Stability and Copolymerization of Concentrated Emulsion of Styrene and Butyl Acrylate in the Presence of Polyurethane Macromonomer

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ABSTRACT: A study has been made of the stability and copolymerization of concentrated emulsion of styrene (St) and butyl acrylate (BA) in the presence of polyurethane macromonomer (DPUA), which contains C=C at one end. First, the DPUA macromonomer was synthesized from the appropriate amount of 2,4-diisocyanate (TDI), polypropylene glycol (PPG), 2-hydroxyethyl methylacrylate (HEMA), dimethylolpropionic acid (DMPA), and triethylamine (TEA) by four steps. Then, the DPUA was dissolved in St-BA monomer mixtures. The DPUA/St-BA concentrated emulsion copolymerization using sodium dodecyl sulfate/cetyl alcohol (SDS/CA) as composite surfactant and polyvinyl alcohol (PVA) as liquid film reinforcer, and ammonium persulfate/sodium hydrogen sulfate (APS/SHS) as redox initiator system was carried out at 30°C. The effect of NCO/OH molar ratio, surfactants' concentration, mass ratio of DPUA/St-BA, initiators' concentration, volume fraction of the monomer phase (Φ), and temperature on the stability or the copolymerization of the concentrated emulsion of DPUA/St-BA were investigated. The average size and distribution of the latex particles obtained under different conditions were also analyzed. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1992–1999, 2007

Key words: concentrated emulsion copolymerization; polyurethane macromonomer; stability; polymerization

INTRODUCTION

Polyurethane (PU) is an elastomeric material and has very extensive applications. Styrene and butyl acrylate copolymers, P(St-BA), are common thermoplastic materials. However, it is not practical to make PU/P(St-BA) blend materials through simple mixing because the compatibility of PU and P(St-BA) is poor. Materials based on PU and P(St-BA) copolymers are expected to have good properties. In this study, we attempted to prepare PU and P(St-BA) copolymers through the copolymerization of α-double bond-containing polyurethane and styrene–butyl acrylate monomers using concentrated emulsion polymerization.

Over the past two decades, various materials have been made via concentrated emulsion polymerization, such as porous materials,[1–7] particles with different morphologies or properties,[8–13] compatibilization of polymer blends, including toughened polymer composites,[14–25] composite membranes for pervaporation separation,[26–29] conducting polymer composites,[30–32]

ion-exchange chromatography columns,[33] etc. This is because concentrated emulsion polymerization possesses quite a number of advantages, such as high rate of polymerization and high molecular weight of polymers produced, high yield per unit volume, favorable reactions at the cell interface, ensured stability, controllable cell uniformity, etc. In addition, some other issues associated with concentrated emulsion polymerization have also been studied, including high-rate polymerization,[34] polymerization initiated by redox systems under lower temperature,[35–40] or self-heating polymerization,[41–43] etc.

In this study, we first synthesized a double bond-containing prepolyurethane (DPUA). Then, the concentrated emulsion copolymerization of St and BA, in the presence of DPUA, was carried out at low temperature (30°C), with APS/SHS as water-soluble redox initiator. The stability of the concentrated emulsion of DPUA/St-BA and its polymerization kinetics were investigated. Particle size and distribution of the lattices produced were also determined.

EXPERIMENTAL

Materials

2,4-diisocyanate (TDI, chemical grade, The Chemical Factory of Hubei University, Wuhan, China), dibutyltin

2mol OCN-D-NCO + 1molHO-G-OH ⟶ OCN-D-NC-O-G-O-CN-D-NCO

TDI   PPG | || || |
                                              H O   O H

↓ 1 mol HEMA

$$CH_3$$
$$CH_2=C\text{-}COCH_2CH_2OCN\text{-}D\text{-}NC\text{-}O\text{-}G\text{-}O\text{-}CN\text{-}D\text{-}NCO$$
$$O \qquad OH \quad HO \qquad O\,H$$

↓ 1 mol DMPA

$$CH_3 \qquad\qquad\qquad\qquad\qquad\qquad CH_3$$
$$CH_2=C\text{-}COCH_2CH_2OCN\text{-}D\text{-}NC\text{-}O\text{-}G\text{-}\text{-}O\text{-}CN\text{-}D\text{-}NC\text{-}O\text{-}CH_2\text{-}C\text{-}CH_2\text{-}OH}$$
$$O \qquad OH \quad HO \qquad OH \quad HO \qquad COOH$$

