

Concentrated Emulsion Copolymerization of α -Double Bond-Containing Polyurethane/Styrene Initiated by Redox System

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ABSTRACT: Copolymers of α -double bond-containing polyurethane (DPU) and styrene (ST) were prepared by concentrated emulsion copolymerization, using a cumyl hydroxy peroxide/tetraethylene pentamine (CHPO/TEPA) redox system as initiator, sodium dodecyl sulfate/cetyl alcohol (SDS/CA) as surfactant, and polyvinyl alcohol (PVA) as a liquid film reinforcer (LFI). DPU was first synthesized from the appropriate precursors, then diluted with ST and dissolved completely in ST. This solution was subsequently used as the dispersed phase of a concentrated emulsion in water. Finally, the DPU/ST (PUS) copolymers were obtained by the copolymerization of DPU and ST in the above concentrated emulsions with a volume fraction of the dis-

persed phase up to 80–90%. The effects of surfactants, initiators, and monomer volume fractions, on the stability of the concentrated emulsion copolymerization procedure and the average sizes of PUS copolymer latex particles, were evaluated. IR spectral results verified that PUS copolymers were obtained, and the DSC diagrams of DPU precursor and PUS copolymers with different weight ratios of DPU/ST were presented. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1–8, 2004

Key words: emulsion polymerization; styrene; redox initiation system; stabilization; polyurethanes

INTRODUCTION

Polystyrene (PS) is a common thermoplastic material, but it is easy to craze and/or crack while in processing. Polyurethane (PU) is an elastomeric material and has very extensive applications. However, it is not practical to use PU/PS blend materials through simple mixing because the compatibility of PU and PS is poor. Materials based on PU and PS copolymers (PUS) are expected to have outstanding properties. In this study, we attempted to prepare PUS copolymers through the copolymerization of α -double bond-containing polyurethane (DPU) and styrene (ST) by using a recently developed procedure—concentrated emulsion polymerization.

A concentrated emulsion is a gel-like emulsion in which the volume fraction of the dispersed phase is larger than 0.74 (which is the most compact arrangement of spheres of equal size) and can be as large as 0.99. The dispersed phase is in the form of spherical or polyhedral cells, separated by a network of thin films of continuous phase.^{1–4} The repulsive force, between

the surfactant molecules adsorbed on the surface of neighboring cells, is responsible for the stability of the concentrated emulsions. Because of its unique structure, polymerization based on concentrated emulsion has a number of advantages^{5,6}: (1) Because of the small size of the cells ($<1 \mu\text{m}$) and the presence of a dispersant on their interface, the mobility of the high molecular weight species in each cell is hindered. As a result of this “gel effect,” biradical termination is sharply decreased, and the so-called self-acceleration appears from the beginning of polymerization. Therefore, a high rate of polymerization and high molecular weight products are achieved. (2) The shape and size of the cells in the concentrated emulsions remain relatively unchanged during subsequent polymerization. Consequently, by adjusting the type and concentration of the surfactant, or by changing the ionic strength and other conditions, better control of the size and dispersion of polymer particles becomes possible.

In earlier studies, concentrated emulsion polymerizations were achieved by using thermolytic initiators,^{7,8} such as AIBN, $\text{K}_2\text{S}_2\text{O}_8$, and BPO. In those studies, high temperature was indispensable, which led to high monomer volatility and energy consumption. In recent years, we also investigated concentrated emulsion polymerizations initiated by AIBN in our laboratory.^{9–11} It was found that high temperatures reduced the stability of concentrated emulsions. It is well known that polymerization can be achieved at low

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TABLE I
Basic Recipe in the Preparation of the Concentrated Emulsions^a

Component	Amount
Toluene	3.0 g (0.0172 mol)
2,4-diisocyanate (TDI)	3.0 g (0.0172 mol)
Polypropylene glycol (PPG)	9.646 g (0.0086 mol)
Dibutyltin dilaurate (DBTL)	Three drops
2-Hydroxyethyl methacrylate (HEMA)	2.256 g (0.0086 mol)
Dispersed phase: styrene (ST)	32.5 g (0.313 mol)
Continuous phase: water	5×10^{-3} L (5 g)
Surfactant: sodium dodecyl sulfate (SDS)	0.5 g (1.74×10^{-3} mol)
Cetyl alcohol (CA)	0.25 g (1.2×10^{-3} mol)
Liquid film reinforcer (LFI): Polyvinyl alcohol (PVA)	0.05 g
Oxidant: cumine hydroperoxide (CHPO)	0.29 g (1.93×10^{-3} mol)
Reducer: tetraethylene pentamine (TEPA)	0.23 g (1.13×10^{-3} mol)

