

Thin Layer Concentrated Emulsion Copolymerization of PUASi/Styrene/Methyl Methacrylate

Hongtao Zhang, Li Chen, Lingli Duan, He Huang

Faculty of Chemistry and Materials Science, Hubei University, Wuhan 430062, People's Republic of China

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ABSTRACT: Stable concentrated emulsions of polymerizable polysiloxane-containing polyurethane (PUASi)/Styrene (St)/Methyl methacrylate (MMA) were prepared using sodium dodecyl sulphate (SDS)/nonyl polyoxyethylene ether (OS15)/polyvinyl alcohol (PVA) as composite surfactant and azobisisobutyronitrile (AIBN) as initiator. A novel polymerization method, thin layer polymerization was used to carry out the concentrated emulsion copolymerization at 55°C. The effects of TDI/PPG molar ratio, surfactant concentration, different kinds of surfactants, and temperature on polymerization stability were studied. The effects of the thickness of the thin layer, the outside temperature of the reactor, as well as

polymerization environment on the volatilization rate of water, and monomer in the system were investigated. The conversion-time relationships of the thin layer polymerization and the tube polymerization, as well as the effect of polymerization environment on the polymerization rate were also investigated. The morphology of latex particles was determined with transmission electron microscope (TEM). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3993–3999, 2008

Key words: concentrated emulsion; thin layer copolymerization; volatilization rate; polymerization kinetics; polymerization stability

INTRODUCTION

Polymerizable polysiloxane-containing polyurethane (PUASi) is an important elastomer that consists of two different chain segments (“soft” and “hard”). In PUASi, the soft segment is composed of polysiloxane chains and polyether chains, while the hard segment consists of diisocyanate chains. PUASi, optimally carrying various functional groups, can be used in a wide variety of applications, such as coatings¹ and semi-permeable membranes.² PUASi may also be a good candidate to toughen some brittle plastics, like polystyrene (PS), through copolymerization. In this study, we are trying to prepare PUASi-PS copolymers through the copolymerization of α -double bond-containing PUASi and styrene (St) by employing a novel polymerization method—thin layer concentrated emulsion polymerization.

Concentrated emulsions are gel-like emulsions in which the volume fraction of the dispersed phase is greater than 0.74.^{3–6} The dispersed phase takes the form of spherical or polyhedral cells separated by thin films of composite surfactants. Concentrated emulsions have three important characteristics^{7–9}: (1) The reduced monomer mobility between cells, due

to the presence of a reinforced surfactant layer, can generate an earlier gel effect, which leads to a delay in the bimolecular termination reaction and, therefore, a higher molecular weight; (2) particle size can be controlled easily by the selection of a suitable surfactant type and concentration; and (3) containing little water, from which powdery resins are easily formed, can be obtained. When the volume of reactor is large, the heat generated could accelerate the polymerization reaction, a so-called self-heating phenomenon, leading to instability in concentrated emulsion polymerization.

To solve the heat conduction problem in concentrated emulsion polymerization and carry out a big batch production, a novel polymerization method—thin layer polymerization of concentrated emulsion was developed in our laboratories.¹⁰ Compared with polymerizations carried out in test tubs or flasks, where the area of heat conduction is very small per volume of concentrated emulsion, thin layer polymerization facilitates the heat conduction, due to the large heat conducting area. Besides, for concentrated emulsion polymerizations in test tubs or flasks, heat conduction problem also leads to quick monomer volatilization and low monomer conversion.^{11–13} The thin layer polymerization approach, however, ensures a high polymerization rate and the stability of the concentrated emulsion, and monomer loss. Therefore, polymer colloids, powdery resins, and decomposable composites of super high content can be directly prepared. The procedure of thin layer

Correspondence to: H. Zhang (zhanghongtao2000@sina.com).