or HEMA- - TDI- -PPG - TDI- -DMPA- -TDI - PPG - TDI- -DMPA

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↓ N(CH₂CH₃)₃

══════⌇⌇⌇⌇⌇⌇⌇⌇⌇⌇⌇⌇⌇⌇⌇COO⁻ NH⁺(CH₂CH₃)₃

Scheme 1

dilaurate (DBDL, analytical grade, Beijing Taopu Chemical Factory, China), triethylamine (TEA), and 2-hydroxyethyl methylacrylate (HEMA, chemical grade, Tianjin Institute of Chemical Reagent, China) were purchased and used directly. Dimethylolpropionic acid (DMPA) was purchased from Chengdu Factory of Polyurethane, Sichuan, China. Polypropylene glycol (PPG N_{210}, $M_n = 1120$, Nanjing Taiping Chemical Factory, China) was dried in vacuum for 3 h at 120°C. Styrene (St, industrial product) and butyl acrylate (BA, industrial product, Beijing Dongfang Chemical Factory, China) were distilled under reduced pressure to remove the inhibitor and then were stored at low temperature. Sodium hydrogen sulfate (SHS, chemical grade) and ammonium persulfate (APS, chemical grade, The Chemical Plant of Hubei University) were recrystallized. Sodium dodecyl sulfate (SDS, chemical grade) and cetyl alcohol (CA, chemical grade) were purchased from Shanghai Supply Depot of Chemical Reagent, China, and were used directly. Polyvinyl alchohol (PVA-1788, chemical grade) and hydroquinone (Analytic grade, Shanghai Chemical Reagent Factory, China) were purchased and were used directly. Water was deionized before use.

Synthesis of prepolyurethane macromonomer

The synthesis of DPUA was carried out in four steps (Scheme 1).

2 mol of TDI was first mixed with 1 mol of N_{210} and catalyst DBTL, at 45°C for 7 h. The change of NCO value during the reaction was determined using the dibutylamine back titration method to find the end point of reaction. In the second step, 1 mol HEMA was added slowly to react with residual isocyanate group at 45°C for 4 h, which introduced C=C into the molecular chain. The end point of this step was determined by the fact that the NCO value did not change with reaction time. After that, 1 mol of DMPA was added to induce some carboxyl groups onto the prepolyurethane. Finally, triethylamine (TEA) was added to neutralize the carboxyl groups induced.

Figure 1 shows the IR spectrum of purified final product. No peak in 2270–2240 cm^{-1} shows that NCO had been thoroughly reacted. The weak peak shoulder at 1415 cm^{-1} is the characteristic peak of CH$_2$=CH— group, which indicates that the double bond has been successfully introduced onto the polyurethane molecular chain.
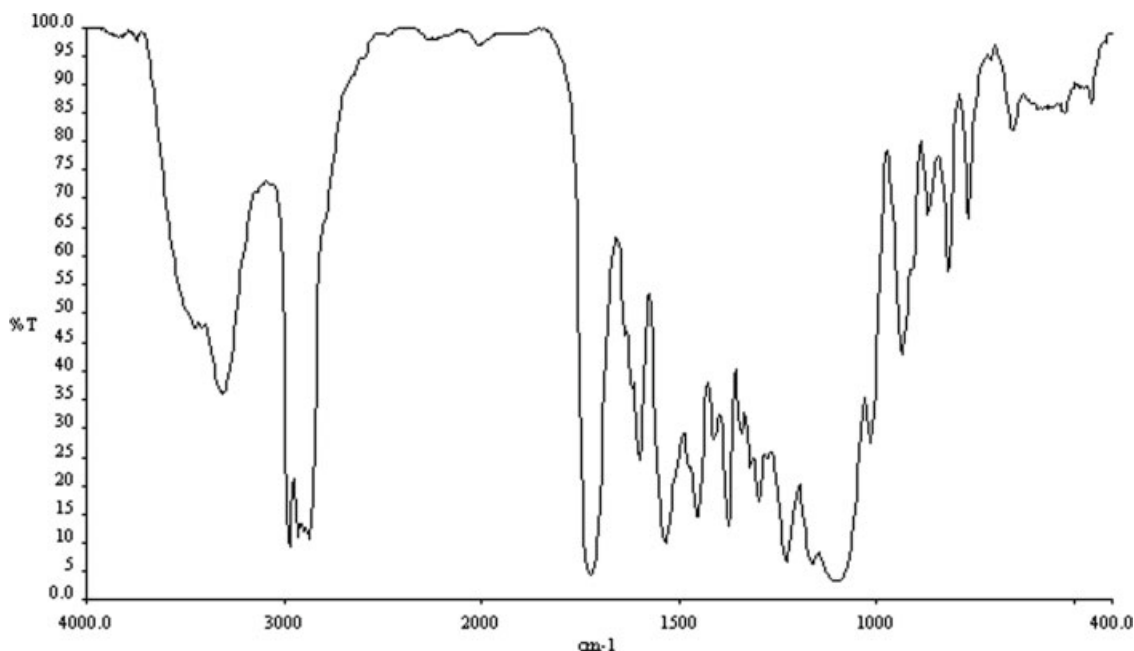
Figure 1 IR of DPUA prepolymer.

