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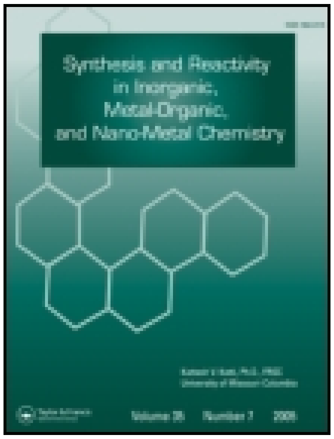

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Synthesis and Characterization of Monoallyl-End-Capped Diethylene Oxide-Based Polyurethane Surfactant

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Synthesis and Characterization of Monoallyl-End-Capped Diethylene Oxide-Based Polyurethane Surfactant

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Diethylene glycol monoallyl ether (DGME) was synthesized by reaction of diethylene glycol with allyl chloride. Then, a novel nonionic functional polyurethane surfactant (PUS) was synthesized by the polycondensation of hexamethylene diisocyanate (HMDI) with polypropylene glycol (PPG-1000) and DGME. Next, a series of polyvinyl acetate (PVAc), polybutyl acrylate (PBA), and polystyrene (PSt) latexes have been successfully synthesized, each one throughout by the emulsion copolymerization in the presence of a PUS. This polymeric surfactant exhibited excellent surface activity, and the surface tension decreased with an increase in the concentration of the polyurethane surfactant.

Keywords diethylene glycol monoallyl ether, polyurethane, surface tension, surfactant

INTRODUCTION

Polymeric surfactants, which contain both hydrophobic segments and hydrophilic segments, have attracted great interest in recent years because of their unique solution properties as a result of their amphiphilic molecular structure. They are among the most versatile products and have found potential applications in emulsion polymerization[1,2], oil enhanced recovery [3], biomedical materials [4], Langmuir-Blodgett (LB) films [5], biomimetism[6], and so on.

Compared with low-molecular-weight surfactants, polymeric surfactants usually have low surface activity because of their high molecular weight. Ogino et al.[7] once pointed out that polymeric surfactants with high molecular weights generally are unable to reduce the surface tension to approximately 50 mN/m. To improve the surface activity of polymeric surfactants, some intensive research has been carried out. Baines et al.[8] synthesized a series of diblock copolymers of 2-(dimethylamino) ethyl methacrylate and methyl methacrylate and found that the surface tension of one sample was about 45 mN/m at a concentration of 0.15 wt%. Vamvakaki et al.[9] showed that lightly quaternized diblock copolymers of 2-(dimethylamino) ethyl methacrylate and 2-(diethylamino) ethyl methacrylate exhibited surprisingly high surface activities (37.5 mN/m), which were comparable to that found for the corresponding 2-(dimethylamino) ethyl methacrylate/ 2-(diethylamino) ethyl methacrylate diblock precursor (34.6 mN/m). Recently, the synthesis of diblock and triblock copolymers of ethylene oxide and ethyl acrylate, by atom transfer radical polymerization, was reported by Dai et al.[10]. The surface tension of these polymeric surfactants in aqueous solutions was about 44 mN/m. However, the results that those groups obtained were not optimistic. In the past decade, extensive studies in academic and industrial laboratories have focused on the development of functional surfactants, especially surfactants containing unsaturated bonds. Such polymeric surfactants can be used as emulsifiers in emulsion polymerization and can copolymerize with latex, thus imparting to the latex excellent stability against high electrolyte concentrations, freeze-thaw cycling, and high shear rates. Liu et al. [11,12] synthesized an amphiphilic poly(ethylene oxide) (PEO) macromonomer [ω-methoxypoly(ethylene oxide)$_{40}$undecyl α-methacrylate] and subsequently used it as a polymerizable surfactant in the synthesis of monodisperse polystyrene microlatexes by emulsion polymerization. Wang et al.[13] studied the emulsion polymerization of styrene with the homopolymer of sodium dodecyl allyl sulfosuccinate as a polymeric surfactant. In recent years, much attention has also been paid to the development of hydrophobically associating polymers, [14,15] which are of great interest for their unique rheological behaviors. However, one major difficulty in the synthesis of hydrophobically modified polymers originates from the insolubility of the hydrophobic comonomer in water. Polymerizable polymeric surfactants are helpful for solving this difficulty.