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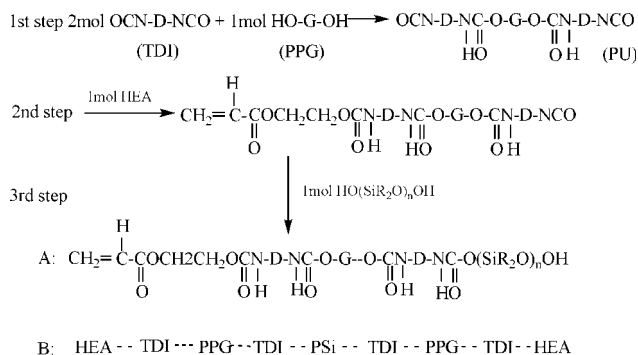


Figure 1 The synthesis of PUASi.

polymerization is similar to the test tube/flask polymerization except the use of a special mold as the reactor. Concentrated emulsion was first centrifuged to expel air bubble and transferred into the special mold designed in our laboratories; then the air in the mold was replaced with nitrogen. The mold was sealed and placed in an oven or a temperature-controlled water bath to carry out the polymerization.

In this study, we first synthesized a nonionic polymerizable polyurethane-containing polysiloxane (PUASi). Then, the thin layer copolymerization of St, MMA, and PUASi concentrated emulsion was carried out at 55°C, with AIBN as initiator. The morphology of particle was studied by TEM (transmission electron microscope).

EXPERIMENTAL

Materials

2,4-Diisocyanate (TDI, chemical grade, the Chemical Factory of Hubei University, Wuhan, China), dibutyltin dilaurate (DBTL, analytical grade, Beijing Taopu Chemical Factory, China), β -hydroethyl acrylate (β -HEA, chemical grade, Tianjin Institute of Chemical Reagent, China) were purchased and used directly. Polypropylene glycol (PPG N₂₁₀, $M_n = 1120$, Nanjing Taiping Chemical Factory, China) and polysiloxane (PSi, $M_n = 1000$, Nanjing Taiping Chemical Factory, China) were dried in vacuum for 3 h at 120°C. Styrene and Methyl methacrylate (St and MMA, analytic grade, the Sixth Factory of Tianjin Chemical Reagents, China) were distilled under reduced pressure, dried, and then stored in a refrigerator. Azobisisobutyronitrile (AIBN, chemical grade The Chemical Factory of Hubei University) was recrystallized. Alkyl phenolic polyoxyethylene ether sulfonic succinic disodium salt (MS-1, chemical grade, The Chemical Factory of Shangdong Zibo), sodium dodecyl sulphate (SDS, chemical grade), and nonyl polyoxyethylene ether (OS₁₅, chemical grade) were purchased from Shanghai Supply Depot of Chemical Reagent, China) and were used directly.

Polyvinyl alcohol (PVA-1788, chemical grade) and hydroquinone (Analytic grade, Shanghai Chemical Reagent Factory, China) were purchased and used directly. Water was deionized before use.

Synthesis of pre-polyurethane macromonomer (PUASi)

The synthesis of PUASi was carried out in three steps (Fig. 1). Two moles TDI was first mixed with 1 mole PPG and catalyst DBTL at 80°C. The change of NCO value during the reaction was determined using the dibutylamine back titration method¹⁴ to find the end point of reaction. In the second step, 1 mole β -HEA was added slowly to react with residual isocyanate group at 70°C, which introduced C=C double bond into the molecular chain. The end point of this step was determined by the observation that the NCO value did not change with reaction time.¹⁵ After that 1 mole PSi was added at 60°C, and the hydroxyl groups will react with the NCO end groups of pre-polyurethane formed in the second step Figure 2 is the IR spectrum of purified PUASi. No peak at 2270–2240 cm^{-1} shows that NCO had been completely consumed. The weak peak shoulder at 1452 cm^{-1} is the characteristic peak of $\text{CH}_2=\text{CH}$ group, which indicates that the double bond has been successfully introduced onto the polyurethane molecular chain.

Preparation of concentrated emulsion

Table I shows a typical recipe used in the preparation of PUASi/MMA/St concentrated emulsion. A known volume of an aqueous solution of SDS, OS₁₅, PVA-1788 was added into a three-neck flask at 55°C, equipped with mechanical stirrer, a funnel, and a nitrogen inlet. The monomers of St, MMA and