It should be noted that, because the hydroxyl and carboxyl groups of DMPA can react with the NCO end groups of prepolyurethane oligomers formed in the second step, DPUA formed in the final step will be a mixture also containing macromonomers with only OH end groups, though the form shown in Scheme 1 is preferred. This, however, will not change the copolymerization of DPUA with St and BA. As mentioned in our previous work,[36] copolymerization of DPUA with St or other monomers could be a promising way to make new materials.

Preparation and polymerization of concentrated emulsion

Table I shows a typical recipe used in the preparation of DPUA/St-BA concentrated emulsion. A known volume of an aqueous solution of SDS, CA, PVA-1788, and APS was added into a four-necked flask at room temperature, equipped with mechanical stirrer, a funnel, and a nitrogen inlet. Monomer mixture of BA and St with DPUA was dropped into the flask under stirring at a suitable rate to avoid phase separation. The whole process was under the protection of nitrogen. After the entire dropping process, solution of reducer SHS was injected into the system. Vigorous stirring stopped after 5 min. The prepared gel-like concentrated emulsion was transferred to a 10-mL centrifugal tube and centrifuged at a moderate rate (1500 rpm) 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. The tube was placed in a temperature-controlled water bath to carry out polymerization.

Determination of stability of the concentrated emulsion

Each concentrated emulsion (free of initiator) was transferred into a 10-mL centrifugal tube. After a mild centrifugation at a speed of 1500 rpm for 10 min, the tube was placed in water bath at polymerization temperature for 24 h. The stability was measured in terms of weight fraction (α) of the bulk phase separated from the concentrated emulsion. The larger the value of α, the less stability of the concentrated emulsion is.

Determination of conversion

Samples were withdrawn from the reaction vessel at regular time intervals and transferred to a preweighed glass container containing hydroquinone. Then the samples were dried in a vacuum oven until their weight remained constant. The conversion was calculated gravimetrically.

TABLE I
A Typical Recipe Used in the Preparation of DPUA/St-BA Concentrated Emulsion

Component	Amount (g)
DPUA	22.00
Dispersed phase, m(St)/m(BA) = 9/1	66.00
Continuous phase, H_2O	17.00
Surfactant, SDS	1.70
Cosurfactant, CA	0.70
Liquid film reinforcer, PVA-1788	0.18
Oxidant, APS	0.32
Reducer, SHS	0.12

TABLE II
The Effect of TDI/PPG Molar Ratio on the Stability (α)

No.	TDI/PPG	α
1	1.2/1	24.6
2	1.5/1	18.7
3	1.8/1	9.2
4	2.0/1	4.9

[E] = 0.12g/mL H_2O, SDS/CA = 2/1, DPUA/St-BA = 1/3, $T = 30°C$, $\Phi = 0.83$.

Measurement of size and distribution of the latex particles

Withdrawn from the reaction vessel at regular intervals, samples were transferred to 10-mL tubes, and then dispersed in deionized water. The size and distribution of the particles were measured on an Autosizer Loc-FC963 apparatus (Malvern Instruments, Worcester, UK).

RESULT AND DISSCUSSION

The stability of DPUA/St-BA concentrated emulsion

In Scheme 1, we used the empirical TDI/PPG molar ratio of 2/1 to demonstrate the steps for the synthesis of DPUA. To compare the experimental result on the stability, we synthesized four kinds of prepolyurethane by changing the TDI/PPG molar ratio. Table II shows the effect of TDI/PPG molar ratio on the bulk phase separated from the concentrated emulsion. When the molar ratio of TDI/PPG increases, the α value decreases, indicating a more stable concentrated emulsion system. A lower molar ratio of TDI/PPG leads to a higher molecular weight of prepolyurethane and higher viscosity of the disperse phase. When the molar ratio of TDI/PPG approaches 1, the molecular weight of DPUA becomes very big, which makes dissolution or swelling of DPUA in St-BA impossible, leading to a worse stability of the concentrated emulsion produced.