^a Monomer volume fraction $\phi = 0.85$, $[E] = 0.15$ g/mL H_2O , $[SDS]/[CA] = 2/1$, $[I] = 1.6$ wt % of monomer. $[E] = [SDS + CA]$, the concentration of surfactant, g/mL water; $[I] =$ concentration of initiator.

hol (CA) were purchased from Tian Tai Fine Chemicals (Guangzhou, China), and used as received. Cumine hydroperoxide (CHPO), tetraethylene pentamine (TEPA), hydroquinone, chloroform, and polyvinyl alcohol (PVA) were all used without further purification (analytical grade). Water was deionized and distilled.

Synthesis of DPU

The reaction was carried out in a four-neck flask equipped with a stirrer, thermometer, reflux condenser, and inlet system for nitrogen gas. As an example, the reaction procedure and molecular structure of PU and PUS copolymers are shown in Scheme 1. TDI (x mol) and PPG (y mol) were mixed in the flask and nitrogen gas was purged to eliminate the residual

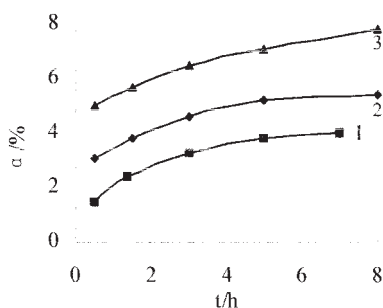


Figure 1 Effect of NCO/OH on stability of the concentrated emulsions NCO/OH: 1 : 2/1; 2 : 1.5/1; 3 : 1.2/1 ($[E] = 0.15$ g/mL H_2O , $[SDS]/[CA] = 2/1$, $[I] = 1.6$ wt % of St, DPU/ST = 1/3, $T = 30^\circ C$, $\Phi = 0.80$).

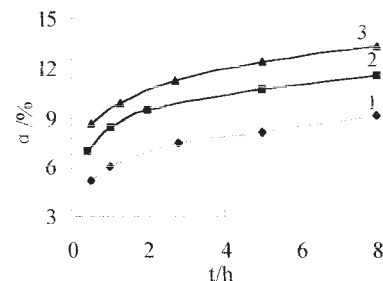


Figure 2 Effect of DPU/ST on stability of the concentrated emulsions DPU/ST: 1 : 1/4; 2 : 1/3; 3 : 1/2 ($[E] = 0.15$ g/mL H_2O , $[SDS]/[CA] = 2/1$, $[I] = 1.6$ wt % St, $NCO/OH = 2/1$, $T = 30^\circ C$, $\Phi = 0.80$).

moisture at room temperature. After the catalyst DBTL was added to the system under stirring, the flask was placed in a water bath at $80^\circ C$ for 3 h to allow the formation of polyurethane (PU) bearing NCO end groups. When the temperature was reduced to $60^\circ C$, HEMA (z mol) was added to the flask within 3 h to introduce $C=C$ double bonds onto the PU molecular chains [i.e., obtaining double bond-containing polyurethane (DPU)]. Then the DPU was cooled to $50^\circ C$, and a certain amount of styrene monomer was added. After being stirred for 1 h, the solution was kept at room temperature for 12 h. TDI : PPG : HEMA = $x : y : z$ mol.

Preparation and polymerization of concentrated emulsions

At room temperature, a known volume of an aqueous solution of PVA, SDS, and CA was charged to a four-neck flask of 100 mL capacity, equipped with a mechanical stirrer, a funnel, and a nitrogen inlet and saturated with nitrogen after addition of each chemical. ST monomer containing the oxidant CHPO was dropped at a suitable rate into the aqueous solution under stirring. After the entire dropping process, which lasted for 15–20 min, reducer TEPA was injected into the system and dispersed completely. Stir-

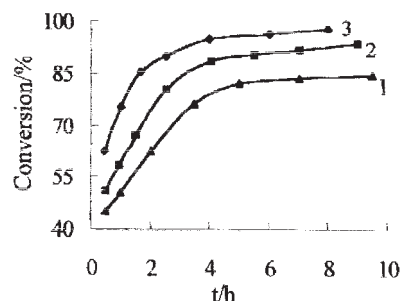


Figure 3 Effect of $[E]$ on conversion (1 : 0.06; 2 : 0.15; 3 : 0.21 g/mL H_2O , $[I] = 1.6$ wt % monomer, $CHPO/TEPA = 1.25$, $\Phi = 85\%$, $[SDS]/[CA] = 2/1$, $T = 30^\circ C$).