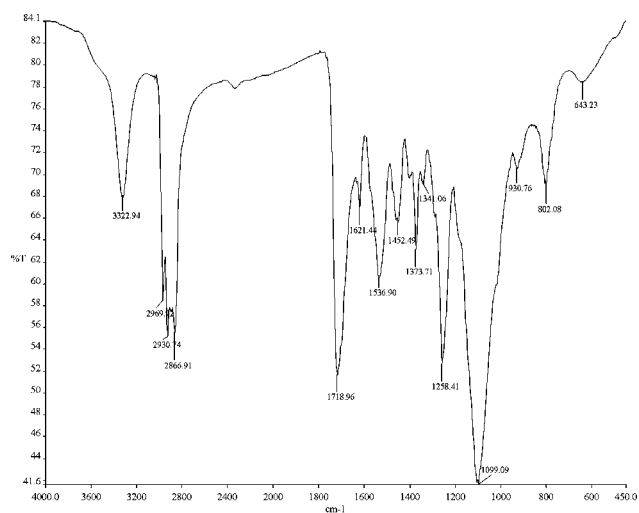


Figure 2 Infrared spectrum of PUASi prepolymer.

TABLE I
A Typical Recipe Used in the Preparation of PUASi/MMA/St Concentrated Emulsion

Component	Amount (g)
Dispersed phase	
PUASi	5
MMA	5
St	15
Continuous phase	
H ₂ O	5
Composite surfactant	
SDS	0.6
OS ₁₅	0.3
PVA-7188	0.05
Initiator	
AIBN	0.2

PUASi containing the AIBN initiator were added dropwise to the above mentioned aqueous solution under stirring at a suitable rate to avoid phase separation. The whole process was under the protection of nitrogen. Stirring stopped after 5 min of the entire dropping process.

Test-tube polymerization

The prepared gel-like concentrated emulsion was transferred to a 10-mL centrifugal tube and centrifuged at a moderate rate (1500 r/min) for 10 min to expel air bubble. Then the air in the tube was replaced with nitrogen and the tube was sealed with a rubber septum. Tube polymerizations were conducted in a temperature-controlled water bath.

Thin-layer polymerization

Each prepared gel-like concentrated emulsion was transferred to a special mold as shown in Figure 3 to

form a thin layer. The thickness of the thin layer can be controlled by the amount of concentrated emulsion added and the pressure put on the concentrated emulsion. The pressure can be adjusted by turning the screw. The air in the mold was replaced with nitrogen. The mold was then placed in a temperature-controlled water bath or oven to carry out the polymerization. Sheet product can be obtained finally.

Polymerization stability

The polymerization stability was measured in terms of weight fraction (α) of the bulk phase separated from the concentrated emulsion at regular intervals. The larger the value of α , the lower polymerization stability of the concentrated emulsion is. And α was calculated according to eq. (1):

$$\alpha\% = \varphi_1/\varphi_0 \times 100\% \quad (1)$$

where φ_1 represents the weight of the bulk phase separated from the concentrated emulsion, φ_0 represents the total weight of the concentrated emulsion.

Volatilization rate of water and monomer

After mild centrifugation, each concentrated emulsion was transferred into a pre-weighted mold. The amount of volatilization of water and monomer in the system was measured gravimetrically by changing the thickness or area of thin layer or outside temperature of the mold/reactor. And then the volatilization rate of water and monomer ($m_0 \times 10^{-4}/\text{g cm}^{-3} \text{ min}^{-1}$, the volatilization rate was defined as the total amount of volatilization of water and monomer in per unit time and volume) was



Figure 3 A schematic of the mold used in the thin-layer concentrated emulsion polymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

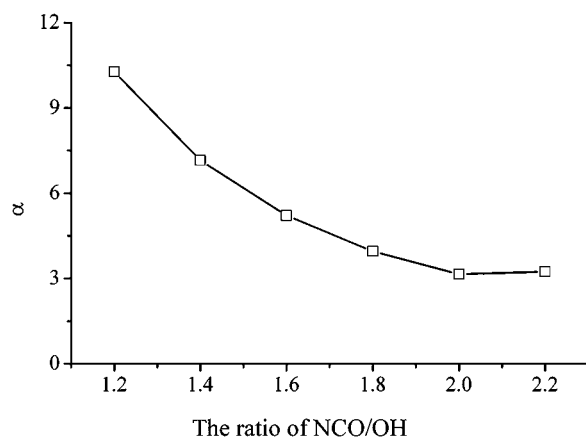


Figure 4 The effect of TDI/PPG molar ratio on α . $[E] = 0.19$ g/mL H_2O , $SDS/OS_{15} = 2 : 1$, $PVA = 0.01$ g/mL H_2O , $H_2O = 5$ g, $PUASi/MMA/St = 1/1/3$, $T = 328$ K, $[I] = 0.8\%$ g/g (PUASi/MMA/St), $\Phi = 80.39\%$.