Figure 2 shows the effect of concentration of the surfactant on the emulsion stability. The stability of concentrated emulsion increases, when the surfactant concentration increased in a certain range, probably generating thicker cell film. Whereas surfactant concentration is larger than 0.12 g/mL H_2O, the stability of concentrated emulsion decreases. This probably happened because of the high viscosity of the highly concentrated aqueous solutions of surfactant that impedes the formation of the cells.[44]

Figure 3 demonstrates the bulk phase separated from concentrated emulsion with time at different mass ratio of DPUA/St-BA. The higher the mass ratio of DPUA/St-BA, the poorer is the stability of the
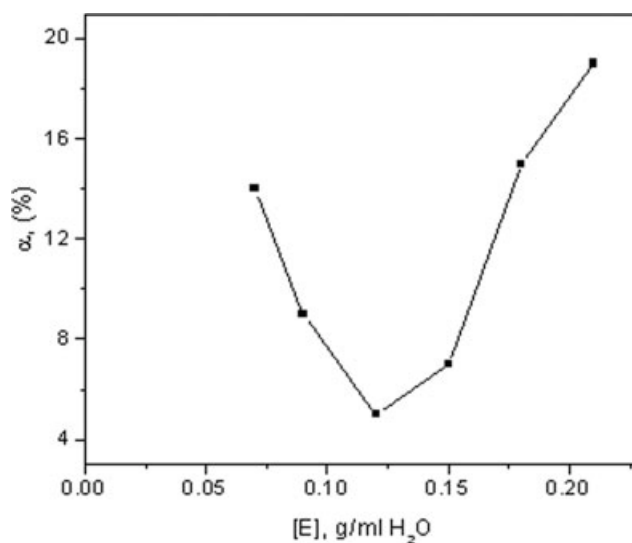

Figure 2 Effect of surfactant concentration [E] on the stability of the DPUA/St-BA concentrated emulsion. SDS/CA = 2/1, DPUA/St-BA = 1/3, $T = 30°C$, $\Phi = 0.83$, NCO/OH = 2/1.

concentrated emulsion prepared. This indicates that the surfactants used have less emulsifying power to prepolyurethane, compared with that of St and BA. This is quite understandable because prepolyurethane has much higher molecular weight than St and BA. The strong intra- and intermolecular hydrogen bonding interactions in prepolyurethane molecules also makes it harder to be emulsified and easier to aggregate, both contributing to a worse stability of the final emulsion produced.
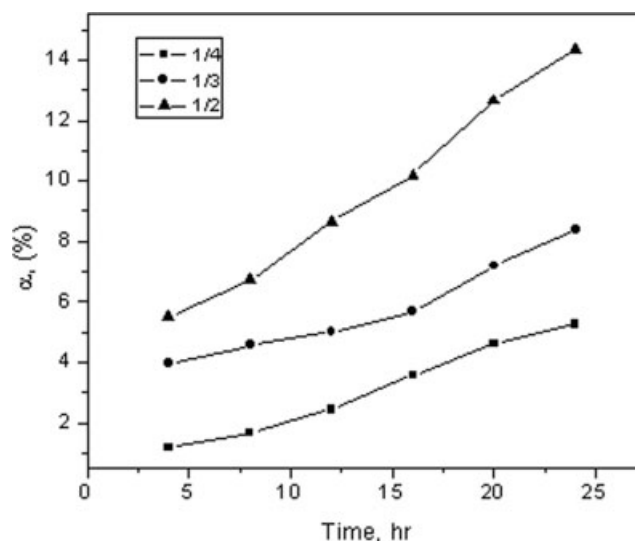

Figure 3 Stability of the DPUA/St-BA concentrated emulsion under different mass ratio of DPUA/St-BA. $\Phi = 0.83$, NCO/OH = 2/1, SDS/CA = 2/1, [E] = 0.12 g/mL H_2O, $T = 30°C$.
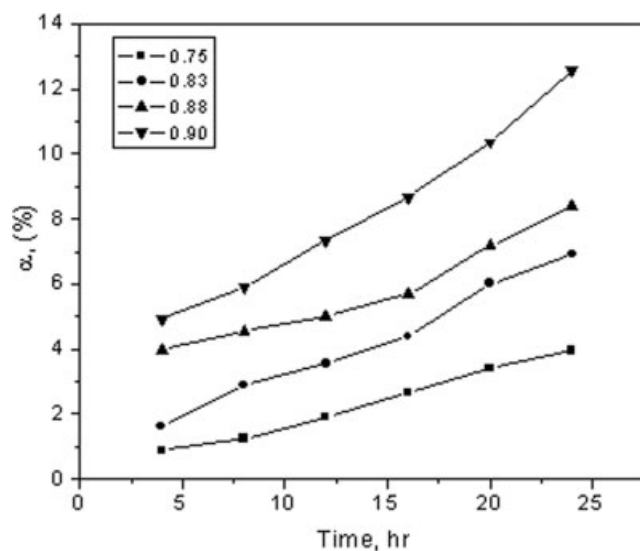
Figure 4 Effect of the volume fraction of disperse phase (Φ) on the stability of concentrated emulsion of DPUA/St-BA. SDS/CA = 2/1, DPUA/St-BA = 1/3, T = 30°C, NCO/OH = 2/1, [E] = 0.12 g/mL H_2O.