Thus, it is desirable to synthesize polymeric surfactants that have high surface activity and contain polymerizable functional groups. Because polycondensation and polyaddition reactions are generally much easier and cheaper for the preparation of block copolymers of low molecular weights (e.g., from 1000 to 50,000), we synthesized a novel polyurethane surfactant that contained functional polymerizable double bonds. The polyurethane surfactant that we discuss in this article can reduce the surface tension to as low as 37.6 mN/m. The sample that we synthesized, had low critical micelle concentration (cmc).

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As discussed previously, this functional polyurethane surfactant may find potential application in emulsion polymerization and, as the hydrophobic part, in the synthesis of hydrophobically associating water-soluble polymers.

EXPERIMENTAL

Materials and Equipment

The monomers, St (Aldrich), BA (Aldrich) and VAc (Fisher Scientific Co) were freed from the inhibitor by shaking with 10% aqueous NaOH, washing with water, and drying over Na_2SO_4. Then, they were distilled under reduced pressure before use and stored at $-20°C$ to avoid thermal polymerization. The initiator, KPS, hexamethylene diisocyanate (HMDI), diethylene glycol, allyl chloride, and tetrahydrofuran (THF) were supplied by Merck, Hohenbrunn, Germany, and were used as received. Polypropylene glycol 1000 (PPG-1000, Korea Polyol Ltd., Korea) was dried and degassed at 65°C, under vacuum. Dibutyltin dilaurate (DBTDL, Aldrich, Gillingham, UK) was analytical grade and used directly without further purification. Water used in this experiment was twice distilled and then deionized.

Fourier-transform infrared (FT-IR) spectroscopy analysis was performed with a Nicolet Impact 400D Model spectrophotometer (Nicolet Impact, Madison, USA) using KBr pellets. The spectra were obtained over the wave-number range 4000–400 cm^{-1} at a resolution of 2 cm^{-1} using an MCT detector with co-addition of 64 scans. NMR Spectra were recorded on a Bruker AV600 NMR Spectrometer (^1H, 600 MHz, ^{31}C, 150 MHz). Chemical shifts were reported in ppm and referenced to residual solvent resonances (^1H, ^{13}C) or an internal standard. Scanning electron micrographs were taken on a JEOL-JXA 840 A SEM (JEOL, Boston, USA). The specimens were prepared for SEM by freeze-fracturing in liquid nitrogen and the application of a gold coating of approximately 300 A° with an Edwards S 150 B sputter coater. A gel permeation chromatograph (Model 500, Analytical Scientific Instruments, USA) with a refractive index detector (RI2000, Schambeck, Germany), and two Jordi gel divinyl benzene mixed bed (Jordi FLP, USA) columns were used to measure the molecular weight, relative to the polystyrene standards at 30°C. The carrier solvent was tetrahydrofuran at a flow rate of 1 ml/min. The surface tension was measured using German du Nouy surface tension equipment. The measured temperature was established at $(25 \pm 0.1)°C$.

Synthesis of Diethylene Glycol Monoallyl Ether (DGME)

(4.0 g, 0.1 mol of) NaOH and the solvent (dioxane) were introduced into a 100 mL three-necked round bottomed flask. Then (7.6 g, 0.1 mol of) allyl chloride and (21.2 g, 0.2 mol of) diethylene glycol were added drop-wise with rapid stirring at 50–55°C. After the completion of the addition, stirring was continued for 6 h at 50–55°C. The crude product was dried with magnesium sulfate. The solid material was filtered off. The solvent was distilled off and the residue was purified by column chromatography to give the compound in a yield of 82.5% and a purity of 99.2% (Agilent 7890A gas chromatography). The structure of the compound was confirmed by FT-IR, ^1H NMR and ^{13}C NMR. The reaction process is outlined in Scheme 1.