obtained at a certain time (20 min). The volatilization rate of water and monomer in the system was calculated according to eq. (2):

$$Q = W/(V \times t) \quad (2)$$

where W ($W = W_0 - W_n$) represents the amount of volatilized of water and monomer in the system, W_0 and W_n represents the initial and final weight of concentrated emulsion respectively; V represents the volume of concentrated emulsion; t is the time of volatilization, i.e., 20 min.

Kinetics of thin layer polymerization

During the polymerization process, 0.5 g samples were withdrawn from the mold at regular intervals and transferred to a pre-weighed glass container containing hydroquinone. The samples were dried at about $100^\circ C$ for 12 h, and then the weight of the PUASi/MMA/St copolymer (W_1) was obtained. Polymerization conversion (C %) was calculated according to eq. (3).

$$C\% = W_1/W_2 \times 100\% \quad (3)$$

where W_2 denotes the mass of all monomers used in the polymerization. The total mass of the batch in the mold was about 30 g.

The size and morphology of the latex particles

The copolymer particles were dispersed in deionized water and then coated onto a copper grid. After being dried at room temperature, the samples were examined with TEM (JEM-100SX, JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

The polymerization stability of PUASi/MMA/St concentrated emulsion

Concentrated emulsions should remain stable not only at room temperature but also at the reaction temperature. The stability of the concentrated emulsions is closely related to the subsequent polymerization reaction. The polymerization stability of the concentrated emulsions refers to the resistance to the formation of two separate phases during polymerization. Here we discuss the effects of TDI/PPG molar ratio, different surfactants, the concentration of the composite surfactant ($[E]$), and temperature on the polymerization stability.

In Figure 1, we used the empirical TDI/PPG molar ratio of 2/1 to demonstrate the steps for the synthesis of PUASi. To compare the experimental result on the polymerization stability, we synthesized six kinds of pre-polyurethane by changing the TDI/PPG molar ratio. Figure 4 shows the effect of TDI/PPG molar ratio on the bulk phase separated from the concentrated emulsion. The α -value decreased with increasing the molar ratio of TDI/PPG, indicating a more stable concentrated emulsion polymerization system. A lower molar ratio of TDI/PPG led to a higher molecular weight of pre-polyurethane and higher viscosity of the disperse phase. When the molar ratio of TDI/PPG approached 1, the molecular weight of PUASi became very big, which made dissolution or swelling of PUASi in St and MMA impossible, leading to a worse polymerization stability of the concentrated emulsion produced.

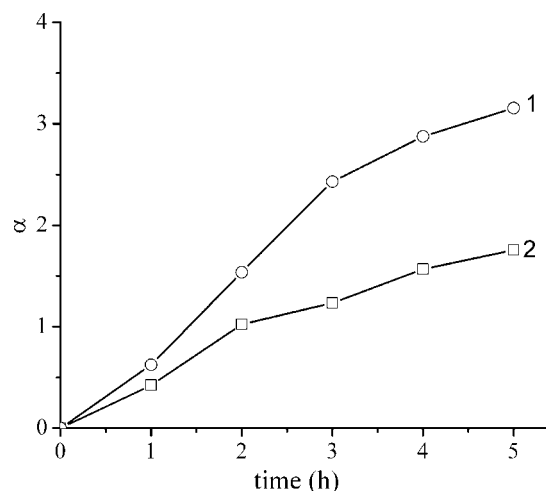


Figure 5 The effect of different kind of surfactants on polymerization stability. $[E] = 0.19$ g/mL H_2O , $SDS/OS_{15} = 2 : 1$, $PVA = 0.01$ g/mL H_2O , $PUASi/MMA/St = 1 : 1 : 3$, $[I] = 0.8\%$ g/g (PUASi/MMA/St), $TDI/PPG = 2 : 1$, $H_2O = 5$ g, $\Phi = 80.39\%$, 1-SDS; 2-MS-1.