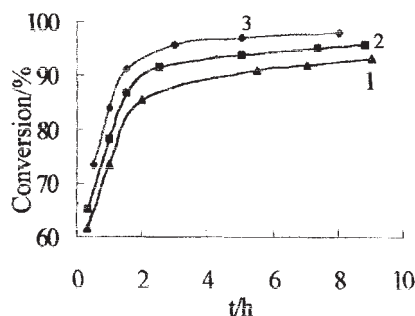


Figure 4 Effect of DPU/ST on conversion (1 : 1/4; 2 : 1/3; 3 : 1/2, $[I] = 1$ wt % monomer, CHPO/TEPA = 1.25, $[E] = 0.15$ g/mL H_2O , SDS/CA = 2/1, $\Phi = 85\%$, $T = 30^\circ C$).

ring was stopped after 5 min. The prepared concentrated emulsion was transferred to a tube (10 mL capacity), sealed with a rubber stopper, and centrifuged at a moderate rate. When no obvious bubble formation was observed, the tube containing the emulsion was placed in a temperature-controlled water bath and copolymerization was conducted for a prescribed time at $30^\circ C$. The copolymer was washed with methanol and dried in a vacuum oven. A typical recipe for the preparation of the concentrated emulsions is presented in Table I.

Stability of polymerization procedure

The stability of the polymerization procedure was measured in terms of the weight fraction (α) of bulk phases that separated from the concentrated emulsion: the larger the value of α , the less stability of the concentrated emulsion.

Determination of conversion

Samples were withdrawn from the reaction vessel at regular time intervals during the polymerization and transferred to a preweighed glass container containing hydroquinone. Then the samples were dried in a vacuum oven at $110\text{--}120^\circ C$ until their weight remained constant. The percentage conversion was calculated gravimetrically.

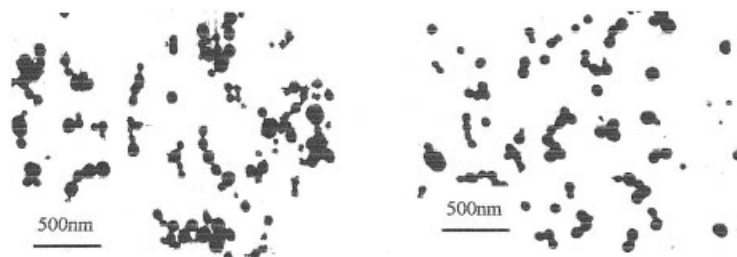


Figure 6 TEM microphotographs of latex particles obtained by using different surfactant concentrations ($[I] = 1.6$ wt % of monomer, CHPO/TEPA = 1.25, $\Phi = 85\%$, SDS/CA = 2/1, DPU/ST = 1/3, $t = 8$ h, $T = 30^\circ C$).

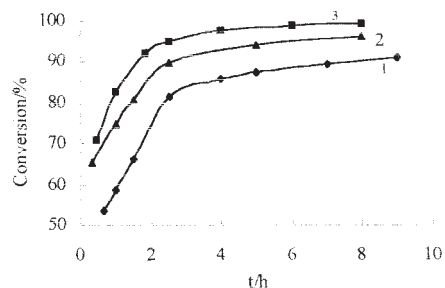


Figure 5 Effect of $[I]$ on conversion: 1 : 0.4%; 2 : 1%; 3 : 1.6 wt % of monomer weight ($[E] = 0.15$ g/mL H_2O , SDS/CA = 2/1, $\Phi = 85\%$, DPU/ST = 1/3, $T = 30^\circ C$, CHPO/TEPA = 1.25).