TABLE 1
Recipe for the synthesis of PUD

Ingredients	Charge (g)
PPG(M.W.: 1000)	80.00
HMDI	13.44
DGME	11.68
TEA	1.50
D.D.W	80.00

Preparation of the Polyurethane Surfactant

A 250 mL, round bottomed, 4-necked-flask, separable glass reactor with mechanical stirrer, thermometer, condenser, and nitrogen purge was used. Basic recipe for the synthesis of the non-ionic polyurethane surfactant is listed in Table 1. Polyaddition reaction was carried out in a N_2 atmosphere in a constant-temperature water bath. DGME and HMDI were first charged into the reactor and heated to 80°C under stirring to obtained NCO end caped polyurethane (NCO-PU), and then dibutyltin dilaurate was dropped into the reactor, while keeping the temperature at 80°C. The reaction proceeded over approximately 2 h, PPG was subsequently charged, and reaction proceeded for another 3 h at the same temperature. This PU was then neutralized by the addition of TEA at 25°C, followed by dispersion at high speed (1200 rpm) with distilled water, which was added drop-wise to produce a waterborne PU dispersion. The reaction process is outlined in Scheme 2.

Semi-Continuous Emulsion Polymerization Using Polyurethane Surfactant

Semi-continuous emulsion copolymerization of vinyl acetate (VAc), butyl acrylate (BA) or styrene (St) with polyurethane surfactant were carried out using a 500 mL four-necked round-bottom flask equipped with a reflux condenser, a stainless-steel stirrer, a sampling device, and one feed stream. The feed stream was a solution of VAc, BA or St each one through emulsion copolymerization. Before emulsion copolymerization start-up, the reaction vessel was first charged with the desired amounts of water, polyurethane surfactant, $NaHCO_3$, and initiator solution (2.8×10^{-3} $molL^{-1}$), respectively. During polymerization, the reaction mixture was stirred at a rate of 100 rpm, and the temperature was maintained at 65°C. After 5 min, 10 w% of total amount of the monomer was added to the flask in a period of 20 min. Then, the temperature was kept at 80°C until the end of polymerization (4 h). The polymerization was performed with feeding rate of 1.0 mL/min under N_2 atmosphere, to investigate the effect of surfactant concentration on monomer conversion. A typical recipe for the preparation of a product is given in Table 2. In order to determine the conversion percentage during

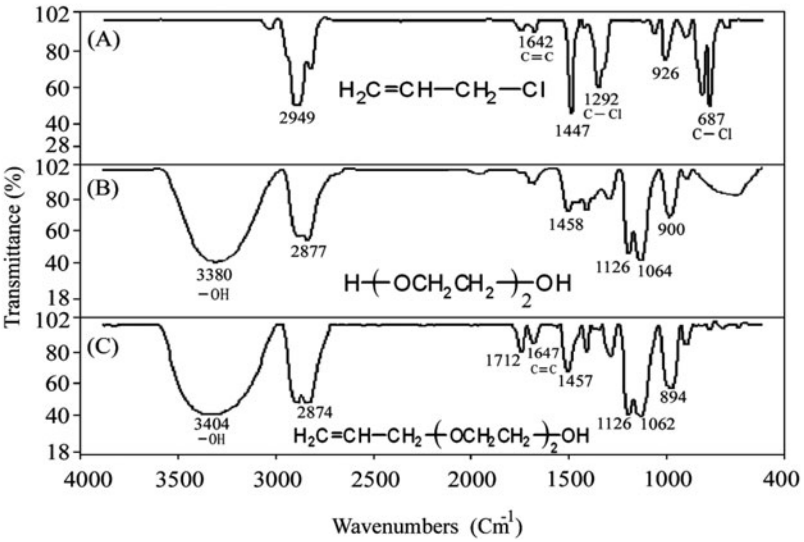

FIG. 1. FT-IR spectra of (A) allyl chloride, (B) diethylene glycol, (C) DGME.