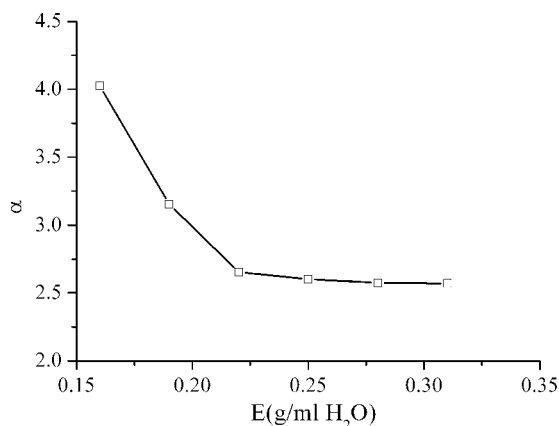


Figure 6 The effect of $[E]$ on polymerization stability. SDS/OS₁₅ = 2 : 1, PVA = 0.01 g/mL H₂O, PUASi/MMA/St = 1 : 1 : 3, $[I]$ = 0.8% g/g (PUASi/MMA/St). TDI/PPG = 2 : 1, H₂O = 5 g, Φ = 80.39%.

Figure 5 shows the effect of different kinds of surfactants on the polymerization stability. The polymerization stability of the concentrated emulsion increased when surfactant SDS was replaced by MS-1. We also found that the concentrated emulsion polymerization was instable when using SDBS and OP-10 as composite surfactant.

Figure 6 shows the effect of the surfactant concentration on polymerization stability of concentrated emulsion. The polymerization stability of concentrated emulsion increased with increasing the surfactant concentration in a certain range, probably generating thicker cell film. Whereas surfactant concentration was larger than 0.22 g/mL H₂O, the polymerization stability of concentrated emulsion changed little.

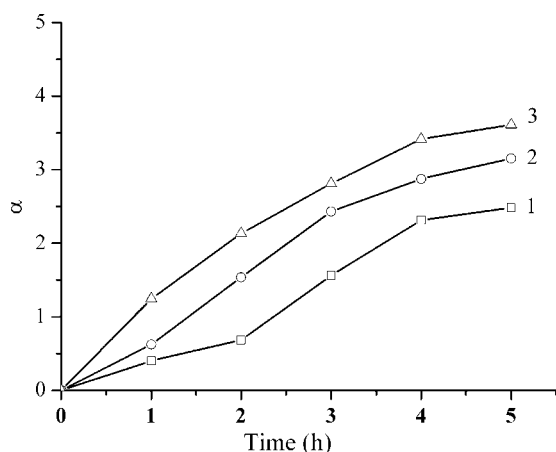


Figure 7 The effect of temperature on polymerization stability. $[E]$ = 0.19 g/mL H₂O, SDS/OS₁₅ = 2 : 1, PVA = 0.01 g/mL H₂O, PUASi/MMA/St = 1/1/3, $[I]$ = 0.8% g/g (PUASi/MMA/St), TDI/PPG = 2 : 1, H₂O = 5 g, Φ = 80.39%, 1–45°C; 2–55°C; 3–65°C.

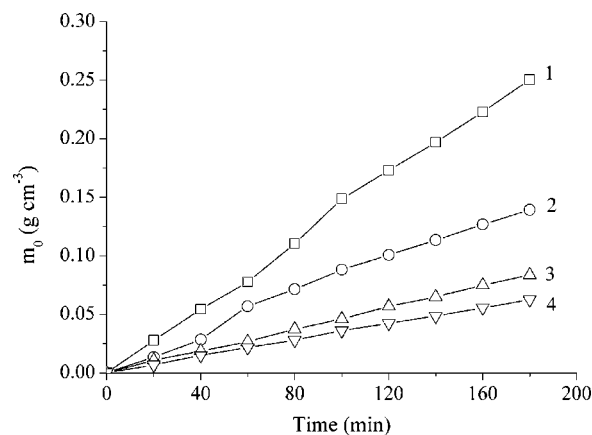


Figure 8 The amount of volatilization per unit volume versus time at various thickness. (SDS)/m(OS₁₅) = 2 : 1, $[E]$ = 0.19 g/mL H₂O, PVA = 0.01 g/mL H₂O, S = 23.75 cm² 1-h = 0.2 mm; 2-h = 0.4 mm; 3-h = 0.6 mm; 4-h = 0.8 mm, m_0 represents the amount of volatilization per unit volume of water and monomer.