Particle size and distribution

The copolymer particles were dispersed in water and then coated onto a copper grid. After being dried at room temperature, the samples were examined with a JEM-100SX (JEOL, Tokyo, Japan) transmission electron microscope. The size and polydispersity of the particles were also measured on an Autosizer Loc-FC963 apparatus (Malvern Instruments, Worcester, UK). Here polydispersity was represented with a "Poly" value (the deviation of average diameter in particles.)

IR spectra of the PU and PUS copolymers

The polymers were extracted by toluene and *N,N*-dimethyl formamide with a Soxhlet apparatus, refluxing for 24 h, respectively. The IR spectra of the DPU precursor and PUS copolymers were determined on an IR-400 instrument (Perkin-Elmer Co., USA).

Thermal transition temperature

The thermal transition temperatures of the samples of separated DPU and PUS, of the above-mentioned copolymer lattices, were measured by differential scanning calorimetry (DSC) with a Delta Series DSC-7 instrument (Perkin Elmer Cetus Instruments, Nor-

TABLE II
Relationship Between ϕ and Particle Size^a

Number	ϕ	Z (nm)	Poly ^b
1	0.80	138.1	0.136
2	0.85	139.9	0.182
3	0.90	143.7	0.197

^a [I] = 1.6 wt % of monomer. DPU/ST = 1/3, CHPO/TEPA = 1.25, SDS/CA = 2/1, [E] = 0.15 g/mL H₂O, *t* = 8 h, *T* = 30°C.

^b Polydispersity is represented with a "Poly" value, which is the deviation of average diameter in particles.

walk, CT). Each sample was heated from -60 to 150°C, at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Stability of the concentrated emulsions

Figure 1 shows the effect of NCO/OH mole ratio in the DPU (maintaining DPU/ST at 1/3) on the stability of the concentrated emulsions.

The fraction α represents the weight percentage of bulk phases separated from the concentrated emul-

sions. It can be seen that the stability of the concentrated emulsions increases with increasing NCO/OH mole ratio in the experimental range. The increased stability of the concentrated emulsion with increasing NCO/OH mole ratio might be attributable to reaction of excess NCO groups with PVA, water, and so forth, which makes the interfacial film stronger because the interfacial film is fixed by forming a crosslinked net of PU/PVA.

The effect of DPU/ST weight ratio on the stability of the concentrated emulsions is presented in Figure 2. It can be seen that the larger the DPU/ST weight ratio, the poorer is the stability of the concentrated emulsion because the polarity and H bonds of DPU are larger than those of ST in the system.

Polymerization kinetics

The conversion of concentrated emulsion polymerization, as a function of time, depends on the concentrations of initiator ([I]) and surfactant ([E]), and DPU/ST weight ratio, for example.

Figure 3 shows the effect of surfactant concentration on conversion with time. It is obvious that, when the

