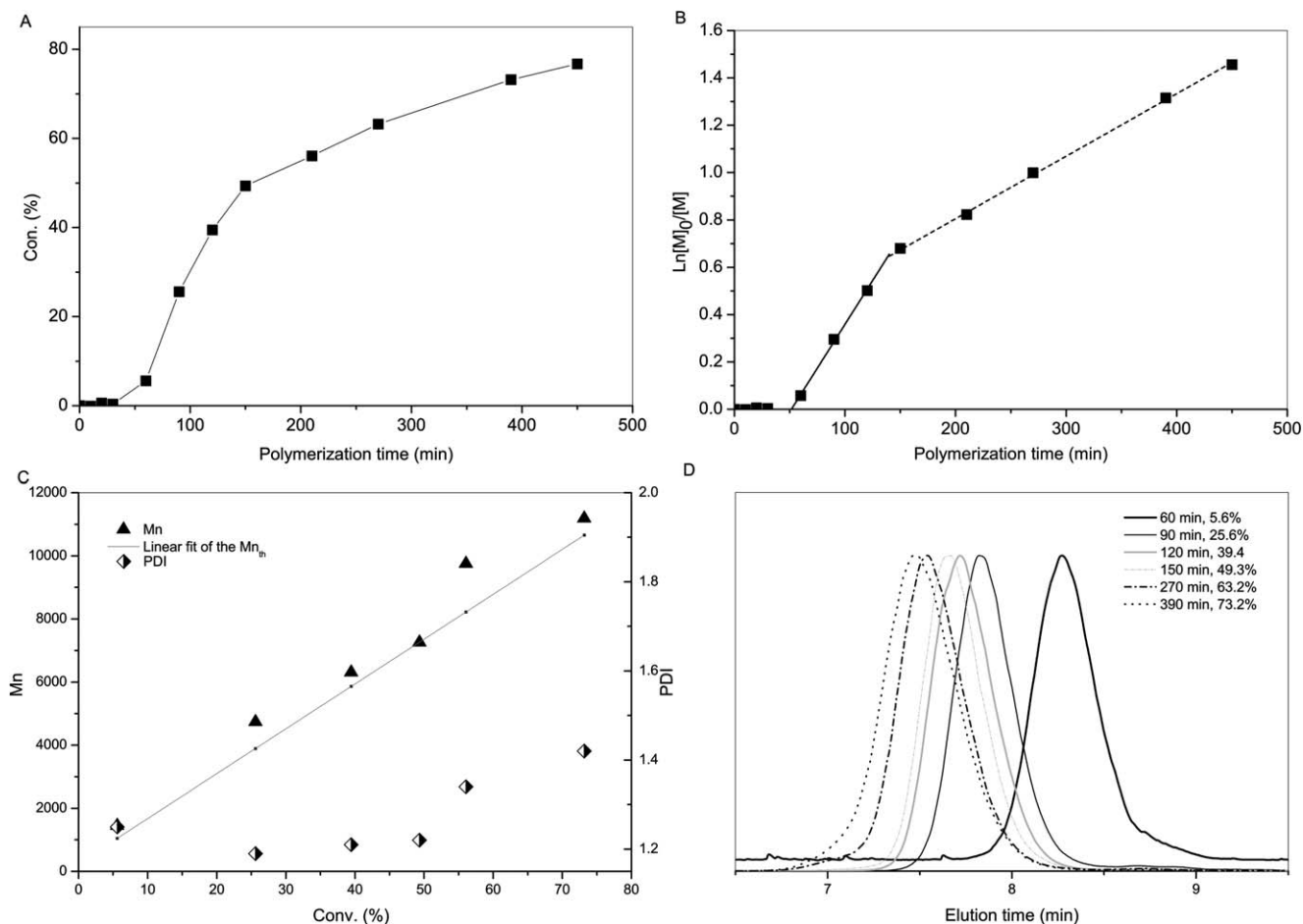
conversion. The residual monomers in the reaction system were analyzed by brominate titration to determine the conversion of AM aqueous two-phase polymerization. In detail, the weighed sample was completely dissolved into 100 mL water, and then 20 mL 0.1M aqueous solution of bromine prepared by dissolving 3 g of potassium bromate and 25 g of potassium bromide in 1 L distilled water, and 10 mL HCl aqueous solution (1:1 volume ratio of 37% hydrochloric acid aqueous solution:water) were introduced into the aqueous solution of sample. The iodine flask containing the aforementioned mixture was put into a dark closet for 30 min, and then 10 mL aqueous solution of potassium iodide (20 wt %) was added. The iodine was titrated by the aqueous solution of sodium thiosulfate (0.1 mol/L). The residual AM can be calculated by  $AM = (V_1 - V_2) \times c \times 0.03554$ , in which  $c$  is the concentration of aqueous solution of sodium thiosulfate, and  $V_1$  and  $V_2$  represent the consumed volume of aqueous solution of sodium thiosulfate for the blank and sample

titration, respectively. The value of 0.03554 represents the mass of AM which is consumed by 1 mL aqueous solution of sodium thiosulfate (1 mol/L).