Therefore, 0.22 g/mL H₂O was the suitable surfactant concentration for this system.

Temperature has remarkable effect on polymerization stability of the concentrated emulsion (Fig. 7). The stability of concentrated emulsion decreased with the increase of temperature, since molecular mobility was getting higher with increasing temperature, which results in easier transfer of monomer phase through cell film.

The volatilization rate of water and monomer

The effects of thickness of the thin layer, outside temperature, polymerization environment, etc. on the amount of volatilization of water and monomer in the thin layer polymerization of concentrated emulsion were shown in Figure 8 (Tables II and III).

At 55°C, the amount (m_0) of volatilization per unit volume of water and monomer under different thickness of the thin layer was presented in Figure 8. The amount of volatilization per unit volume-time, i.e., the volatilization rate (dm_0/dt) was calculated by the linear regression method and shown in Table II. Although the area of the thin layer and the outside condition (1 kp, 55°C) of the reactor remained constant, it was found that with the increase of the thin

TABLE II
The Effect of the Thickness of the Thin Layer on the Volatilization Rate of Water and Monomer

Thickness (cm)	0.2	0.4	0.6	0.8
The volatilization rate ($V_0 \times 10^4$)	13.9	6.95	4.63	3.48

$m(\text{SDS})/m(\text{OS}_{15}) = 2 : 1$, $[E] = 0.19$ g/mL H₂O, $S = 23.75$ cm², PVA = 0.01 g/mL H₂O.

TABLE III
The Effects of Environment on the Volatilization Rate of Monomer and Water ($\times 10^{-4}$ g cm $^{-3}$ min $^{-1}$)

Polymerization environment	Temperature ($^{\circ}$ C)		
	45	55	65
In air	5.42	6.95	12.58
In water bath	2.05	2.63	5.0

$m(\text{SDS})/m(\text{OS}_{15}) = 2:1$, $[E] = 0.19$ g/mL H $_2$ O, $h = 0.40$ cm, $S = 23.75$ cm 2 , PVA = 0.01 g/mL H $_2$ O.

layer thickness, the volatilization rate of water, and monomer decreased. With the increase of the thin layer's thickness, the volume of the concentrated emulsion increased. But the total amount of volatilization of water and monomer didn't change at certain temperature and pressure while the area of the thin layer remind constant. The effects of environment (air or water) and its temperature on the volatilization rate of water and monomer were presented in Table III. The volatilization rate of water and monomer did not change much from 45 to 55 $^{\circ}$ C, but doubled from 55 to 65 $^{\circ}$ C. This suggests that stable concentrated emulsion polymerization may be carried out between 45 and 55 $^{\circ}$ C. Above 55 $^{\circ}$ C, the stability of concentrated emulsion decreased rapidly with the increasing temperature, since molecular mobility is getting larger with increasing temperature, which results in easier transfer of monomer phase through the cell film. Therefore, temperature has remarkable effect on stability of the concentrated emulsion. Table III also demonstrated that, at three different temperatures, the volatilization rate of water and monomer in water bath was less than half of that in air, indicating that water bath is a better

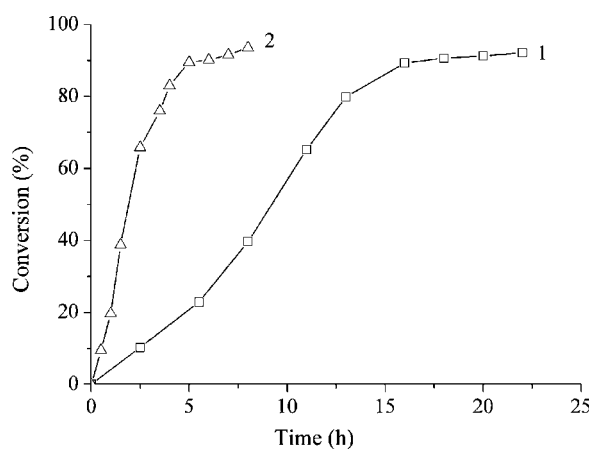


Figure 9 The conversion-time curves of the thin layer and tube polymerizations. $[E] = 0.19$ g/mL H $_2$ O, SDS/OS $_{15} = 2 : 1$, PVA = 0.01 g/mL H $_2$ O, PUASi/MMA/St = 1 : 1 : 3, $[I] = 0.8\%$ g/g (PUASi/MMA/St), TDI/PPG = 2 : 1, H $_2$ O = 5 g, $\Phi = 80.39\%$, 1-thin layer polymerization; 2-tube polymerization.