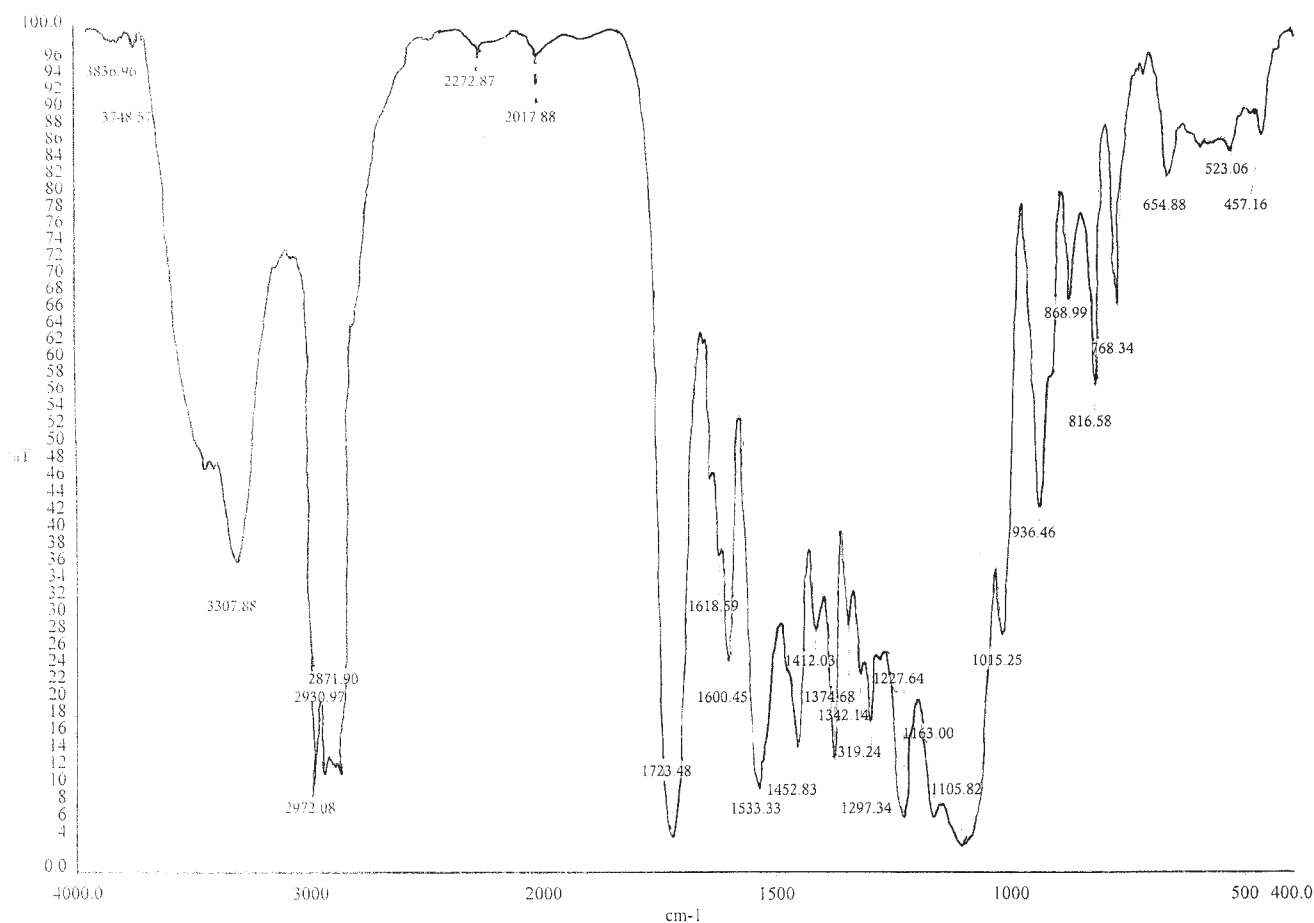


Figure 7 IR spectrum of DPU separated from the samples.