Relationship between the volume fraction of disperse phase (Φ) and the stability of concentrated emulsion is presented in Figure 4, where the surfactants' concentration remains constant. The stability of the concentrated emulsion decreases with the increase of Φ, which is clearly due to the decrease of surfactant molecules absorbed on cell film per area.

Temperature has remarkable effect on stability of the concentrated emulsion (Fig. 5). The stability of concentrated emulsion decreases with the increase of temperature, since molecular mobility is getting higher with increasing temperature, which results in easier transfer of monomer phase through cell film.

Kinetics of concentrated emulsion copolymerization of DPUA/St-BA

Figure 6 plots the conversion against time under different initiator concentrations. Both polymerization rate and conversion increase with increasing initiator concentration. This is a straightforward result and a common phenomenon in all emulsion polymerization methodologies. It complies with the kinetics of polymerization induced by free radicals formulated on the basis of the steady-state approximation, assuming that the conversion for a given polymerization time is proportional to the rate of polymerization.

Figure 7 presents the conversion-time curves under various surfactant concentrations, while other conditions remain constant. Continuous increase in conversion with increasing surfactant concentration was observed. As the effect of initiator concentration on conversion, this is also a rather common phenom-
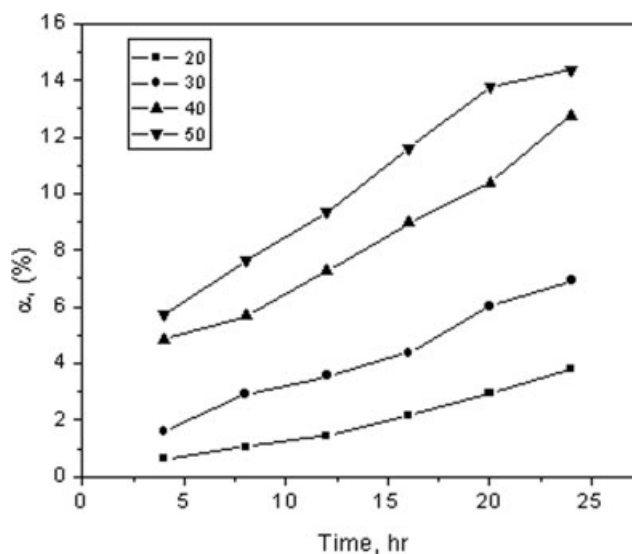

Figure 5 Effect of temperature (°C) on the value of α SDS/CA = 2/1, DPUA/St-BA = 1/3, Φ = 0.83, NCO/OH = 2/1, [E] = 0.12 g/mL H_2O.

enon in emulsion polymerization. A larger amount of surfactant leads to a reduction in the cell size and increase of cell number, which provides more initiating sites. This reduces the chance of bimolecular termination and, therefore, leads to an increased rate of polymerization.

Conversion-time curves of concentrated emulsion polymerization of DPUA/St-BA at different volume fraction of dispersion phase (Φ) are shown in Figure 8. With the increase of Φ, monomer concentration in each cell increases, which leads to the increase in polymerization rate. However, the final conversion decreases when Φ reaches 0.9, where the high poly-
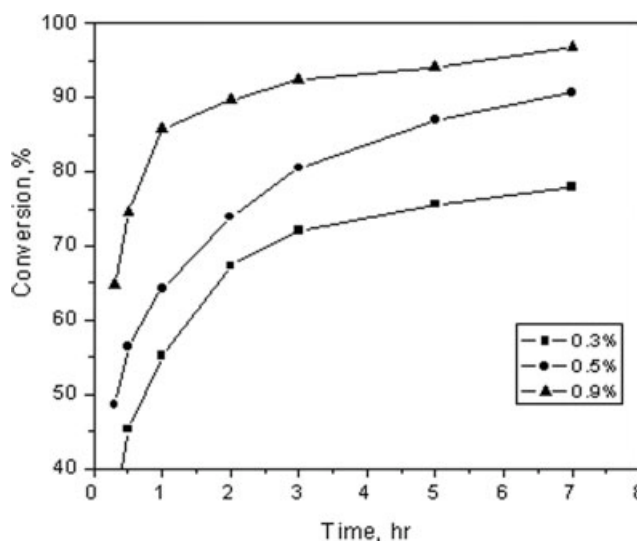