environment for the polymerization to go on. This is, of course, reasonable because the heat conduction in water bath is much easier than that in air.

A comparison between the thin layer polymerization and the tube polymerization

The conversion-time curves of the thin layer and tube polymerizations at 55 $^{\circ}$ C in water bath were plotted in Figure 9. It is clear that the polymerization rate of the tube polymerization is faster than that of the thin layer polymerization. This is due to the larger area for heat dispersion in the thin layer polymerization, which reduces the effect of self-heating phenomenon.¹⁶

Figure 10 plotted the conversion against time under different environment. Conversion of the thin layer polymerization in the oven was higher than that in water bath, while temperature remained constant. Since the efficiency of heat conduction rate in water bath is higher than that in the oven, the heat accumulated in the thin layer polymerization was easier to diffuse in water, leading to lower self-heating temperature. Therefore, the polymerization environment has remarkable effect on polymerization rate of concentrated emulsion.

TEM images of the colloidal particles of thin layer polymerization

Figure 11 presents the latex particle morphologies under different polymerization environments. The average size of latex particles in thin layer polymerization in water bath was smaller than that in the oven, since the efficiency of heat conduction in water

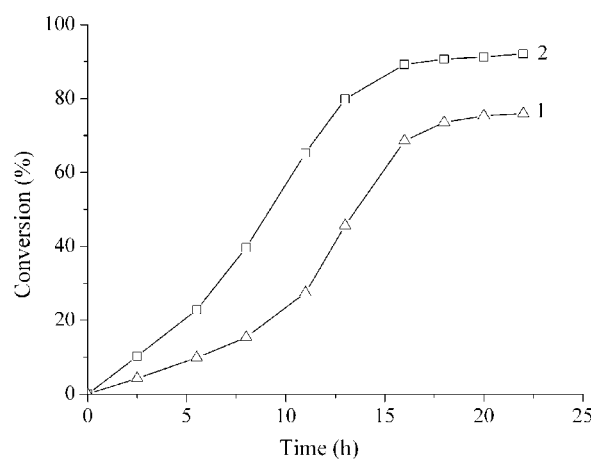


Figure 10 The effects of polymerization environment on the polymerization rate. $[E] = 0.19$ g/mL H $_2$ O, SDS/OS $_{15} = 2 : 1$, PVA = 0.01 g/mL H $_2$ O, PUASi/MMA/St = 1 : 1 : 3, $[I] = 0.8\%$ g/g (PUASi/MMA/St), TDI/PPG = 2 : 1, H $_2$ O = 5 g, $\Phi = 80.39\%$, 1-water bath polymerization; 2-air polymerization.