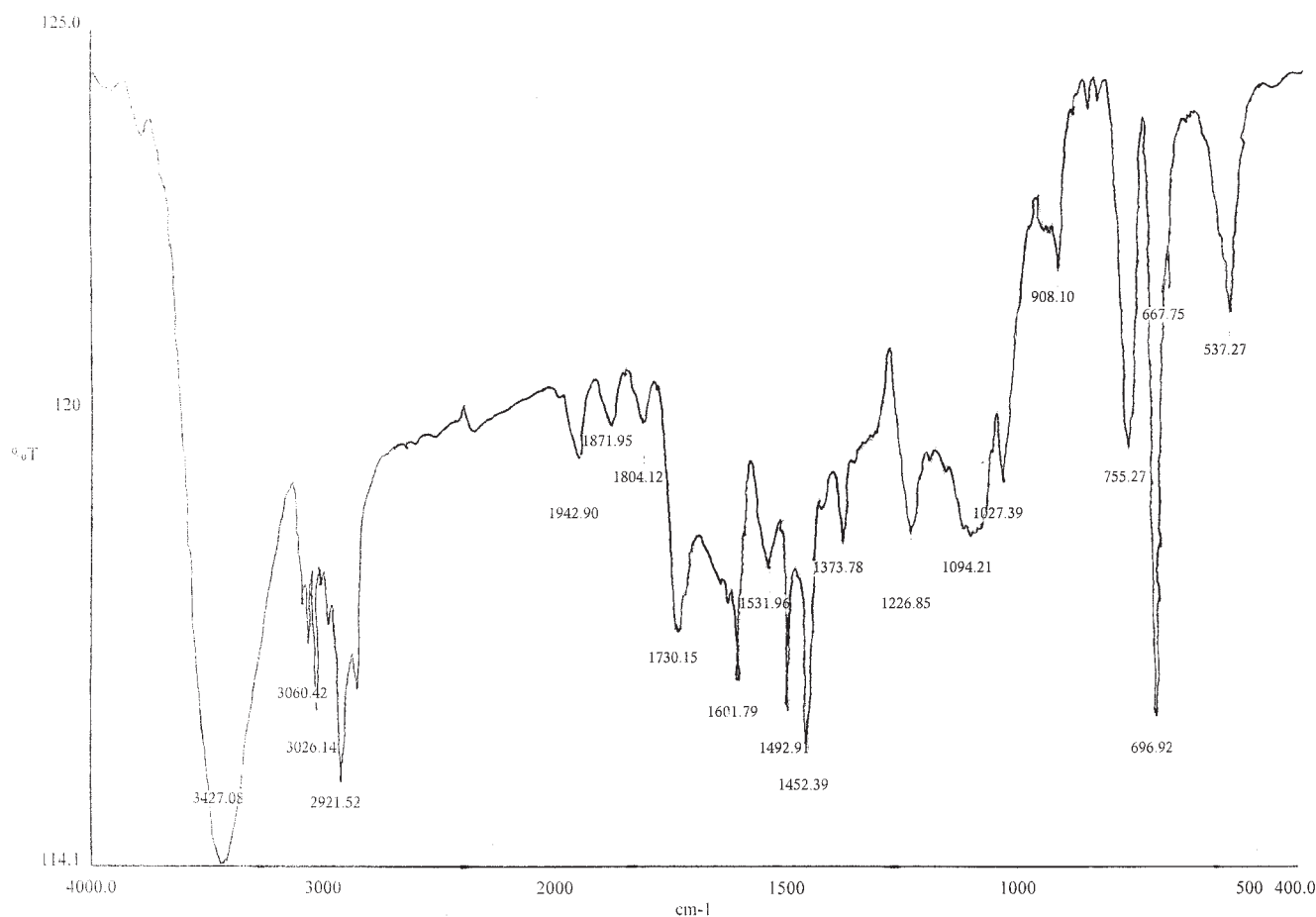


Figure 8 IR spectrum of PUS separated from the copolymer.

surfactant concentration increased, the copolymerization rate also increased. This is a common phenomenon in emulsion polymerization.

It may be observed from Figure 4 that the polymerization rate increases with increasing DPU/ST ratio. This is expected because increasing DPU/ST ratio equals reducing the amount of ST, whereas the amount of initiator is constant. The DPU/ST ratio cannot be too large, however, because increasing the DPU/ST ratio will decrease the stability of the copolymerization procedure, as discussed earlier.

Figure 5 shows the effect of concentration of [I] on conversion. When [I] increases, the concentration of free radicals also increases. This leads to a fast copolymerization rate and high conversion. When [I] is 1.6 wt % of monomer weight, conversion reached nearly 100% after 4 h at 30°C. This polymerization rate is significantly faster than that for systems initiated by a thermolytic initiator at such low temperature.

Analysis of copolymer particles

In conventional emulsion polymerization, radicals are adsorbed into monomer-swollen micelles that are

transformed into polymer particles: monomer droplets provide the source of the monomer to these monomer-swollen micelles. Latices with a rather broad distribution are produced in this manner. In concentrated emulsions, however, the monomer droplets are in the form of polyhedral cells¹⁻⁴: radicals generated by the oil-soluble initiator (CHPO-TEPA) transform the monomers in the cells into polymer. The size and shape of the latex particles depend on the size of the cells of the concentrated emulsions, which, in turn, can be controlled by using appropriate experimental conditions. The effect of the surfactant concentration on particle sizes of PUS copolymer latices is shown in Figure 6.

The average size of particles decreases with increasing surfactant concentration. This is identical to conventional emulsion polymerization because a larger surface area, between the continuous and dispersed phases protected by the adsorbed surfactant, becomes possible as the surfactant concentration increases. At relatively low surfactant concentrations, coalescence of some cells can occur because the interface might not be completely covered with surfactants. On the other hand, when the ionic surfactant concentration be-