the polymerization process, it was necessary to withdraw samples at various intervals from the reaction vessel. These samples are relatively small so that the overall composition in the reactor is not seriously affected; once a sample is removed and put in a watch glass, polymerization is terminated by the addition of 7 ppm hydroquinone. Then, two drops of ethanol were added to the sample as a coagulant, and the contents of the watch glass were evaporated at room temperature and then dried to a constant weight in a vacuum oven. The conversion percentage was determined gravimetrically. The purification and precipitation of the polymer were done using a reported method [16].

Film Formation

Films were prepared with a dry thickness of about 0.5 mm. After casting the emulsion onto glass plates (20 cm × 20 cm), the films were allowed to dry for one week at ambient temperature (25°C).

TABLE 2
Recipe for the semi-continuous emulsion polymerization of VAc, BA or St

Ingredients	Charge (g)
PUS	0.20
Demineralized water	100.00
HEC	0.60
NaCl	0.20
$NaHCO_3$	0.04
Initiator: KPS	0.03
VAc	51.60
BA	51.60
St	51.60

Water Absorption

Dried films (30 mm × 30 mm; original weight designated as W_0) were immersed in water for 24 h at 25°C. After the residual water was wiped from the films using filter paper, the weight (W_1) was measured immediately[17].

It was calculated as follows: water absorption, $R\ (\%) = ((W_1 - W_0)/\ W_0) \times 100$

RESULTS AND DISCUSSION

Spectral Analysis of Diethylene Glycol Monoallyl Ether (DGME)

Figure 1 shows the typical FT–IR spectra of (A) allyl chloride, (B) diethylene glycol, and (C) DGME. In the Figure 1(A) , there are absorption peaks at 2949 and 1292 cm^{-1}, which are ascribed to the vibration of CH_2 and C-Cl. Figure 1(B) indicates strong absorption peak at 3380 cm^{-1}, which is ascribed to the vibration of –OH. According to Figure 1(C), there is strong absorption peak at 3404 cm^{-1}, which is ascribed to the vibration of –OH. The absorption peaks at 1712 and 1457 cm^{-1} were attributed to C=O and C=C stretch vibration, respectively.

The ^{1}H-NMR of DGME was shown in Figure 2, it can be seen that all the relevant peaks of molecule could be found in this Figure. The peaks at 3.6 ppm result from the groups of $–CH_2$ in the chain of $(\text{-}OCH_2CH_2)_2$, in the molecule of DGME. Also, one peak has been observed at 4 ppm, which is belonging to –OH, and two signals of the $CH_2{=}CH–$bond have been obtained at 5.2 ppm. A small peak at 5.9 ppm results from the group of $=CH–CH_2$.

Figure 3 indicates the ^{13}C-NMR spectrum of DGME. The signals at 60–70 ppm were attributed to the $-(OCH_2CH_2)-$ groups. Also, carbon of $–CH_2$ group was seen at 73 ppm. Two peaks have been observed at 117 and 134 ppm, which are belonging to $CH_2{=}CH$-.

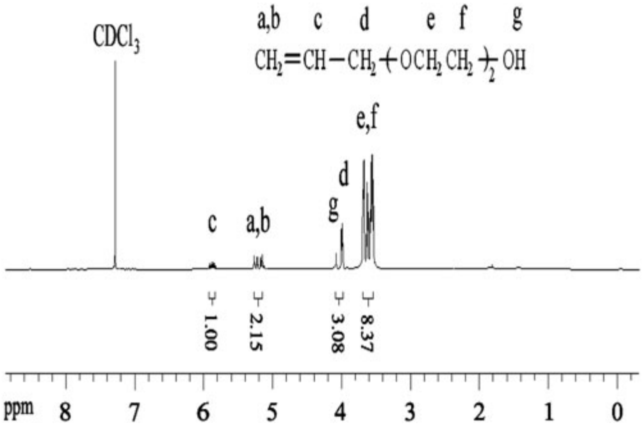

FIG. 2. ^{1}H-NMR spectrum of DGME.