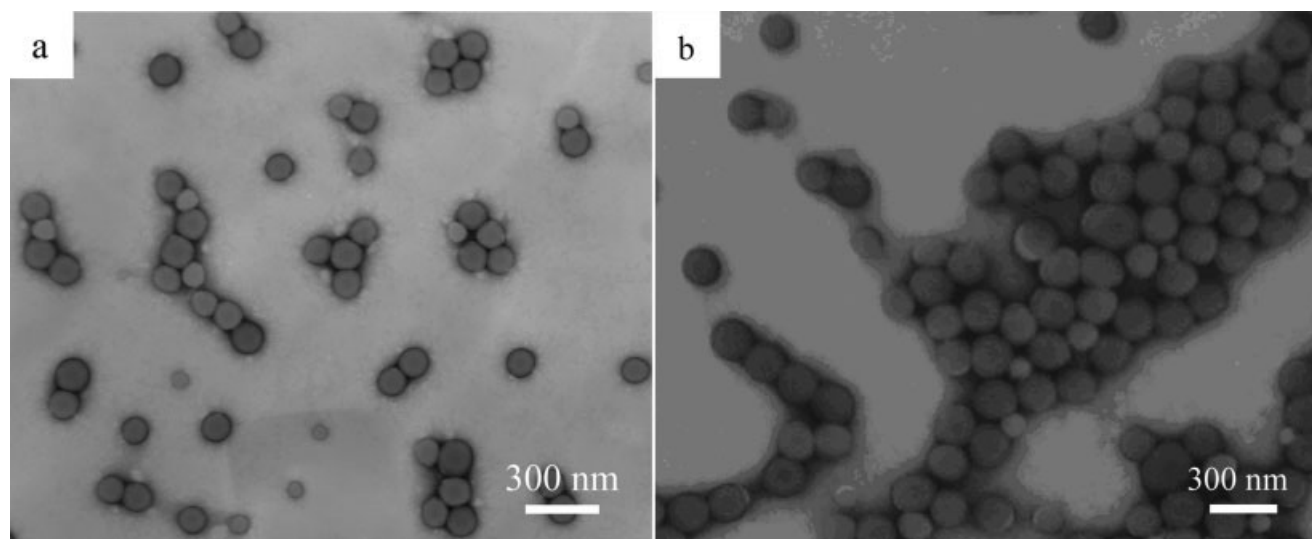


Figure 11 TEM images at different polymerization environments ($\times 20,000$). (a) water bath; (b) oven bath.

bath was higher than that in the oven, reducing the formation of particle aggregations.

CONCLUSION

A novel polymerization method, thin layer concentrated emulsion polymerization was applied to carry out the copolymerization of PUASi, St, and MMA. Stable concentrated emulsions of PUASi/St/MMA were first prepared.

Then the effects of TDI/PPG molar ratio, surfactant concentration, different kinds of surfactants and temperature on polymerization stability were studied. The volatilization rate of water and monomer was also investigated and found that it decreased with the increase of the thin layer's thickness, increased with increasing temperature and was lower in water bath than that in the oven. The polymerization rate of the thin layer concentrated emulsion polymerization was further compared with that of the test tube polymerization. It was concluded that polymerization was faster in the tube than that in the thin layer polymerization. But the thin layer polymerization rate in the oven was faster than that

in the water bath. As a result, the average size of latex particles in thin layer polymerization carried out in water bath was smaller than that in the oven.

References

1. Kozakiewicz, J. *Prog Org Coat* 1996, 27, 123.
2. Czerwiński, W.; Ostrowska-Gumowska, B.; Kozakiewicz, J.; Kujawski, W.; Warszawski, A. *Desalination* 2004, 163, 207.
3. Zhang, H. T.; Chen, L.; Duan, L. L.; Huang, H. *Polym Bull* 2006, 57, 603.
4. Zhang, H. T.; Lin, L. L.; Yin, Z. H. *Chem J Internet* 2000, 2, 24.
5. Zhang, H. T.; Cao, J. H. *Petrochem Technol* 2003, 32, 763.
6. Liao, S. P.; Yang, Y. K. *Chem Adhesion* 1999, 2, 57.
7. Ruckenstein, E.; Gerlinde, E.; Platz, G. *J Colloid Interface Sci* 1989, 133, 432.
8. Ruckenstein, E.; Kim, K. J. *J Appl Polym Sci* 1988, 36, 907.
9. Zhang, H. T.; Li, J. Z. *Polym Commun* 1995, 2, 99.
10. Yun, Q.; Li, H. Q. *Polym Mater Sci Eng* 2001, 5, 144.
11. Zhang, C.; Du, Z. J.; Li, H. Q.; Ruckenstein, E. *Polymer* 2002, 43, 2945.
12. Zhang, H. T.; Huang, H.; Cao, J. H. *J Appl Polym Sci* 2004, 94, 1.
13. Sun, F.; Ruckenstein, E. *J Appl Polym Sci* 1993, 48, 1279.
14. David, D. J.; Staley, H. B. *Journal of High Polymer Series XVI, Part*, Wiley: New York, 1969.
15. Kim, J. Y.; Suh, K. D. *J Colloid Polym Sci* 1996, 274, 920.
16. Zhang, H. T.; Chen, M. *J Appl Polym Sci* 2004, 91, 570.