Figure 6 Effect of initiator concentration [I] on polymerization. NCO/OH = 2/1, [E] = 0.12 g/mL H_2O, Φ = 0.83, SDS/CA = 2/1, DPUA/St-BA = 1/3, T = 30°C.
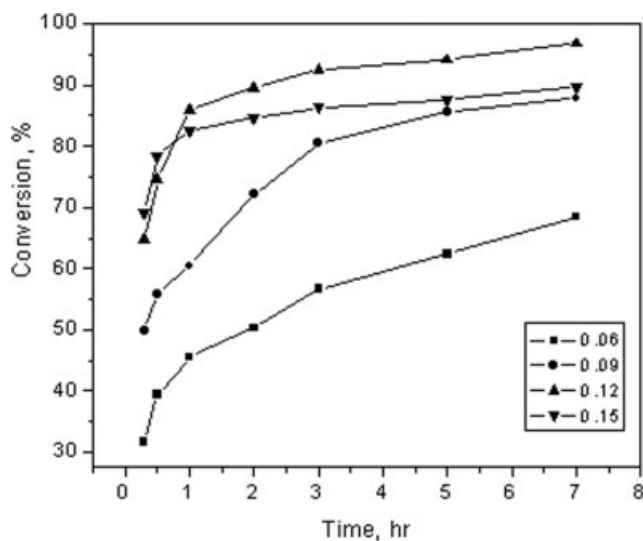
Figure 7 Effect of surfactant concentration [E] (g/mL H$_2$O) on polymerization. NCO/OH = 2/1, SDS/CA = 2/1, DPUA/St-BA = 1/3, T = 30°C, Φ = 0.83, [I] = 0.5%.
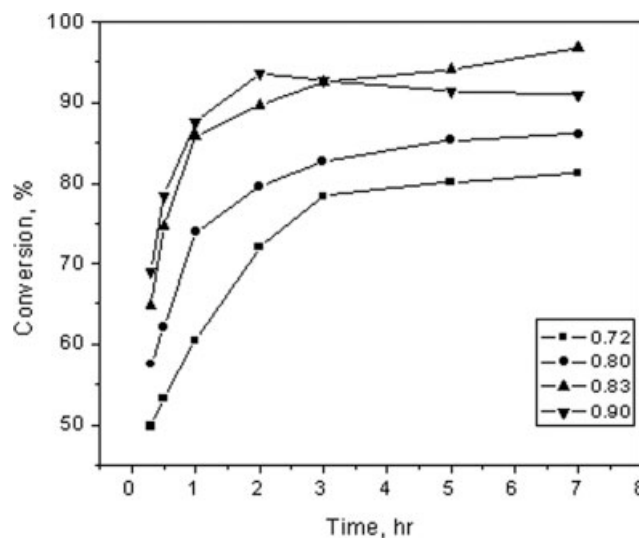

Figure 8 Effect of volume fraction of dispersion phase (Φ) on polymerization. NCO/OH = 2/1, SDS/CA = 2/1, DPUA/St-BA = 1/3, [E] = 0.12 g/mL H$_2$O, T = 30°C, [I] = 0.5%.

merization rate gives rise to the release of large amount of heat, which results in decreased stability of the colloidal system. Therefore, some cells of the gel coalesce and form a bulk phase in which the conversion is smaller. In some extreme cases, loss of monomers could also happen.

The effect of mass ratios of DPUA/St-BA on the polymerization rate and conversion is shown in Figure 9. The higher the mass ratio of DPUA/St-BA, the faster is the polymerization rate and conversion. This can be attributed to the following two reasons. One is that increasing the mass ratio of DPUA/St-BA equals reducing the concentration of monomer mixture of St and BA, while the amount of initiator is constant. This is equal to the increase of initiator concentration. On the other hand, a higher mass ratio of DPUA/St-BA leads to a higher viscosity of the disperse phase, which gives rise to a more significant "gel effect."

Particle size and distribution of polymer lattices

Average particle size and distribution of polymer lattices under different surfactant concentrations are listed in Table III, with the concentration of surfactant lower than 0.12 g/mL H$_2$O. With the increase of composite surfactant concentration in the experimental range studied, average particle size of lattices decreases and particle size distribution becomes narrower, since enough surfactant molecules absorbed on cell film, which impedes coalescence of cells to form a bulk phase.

Average particle size and distribution of the polymer lattices at different temperatures are also listed

in Table III. Lower temperature results in slower polymerization rate, moderate reaction, and less coalescence of cells. Therefore, the average size of latex particles decreases and the particle size distribution becomes narrower.