**Molecular Weights and Molecular Weight Distributions Measurement.** Polymer molecular weights and molecular weight distributions were measured by an Agilent 1100 aqueous gel permeation chromatography (GPC) system at 30°C. The GPC system comprised a G1310A isocratic pump, a RI-G1362A RI detector, and a PL gel Mixed-C column (8 mm, 7.5 × 300 mm). About 0.05M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the mobile phase with a flow rate of 1 mL/min. The column was calibrated with poly(ethylene oxide) standard samples. The GPC samples were prepared according to the following procedure: aqueous solution aliquots of 1 mL were removed during the polymerization, quenched with 0.1 mL 0.1 wt % hydroquinone aqueous solution, and then stored in the fridge at 4°C. The samples were purified by dissolving



**Figure 2.** The aqueous “two-phase” polymerization of AM in PEG aqueous solution at 70°C. (A) The curve of monomer conversion versus polymerization time; (B)  $\ln([M]_0/[M])$  versus polymerization time.



**Figure 3.** The aqueous "two-phase" RAFT polymerization of AM in PEG aqueous solution at 70°C, with  $[AM]/[CTA]/[ACPA] = 600:4:1$ . (A) Monomer conversion versus polymerization time; (B)  $\ln[M]_0/[M]$  versus polymerization time; (C)  $M_n$  and PDI of the product versus conversion; (D) GPC trace of products obtained at different polymerization time.

precipitated method for several times with water as solvent and methanol as precipitation.

**Droplets Morphologies Measurement.** The samples were usually dispersed in methanol. The droplet morphology was observed by TEM (JEOL JSM-1230EXT20).

## RESULTS AND DISCUSSION

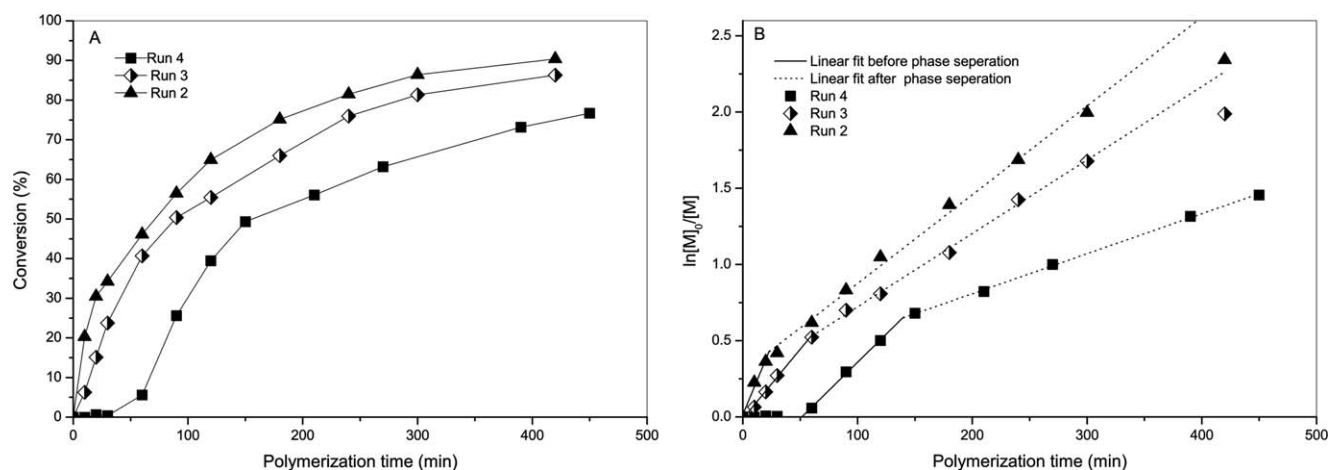
### "Aqueous Two-Phase" Polymerization with and without CTA

Generally, all reagents and products in "aqueous two-phase" polymerization of AM are required to be dissolved in water. In the experiment, V-501 was used as initiator and a water-soluble chain transfer agent, 2-(2-carboxyethylsulfanylthiocarbonyl-sulfanyl) propionic acid was used as RAFT agent. PEG20000 with a concentration of 15 wt % was used in the experiment because of its good stability for the droplets according to the previous researches.<sup>20,27</sup> The concentration of AM was kept constant at 6 wt %. Additionally, all the polymerization ran for a certain time of 20 h to react adequately.

FTIR spectra of CTA and CTA-PAM are shown in Figure 1. The CTA spectrum shows bands at 1689, and 1061  $\text{cm}^{-1}$  which are assigned to vibration frequencies of C=O, and C=S bonds, respectively; the bands at 2863 and 1380  $\text{cm}^{-1}$  are related to

bending vibration of  $-\text{CH}_2-$  and  $-\text{CH}_3$ , respectively. CTA-PAM shows the bands at 3338 and 3196  $\text{cm}^{-1}$  are related to stretching vibration of N-H, the band at 2880  $\text{cm}^{-1}$  is due to bending vibration of  $-\text{CH}_2-$ ; the bands at 1655 and 1059  $\text{cm}^{-1}$  are assigned to vibration frequencies of C=O and C=S, respectively. The results proved the formation of CTA-PAM.