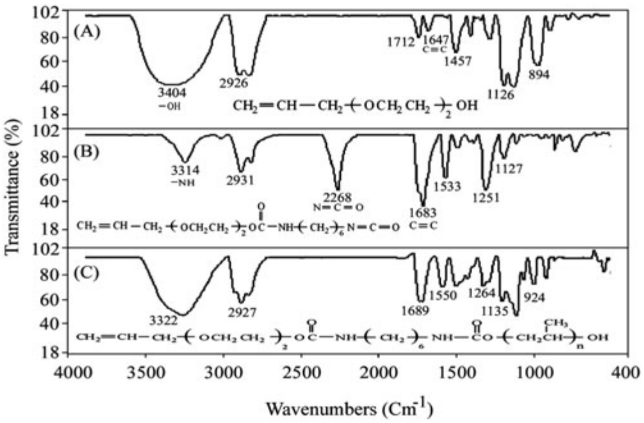

FIG. 4. FT-IR spectra of (A) DGME, (B) NCO-PU, and (C) PUS.

Spectral Analysis of Polyurethane Surfactant (PUS)

Figure 4 illustrates the FT–IR spectra of (A) DGME, (B) NCO-PU, and (C) PUS, respectively. It can be seen from Figure 4(A) that there are strong absorption peaks at 3404 and 2926 cm^{-1}, which are ascribed to the vibration of –OH, and –CH$_2$ groups, respectively. The absorption peaks at 1712 and 1647 cm^{-1} were attributed to C=O and C=C stretch vibration. According to Figure 4(B) there are strong absorption peaks at 3314, 2931, 2268, and 1683 cm^{-1}, which are ascribed to the vibration of –NH, –CH$_2$, N=C=O, and C=C groups. As shown in Figure 4(C), a new sharp peak appeared at 3322 cm^{-1}, which was attributed to N–H absorption. Also, the absorption peak at 1550 cm^{-1} was attributed to N–H bond vibration and C–N symmetry stretch vibration.

The ^{1}H-NMR of NCO-PU was shown in Figure 5, it can be seen that all the relevant peaks of molecule could be found in this Figure. The peaks at 1.2–1.5 ppm results from the groups of –CH$_2$ in the chain of –NH–(CH$_2$)– in the molecule of NCO–PU. Also one peak has been observed at 4.8 ppm, which is belonging to –NH and two signals of the CH$_2$=CH–bond have been obtained at 5.2 ppm, respectively. A small peak at 5.8 ppm results from the group of =CH–CH$_2$.

Figure 6 indicates the ^{13}C NMR spectrum of NCO-PU. The number of carbons in the NCO-PU is compatible with the number of spectra.

The ^{1}H-NMR of PUS was shown in Figure 7, it can be seen that all the relevant peaks of PU could be found in this Figure. Two peaks have been observed at 5.2 ppm, which are belonging to (CH$_2$=CH-). The peak at 5.9 ppm results from the group of –CHCH$_2$, and the peaks at 3.4–3.6 ppm results from the group of –OCH$_2$CH$_2$ in the molecule of PUS. Also a small peak has been observed at 4.9 ppm, which is belonging to -NH group.

Figure 8 indicates the ^{13}C-NMR spectra of PUS. The number of carbons in the PUS is compatible with the number of spectra.