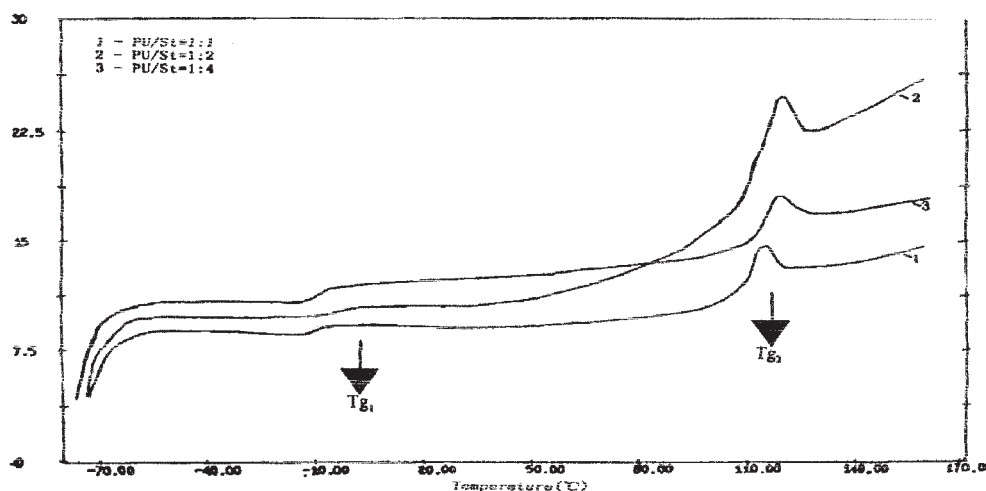


Figure 9 DSC curves of PUS at different DPU/ST weight ratios.

comes too large, the ionic strength in the continuous phase also increases. This shields the electric field and coalescence of some cells can occur. The mixtures of SDS and long-chain alcohol (CA) also affect the particle size. The presence of alcohol molecules, among those of SDS, increases the distance between the charged end groups of SDS molecules, thus decreasing electrostatic repulsion among them and hence increasing the cohesion.

The average diameter and the polydispersity of the particles obtained from different monomer volume fractions are listed in Table II. No significant change of average particle size or polydispersity was observed with increasing Φ (which represents volume fraction of the monomer) in the experimental range. This is not surprising because the relative concentrations of emulsifiers were kept constant while changing the monomer volume fractions.

IR spectra and DSC measurements

Figure 7 shows the IR spectra of a DPU separated from the product. It can be found that the NCO peak around 2270 cm^{-1} is almost undetectable, but a sharp $\text{C}=\text{C}$ peak around 1618 cm^{-1} appears. These indicate that the NCO groups in the PU precursors have reacted with the OH group of HEMA to form the $\text{NH}-\text{COO}$ group, and acryl groups have been introduced onto PU, to form the α -double bond-containing polyurethane (DPU).

The IR spectrum of PUS separated from the product is shown in Figure 8. It can be seen that the $\text{C}=\text{C}$ double bond disappears and there are sharp monophenyl peaks around 3030 , 1601 , 1027 , 755 , and 696 cm^{-1} . These confirm copolymerization between DPU and ST. In Figure 9, the DSC diagrams of DPU precursor and PUS copolymers with different weight ra-

tios of DPU/ST are presented. The glass-transition temperature (T_g) of DPU obtained in the synthesis is about -20°C . After dissolving DPU in ST and starting the copolymerization (see experimental section for details), two T_g values are observed: the one at lower temperature is identical to the T_g of pure DPU; the other at higher temperature corresponds to the T_g of polystyrene. This is a typical result for a block or graft copolymer whose two components are immiscible.

It is interesting to notice that, when the weight ratio of DPU/ST increases, the T_g at lower temperature does not change significantly; however, the T_g at higher temperature moved slightly to a higher temperature, implying that the molecular weight of PS increases when additional ST units are copolymerized onto DPU.

CONCLUSIONS

DPU-ST copolymer lattices, with volume fraction of the dispersed phase up to 80–90%, were prepared by concentrated emulsion copolymerization, using a CHPO-TEPA redox system as initiator, sodium dodecyl sulfate-cetyl alcohol (SDS-CA) as surfactant, and polyvinyl alcohol (PVA) as a liquid film reinforcer (LFI). A fast copolymerization rate and high stability were achieved using the CHPO-TEPA as redox initiator at lower temperature. The copolymerization rate and the size of the resulting PUS latex particles are affected by the monomer volume fractions, and concentrations of surfactants and the redox initiator, similar to conventional emulsion polymerization. The copolymerization of DPU and ST was confirmed by both infrared and DSC measurements.

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