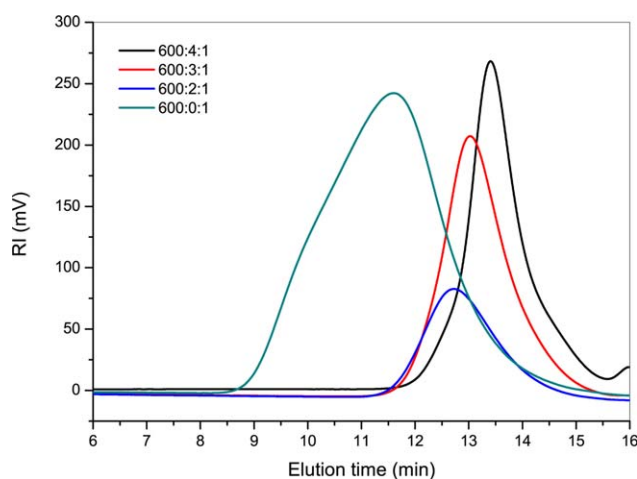
In order to check the effect of CTA on the polymerization behavior, the polymerization absence of CTA was investigated as a comparison. It can be seen from Figure 2(A), that the polymerization absence of CTA begins with no induction period, and the monomer conversion increases rapidly to 85% within 90 min, then slowly approaches to 97% at 240 min. After polymerization began 5 min system turned rapidly from clear solution to white turbid emulsion. This indicates the droplet formation and phase separation takes place at initial period of polymerization. Shan has explained the phase separation in this kind of polymer system from thermodynamic point.<sup>22</sup> It is known that phase separation will take place when the mixing Gibbs free energy of the system is negative.<sup>43</sup> The entropy of mixing is always positive, but it will decrease as many monomers polymerize to a polymer chain in polymerization process. RAFT polymerization is a kind of living radical polymerization,



**Figure 4.** The aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA with various concentration. (A) Monomer conversion versus polymerization time; (B.)  $\ln[M]_0/[M]$  versus polymerization time.

and there is almost no double-base termination bimolecular termination. Therefore, the molecular weight increases linearly with the monomer conversion. Because of hydrogen bond between PAM and PEG, the enthalpy of mixing is positive and increases with molecular weight. It is obvious that the polymerization has a critical monomer conversion, when the mixing Gibbs free energy of the system is negative. Eventually, the reaction solution is changed into latex, and the polymerization reaction is changed from homogeneous to heterogeneous polymerization. In Figure 2(B),  $\ln[M]_0/[M]$  increases linearly with time within 90 min, and after that it deviates from the linear relationship. After 20 h the polymerization reached full conversion, and the final molecular weight  $M_n$  is 75,200 g/mol with quite wide distribution (polydispersity index [PDI] value at 9.25).

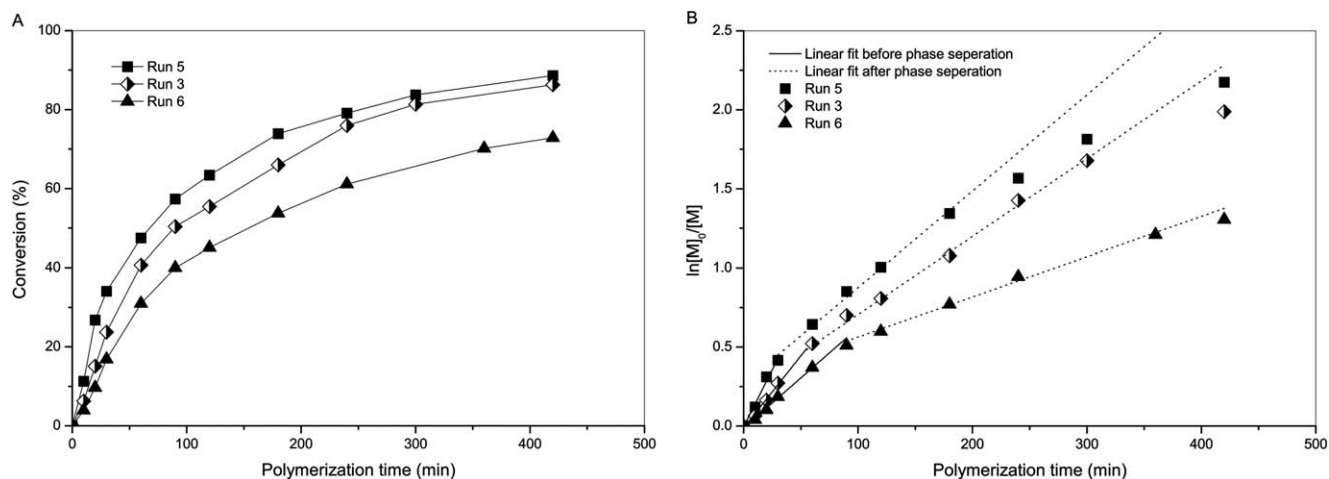
RAFT “aqueous two-phase” polymerization of AM under same conditions was carried out mediated by CTA with a molar ratio of  $[AM]_0/[CTA]_0/[V501]_0 = 600/4/1$ . In Figure 3(A), there is an