In Table III are also listed the average size and distribution of latex particles obtained at different initiator concentrations. High polymerization rate brought by high initiator concentration leads to large amount of heat transfer, which is responsible for the coalescence of cells. As a result, the average particle size increases and the particle size distribution becomes broader.
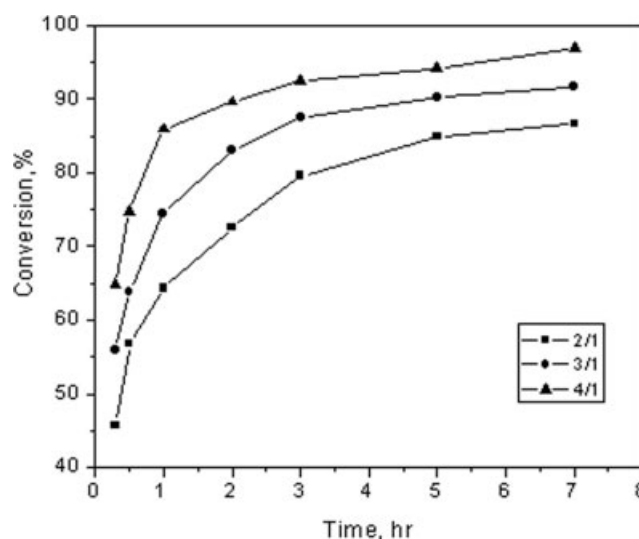

Figure 9 Effect of DPUA/St-BA mass ratio on polymerization. SDS/CA = 2/1, T = 30°C, [I] = 0.5%, [E] = 0.12 g/mL H$_2$O, Φ = 0.83, NCO/OH = 2/1.

TABLE III
Average Particle Size and Distribution of Polymer Latexes under Different Condition

Variable	Condition	D (nm)	Poly	Note
T (°C)	20	128.6	0.097	NCO/OH = 2/1, SDS/CA = 2/1
	25	137.9	0.116	DPUA/St-BA = 1/3
	30	143.5	0.128	[E] = 0.12 g/mL H_2O, Φ = 0.83, [I] = 0.5%
	40	175.2	0.217	
[E] (g/mL)	0.06	198.3	0.245	NCO/OH = 2/1, SDS/CA = 2/1
	0.09	175.4	0.196	DPUA/St-BA = 1/3, T = 30°C
	0.12	143.5	0.128	Φ = 0.83, [I] = 0.5%
[I]	0.3%	117.6	0.073	NCO/OH = 2/1, SDS/CA = 2/1
	0.5%	143.5	0.128	DPUA/St-BA = 1/3, [E] = 0.12 g/mL H_2O
	0.9%	184.3	0.159	Φ = 0.83, T = 30°C

D (nm) represents average diameter, "poly" represents particle size distribution of the latexes. The value of "poly" varies from 0 to 1. The smaller the value, the narrower is the distribution.

CONCLUSIONS

In this preliminary report, prepolyurethane macromonomer DPUA was first prepared. Then a series of stable concentrated emulsion DPUA/St-BA were achieved using sodium dodecyl sulfate/cetyl alcohol (SDS/CA) as composite surfactant and polyvinyl alcohol (PVA) as liquid film reinforcer. The copolymerization of St and BA were carried out in the presence of DPUA with ammonium persulfate/sodium hydrogen sulfate (APS/SHS) as redox initiator.

The experiment result indicates that the most stable concentrated emulsion can be generated when the molar ratio of TDI/PPG in DPUA is 2/1, SDS/CA = 2/1, [E] = 0.12 g/mL H_2O, DPUA/St-BA = 1/3. If the volume fraction of dispersion phase is larger than 0.85, a stable concentrated emulsion is hardly achieved.

The effects of TDI/PPG molar ratio, surfactants' concentration, mass ratio of DPUA/St-BA, initiators' concentration, volume fraction of the monomer phase (Φ), and temperature on the polymerization of the DPUA/St-BA concentrated emulsion were investigated. It complies with the kinetics of common emulsion polymerization induced by free radicals.

The average size and distribution of lattices particles obtained from the concentrated emulsion of DPUA/St-BA decrease with increasing surfactant concentration, but increase with the increase of polymerization temperature and initiator concentration. Relatively small latex particles between 100 and 200 nm were obtained.