**Figure 5.** The aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA with various concentration, GPC trace of products obtained after polymerized for 20 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

induction period of about 60 min in the polymerization. After the induction, monomer conversion reaches at 52% in 150 min, and then further increases at a more slowly rate to 76% in 450 min. Compared with conventional free radical “aqueous two-phase” polymerization mentioned above, the phase separation time in RAFT “aqueous two-phase” polymerization was greatly delayed to 120 min. This may attribute to some degree to the retardation effect caused by CTA, but the main reason is that the RAFT polymerization has unique mechanism that the molecular weight increases with time during polymerization progress. Under this condition, the polymer chain will not aggregate to nuclei or separate from the solution until the molecular weight reach to the critical value. From Figure 3(B), the curve of  $\ln[M]_0/[M] - t$  presents as a fold line after induction period, illustrating the polymerization undergo a “two stage” process from homogeneous to heterogeneous. Ignoring the error caused by the measuring method of kinetics, the turning point at 140 min is corresponding to the time when the clear yellow polymerization solution turned to turbid emulsion, thus it can be treat as phase separation time. Both of the  $\ln[M]_0/[M]$  in two stage increase linearly with time, that suggest pseudo-first-order kinetics of the RAFT polymerization in homogenous and heterogeneous process, respectively. It is noted that the polymerization rate of heterogeneous stage evaluated to be  $4.1 \times 10^5 \text{ mol (L s)}^{-1}$  is much lower than that in homogeneous stage  $[R_p, 11.6 \times 10^5 \text{ mol (L s)}^{-1}]$ . While in common disperse polymerization or emulsion polymerization the reaction rate is usually increased after phase separation because of “radical compartmentalization effect.” This indicates that the polymerization carried in polyethylene glycol (PEG) aqueous solution undergoes a different process from disperse polymerization and emulsion polymerization.

From Figure 3(C), the  $M_n$  values by GPC analysis increases linearly with conversion and are very close to the theoretical ones calculated by Monteria’s equation.<sup>44</sup> PDI value is below 1.3 before the monomer conversion approached to 50%, then it increases apparently and approach to 1.93 after 20 h. The turning point at 50% conversion is consistent with the moment when phase separation takes place. This suggests the



**Figure 6.** The aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA with various initiator concentration, (A) Monomer conversion versus polymerization time; (B)  $\ln[M]_0/[M]$  versus polymerization time.

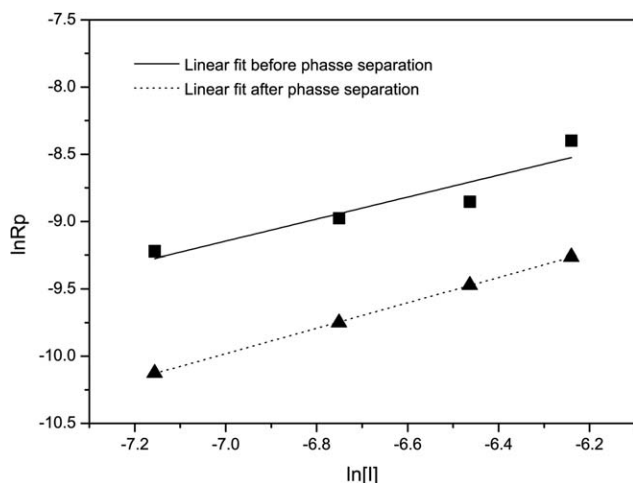
controllability of polymerization after phase separation gets bad. While at heterogeneous stage the PDI value is much lower than that of conventional free radical polymerization in “aqueous two-phase,” suggesting the reaction still keeps some controllability. The GPC analysis of the PAM synthesized at different time are showed in Figure 3(D). All traces are monomial peak with narrow molecular weight distribution and shift from high to low elution time as conversion increases.

From all the results discussed above, conclusions can be drawn that polymerization of PAM in PEG aqueous solution mediated by CTA proceeds from homogeneous to heterogeneous stage and reveals relatively good controllability. However, compared with the similar polymerization free of CTA, the RAFT “aqueous two-phase” polymerization rate is slow, even before phase separation it is only about a quarter of that in the polymerization without CTA. The reaction rate and controllability are most important factors in RAFT polymerization, while in most cases the factors that improve controllability result to a

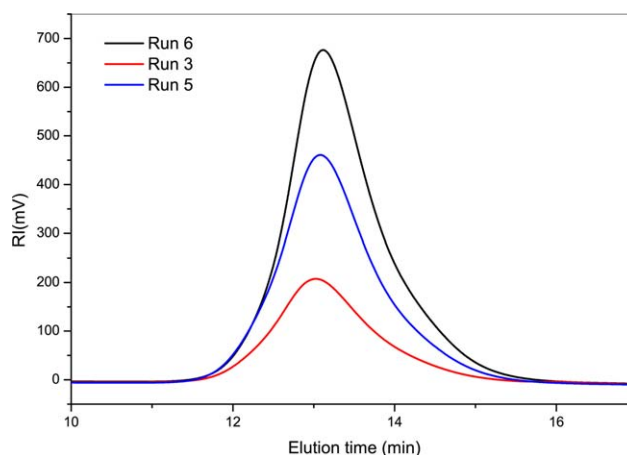
slow reaction rate. To keep a balance between the reaction rate and controllability, the effect of temperature, concentration of CTA and initiator on polymerization rate, and controllability are investigated. The results are list in Table I.

#### The Effect of CTA Concentration on the Polymerization

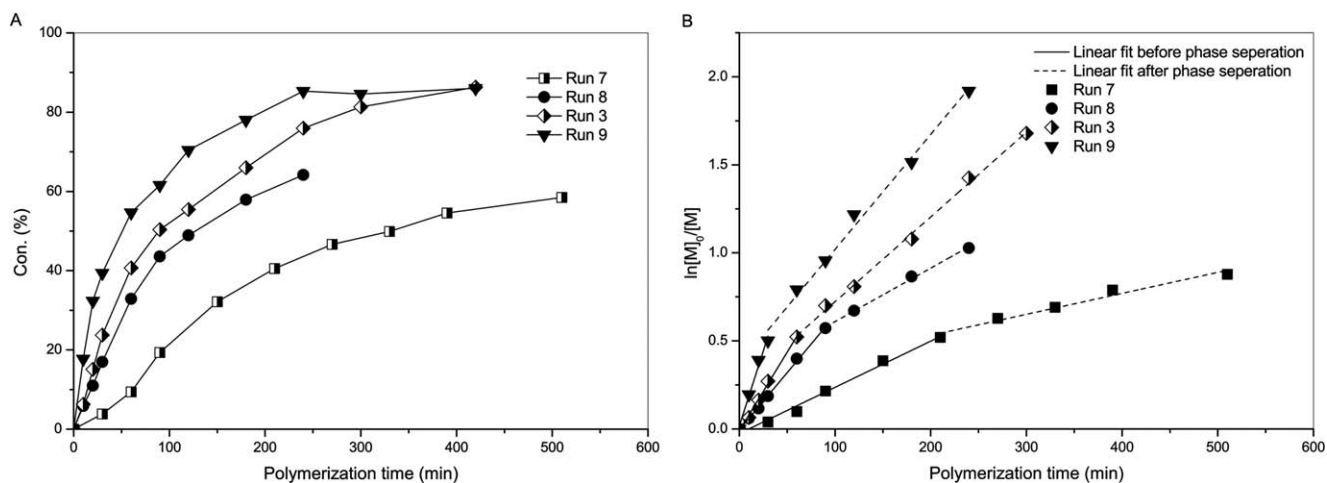
From Figure 4(A), it is clearly seen that the induction period vanishes as CTA concentration decreases, suggesting that the mole ratio of CTA to V501 should be below 4:1. Polymerization rate as well as the final conversion increases with decrease of CTA concentration. Further information on kinetics can obtained from Figure 4(B) and Table I. As shown in Figure 4(B), all of the polymerization with different CTA concentration undergoes a “two stage” process. The  $R_p$  of polymerization before phase separation increases from  $11.6 \times 10^5 \text{ mol (L s)}^{-1}$  to  $28.4 \times 10^5 \text{ mol (L s)}^{-1}$ , and after phase separation it increases from  $4.1 \times 10^5 \text{ mol (L s)}^{-1}$  to  $28.4 \times 10^5 \text{ mol (L s)}^{-1}$  with CTA concentration decrease. It indicates that the CTA concentration has significant



**Figure 7.** The aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA with various initiator concentration, the curve of  $\ln R_p$  versus  $\ln[I]$ .

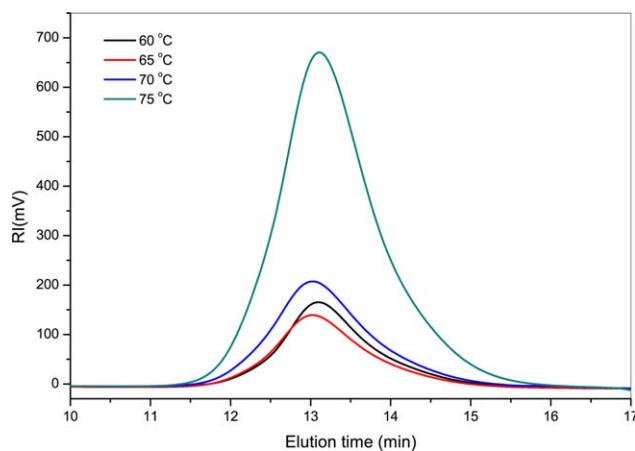


**Figure 8.** The aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA with various initiator concentration, GPC trace of products obtained after polymerized for 20 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 9.** The aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA at various temperature, (A) Monomer conversion versus polymerization time; (B)  $\ln[M]_0/[M]$  versus polymerization time.