References

1. Zhang, H. F.; Cooper, A. I. Soft Mater 2005, 1, 107.
2. Richez, A.; Deleuze, H.; Vedrenne, P.; Collier, R. J Appl Polym Sci 2005, 96, 2053.
3. Butler, R.; Hopkinson, I.; Cooper, A. I. J Am Chem Soc 2003, 125, 14473.
4. Zhang, H. F.; Hardy, G. C.; Rosseinsky, M. J.; Cooper, A. I. Adv Mater 2003, 15, 78.
5. Du, Z. J; Zhang, C.; Li, H. Q. Chem J Chin Univ 2002, 23, 1614.
6. Ruckenstein, E.; Wang, X. Biotechnol Bioeng 1993, 42, 821.
7. Ruckenstein, E.; Hong, L. Chem Mater 1992, 4, 122.
8. Xiang, A. M.; Du, H. J.; Qiao, J. L.; Li, H. Q. Abstr Pap Am Chem Soc (PMSE Part 2, U504-U504) 2003, 226, 294.
9. Xiang, A. M.; Du, Z. J.; Zeng, Q. H.; Zhang, C.; Li, H. Q. Polym Int 2005, 54, 1366.
10. Zhang, H.; Cooper, A. I. Chem Mater 2002, 14, 4017.
11. Yun, Y.; Li, H. Q.; Ruckenstein, E. J Colloid Interf Sci 2001, 238, 414.
12. Li, H. Q.; Zhao, J.; Ruckenstein, E. Colloids Surf A 2000, 161, 489.
13. Sun, F. M.; Ruckenstein, E. J Appl Polym Sci 1993, 48, 1279.
14. Du, Z. J.; Zhang, C.; Li, H. Q. Polym Int 2005, 54, 1377.
15. Du, Z. J.; Zhang, C.; Li, H. Q. Chem J Chin Univ 2004, 25, 184.
16. Li, H. Q.; Du, Z. J.; Huang, H. H. J Appl Polym Sci 2002, 83, 2915.
17. Li, H. Q.; Ruckenstein, E. J Polym Sci, Part B: Polym Chem 2001, 39, 757.
18. Li, H. Q.; Huang, H. H.; Ruckenstein, E. J Polym Sci, Part B: Polym Chem 1999, 37, 4233.
19. Yuan, Y. M.; Ruckenstein, E. J Appl Polym Sci 1998, 67, 913.
20. Ruckenstein, E.; Li, H. Q. Polym Compos 1997, 18, 320.
21. Li, H. Q.; Ruckenstein, E. J Appl Polym Sci 1996, 61, 2285.
22. Li, H. Q.; Ruckenstein, E. Polymer 1996, 37, 1933.
23. Li, H. Q.; Ruckenstein, E. Polymer 1995, 36, 2647.
24. Ruckenstein, E.; Li, H. Q. J Appl Polym Sci 1994, 54, 561.
25. Ruckenstein, E.; Li, H. Q. J Appl Polym Sci 1994, 52, 1949.
26. Ruckenstein, E.; Sun, F. M. J Membr Sci 1995, 103, 271.
27. Sun, F. M.; Ruckenstein, E. J Membr Sci 1995, 99, 273.
28. Ruckenstein, E.; Sun, F. M. J Membr Sci 1993, 81, 191.
29. Ruckenstein, E.; Chen, H. H. J Membr Sci 1992, 66, 205.
30. Park, J. S.; Ruckenstein, E. J Electron Mater 1992, 21, 205.
31. Ruckenstein, E.; Park, J. S. Polym Compos 1991, 12, 289.
32. Ruckenstein, E.; Park, J. S. J Appl Polym Sci 1991, 42, 925.
33. Baharvand H, Rabiee A. J Appl Polym Sci 2004, 91, 2973.
34. Zhang, C.; Du, Z. J.; Li, H. Q.; Ruckenstein, E. Polymer 2002, 43, 5391.

35. Zhang, H. T.; Tan, B.; Wang, A. L.; Cao, J. H. J Appl Polym Sci 2005, 97, 1695.
36. Zhang, H. T.; Huang, H.; Cao, J. H. J Appl Polym Sci 2004, 94, 1.
37. Zhang, H. T.; Chen, M.; Lv, R. J Appl Polym Sci 2004, 91, 570.
38. Zhang, H. T.; Cao, J. H.; Wang, A. L.; Cao, J. H. Chem J Chin Univ 2003, 24, 739.
39. Zhang, H. T.; Wang, A. L.; Cao, J. H.; Acta Polym Sinica 2003, (1), 23.
40. Zhang, H. T.; Lin, L. L.; Yin, Z. H.; Acta Polym Sinica 2001, (2), 200.
41. Zhang, C.; Du, Z. J.; Li, H. Q.; Ruckenstein, E. Polymer 2002, 43, 2945.
42. Li, H. Q.; Du, Z. J.; Ruckenstein, E. J Appl Polym Sci 1998, 68, 999.
43. Ruckenstein, E.; Li, H. Q. Polym Bull 1996, 37, 43.
44. Chen H. H.; Ruckenstein, E. J Colloid Interf Sci 1991, 154, 260.