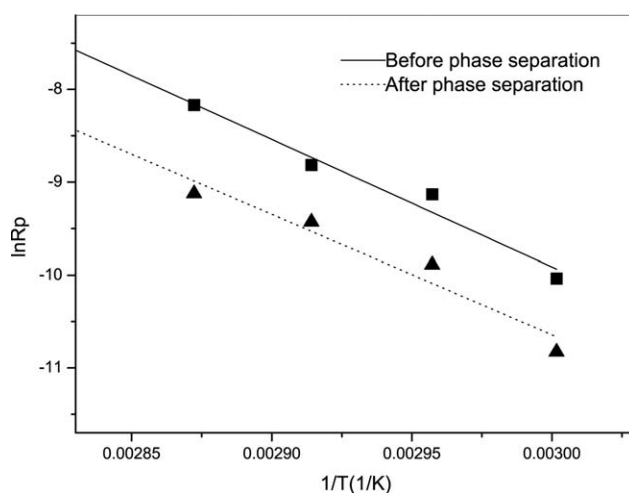
influence on polymerization rate. The  $\ln[M]_0/[M]$  increases linearly with time before phase separation, while after phase separation it deviates at high conversion. The molecular weight of final product after 20 h increases from 10,800 g/mol to 26,200 g/mol, with PDI values increasing from 1.93 to 2.62 as CTA concentration decreases. These suggest that the decrease of CTA concentration will lead faster reaction rate and worsen controllability. Figure 5 shows that all GPC trace of the final product are monomial peak with apparent “trailer” at high elution time, suggesting low molecular weight PAM existing in the product. Because the initiator and monomer are water-soluble, and they can dissolve in both continuous phase and dispersion phase in certain proportion after phase separation. Thus, the initiation and propagation reaction carried out in two phase simultaneously, and a small number of low molecular weight PAM is produced during the polymerization. Another phenomenon is also observed in the experiment, the phase separation time is shortened as CTA concentration decreases. It is a result of increase of polymerization rate.



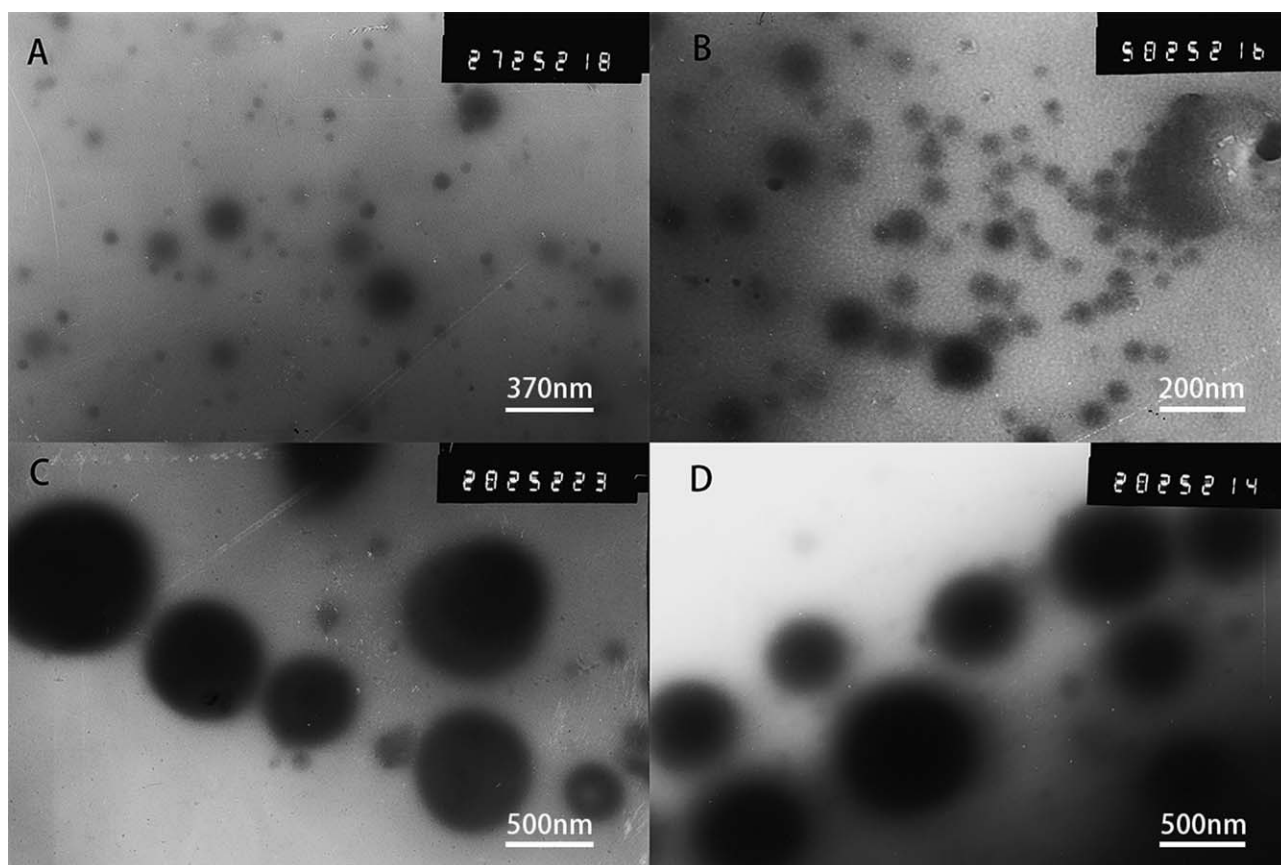
**Figure 10.** The aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA at various temperature, GPC trace of products obtained after polymerized for 20 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### The Effect of Initiator Concentration on the Polymerization

As shown in Figure 6(A), increasing initiator concentration leads to increase in polymerization rate. The  $R_p$  of polymerization before phase separation increases from  $9.9 \times 10^5 \text{ mol (L s)}^{-1}$  to  $22.5 \times 10^5 \text{ mol (L s)}^{-1}$ , and after phase separation it increase from  $4.0 \times 10^5 \text{ mol (L s)}^{-1}$  to  $9.5 \times 10^5 \text{ mol (L s)}^{-1}$ . In Figure 6(B),  $\ln[M]_0/[M]$  increases linearly with time before phase separation at all initiator concentration, while it deviates significantly after phase separation even at medium conversion with initiator concentration increase, indicating the controllability of the polymerization get worse. Final conversion and the molecular weight of the polymer also increase with increase in initiator concentration. The turning point is found to drop with initiator concentration increasing in Figure 6(B), indicating the critical monomer conversion decrease with initiator concentration increasing. In Figure 7, the reaction order value to  $[I]$  is estimated to be 0.82 before phase separation and 0.95 after phase separation, much higher than general solution polymerization, suggesting the double-base termination reaction is hindered in both steps. All GPC trace of the final product are monomial peak with apparent trailer at high elution time (Figure 8), and the PDI value



**Figure 11.** The curve of  $\ln R_p$  versus  $\ln(1/T)$  for aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA.



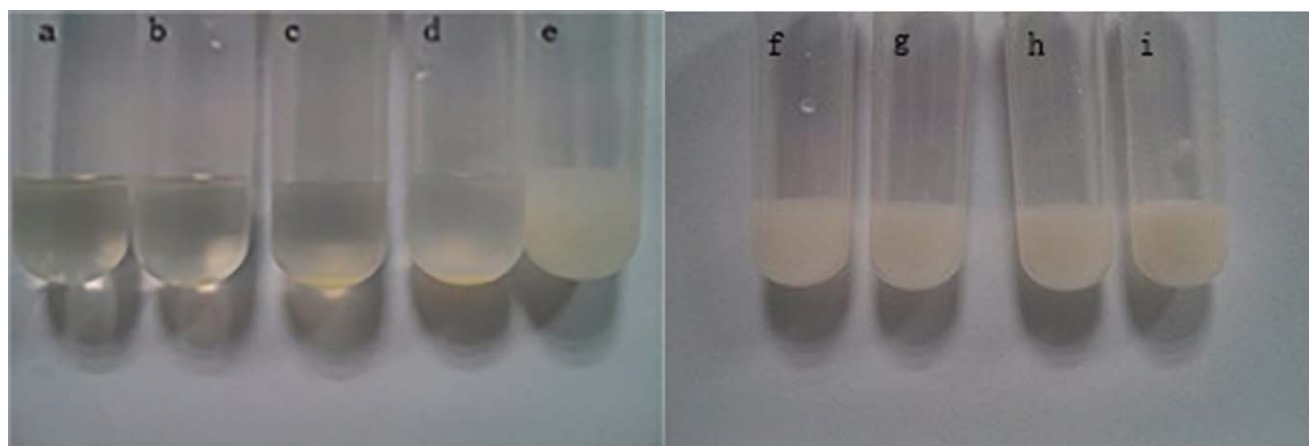
**Figure 12.** The TEM images of dispersed droplets in aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA at various monomer conversion, the polymerization is 70°C. (A) 40.7%; (B) 40.7% at high amplification factor; (C) 55.4%; (D) 81.3%.

increase with initiator concentration also suggesting that increasing initiator concentration will lead the polymerization less controllable. At homogeneous stage of this experiment, the viscosity of the polymerization is high because of the presence of PEG20000 and the PAM produced in polymerization. The high viscosity hinders the motion of propagating chain radicals and leads to the difficulty of double-base termination reaction. At heterogeneous stage, the viscosity of continuous phase increases with polymerization proceeding,

and in the dispersion phase double-base termination reaction is more difficult because of the “radical compartmentalization effect.”

#### The Effect of Temperature on the Polymerization

As shown in Figure 9(A), polymerization rate increases with temperature rising. While the final conversion is increased from 89.6% to 91.1% as temperature increases from 60°C to 70°C and then decrease to 86.3% after temperature approached to 75°C.



**Figure 13.** The emulsion stability of aqueous “two-phase” polymerization of AM (Run 4) in PEG aqueous solution mediated by CTA at various monomer conversion after 1 month standing at ambient temperature. (a) 0.3%; (b) 5.6%; (c) 25.6%; (d) 39.4%; (e) 49.3%; (f) 56.1%; (g) 63.2%; (h) 73.2%; (i) 86.6%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 14.** The emulsion stability of aqueous “two-phase” polymerization of AM in PEG aqueous solution mediated by CTA after 1 month standing at ambient temperature. The number corresponds to the reaction numbers in Table I. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The conversion decreases mainly because the initiator decomposed rapidly at high temperature, which leads the initiator radical consumed quickly. Therefore, there are no initiator to keep the reaction run at the end of polymerization and the monomer conversion decreases. In Figure 9(B),  $\ln[M]_0/[M]$  increases linearly with time before and after phase separation at all temperature, indicating the pseudo-first-order kinetics of the polymerization is not affected by temperature. The  $R_p$  of polymerization before phase separation is  $4.1 \times 10^5 \text{ mol (L s)}^{-1}$ , and after phase separation it is  $1.9 \times 10^5 \text{ mol (L s)}^{-1}$  at  $60^\circ\text{C}$ . As the polymerization temperature increase to  $75^\circ\text{C}$ ,  $R_p$  before phase separation increase to  $26.6 \times 10^5 \text{ mol (L s)}^{-1}$ , and increase to  $10.6 \times 10^5 \text{ mol (L s)}^{-1}$  after phase separation. The polymerization rate at  $75^\circ\text{C}$  before and after phase separation increase over that at  $60^\circ\text{C}$  by a factor of 6 and 5, respectively, indicating that temperature has great influence on polymerization rate.

The GPC trace of final product reveals as a monomial peak with apparent “trailer” in Figure 10, and the PDI value of each product increase with temperature also suggesting that the polymerization less controllable. The turning point at  $\ln[M]_0/[M] - t$  curve is found to rise with temperature increasing from  $60^\circ\text{C}$  to  $65^\circ\text{C}$  first, but drop after that. The initiator decomposed rate increases as temperature increases, which causes the polymerization less controllable. It has a similar effect on molecular weight distribution as increase of initiator concentration and leads the critical monomer conversion decreasing. This is the dominant factor effect on phase separation with temperature continue to increase. The relationship between  $\ln R_p$  and  $1/T$  is showed in Figure 11, and according to Arrhenius equation the apparent reaction activation energy are estimated to be 115.2 kJ/mol before phase separation and 107.1 kJ/mol after phase separation. The reaction activation energy decreases after phase separation. It has been mentioned that the termination reaction gets more difficult after phase increase, which will increase the activation energy of termination reaction and cause the decrease of apparent activation energy.

#### Analysis of the Dispersed Droplets and Emulsion Stability

To better understand the phase separation process, the formation and growth of dispersion droplets were observed by TEM. The sample of reaction mixture was withdrawn at certain time

after phase separation, and observed instantly after diluted by methanol. In Figure 12(A), there are serials of droplets with different size ranging from 20 to 120 nm at 40.7% monomer conversion just after phase separation. From more high resolution picture in B, the tendency of small droplets gathering is observed. It indicates that the small droplets are not stable, and the big droplets are mainly formed by the coalescence of small droplets at this moment. When the monomer conversion increase to 55.4%, the droplets grow to  $1 \mu\text{m}$  along presence of small droplets, and some smaller droplets are also found in the picture. This indicates the phase separation and forming of nuclei still occurs at this time. Smaller droplets are also found when monomer concentration approached to 81.3%, and this result showed that the smaller droplets do not gather and grow little after the monomer conversion is more than 55.4%. These indicate that the droplets can be stably kept at high monomer conversion (Figure 13).

Further investigation on stability of dispersions has been also carried on. Result show that the dispersions can keep stable for weeks and the dispersions at high conversion have better stability (Figure 14). It is mainly caused by the high viscosity of the reaction media at high monomer conversion, which prevents the droplets from gathering.

#### CONCLUSION

In summary, the RAFT polymerization of AM in “aqueous two-phase” system was successfully carried out in PEG aqueous solution. Compared with the similar polymerization free of RAFT agent, a two-stage kinetic profile was observed for these RAFT polymerizations. The value of PDI was low in the initial homogeneous polymerization, and then it became higher in heterogeneous polymerization. The  $M_n$  linearly increases with monomer conversion both in homogeneous and heterogeneous polymerization, and the PDI is still low compared with the similar polymerization free of CTA, indicating the “two-stage” polymerization under good control. The effects of polymerization temperature, concentration of CTA and initiator on RAFT polymerization behaviors have been investigated. It was found that the rate of RAFT polymerization conducted in PEG20000 aqueous solution increases with initiator concentration and

temperature, and decreases significantly with CTA concentration. Similarly with general RAFT polymerization, the polymerization becomes less controllable as the polymerization rate increases. The PDI of final products increases with increasing of initiator concentration and temperature, on the contrary decreases with increasing of CTA concentration.

The droplet morphologies were studied via TEM to understand the evolution of the particles. The result showed that the nuclei are formed throughout the whole polymerization and sphere particles with an average size about 1  $\mu\text{m}$  are produced at the end of polymerization. No aggregation of big droplets was found at the high monomer conversion. Furthermore, it is also found that the dispersion products can stably be kept for several weeks and stability of the system at high conversion is better than that at low conversion after phase separation, suggesting that the viscosity plays a significant role for the stabilization of the dispersion polymer particles.

This work extends the research of “aqueous two-phase polymerization” to RAFT polymerization. The success of performing RAFT polymerization in “aqueous two-phase” system offers a new approach to synthesize well-defined water-soluble polymer. It may be a promising polymerization technique after further investigation.

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