Effect of the PUS Concentration on the Surface Tension

According to Figure 9, the surface tension decreases with an increase in the concentration of the polyurethane surfactant in an aqueous solution. This trend resembles what appears in conventional low-molecular-weight surfactant, but it is noteworthy that, after the critical micelle concentration (CMC) was reached, the surface tension could still be reduced slightly, and there is no inflection point in the curve as known for typical surfactants. As for low molecular-weight surfactants, the surface tension

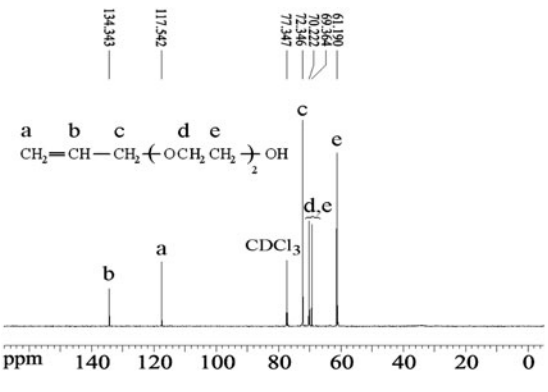

FIG. 3. ^{13}C NMR spectrum of DGME.

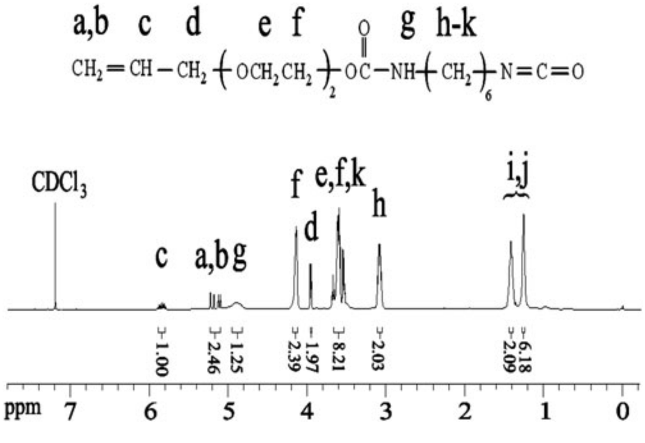

FIG. 5. ^{1}H-NMR spectrum of NCO-PU.

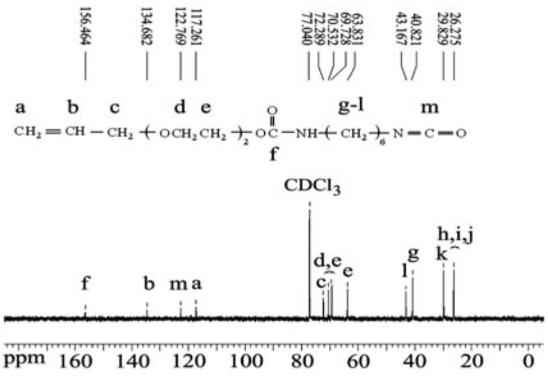

FIG. 6. ^{13}C NMR spectrum of NCO-PU.

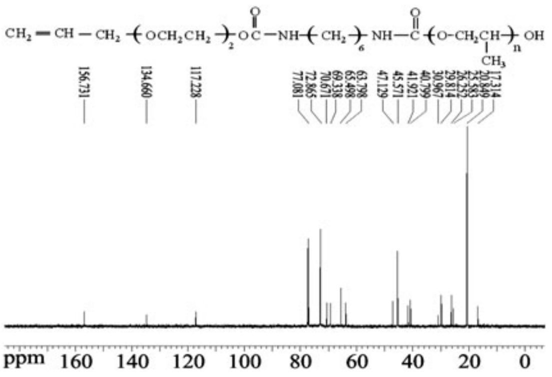

FIG. 8. ^{13}C NMR spectrum of PUS.

usually remains constant after the CMC is reached. Thus, this phenomenon is interesting. To the contrary, Ismail[18] once synthesized a series of water-soluble polyurethane surfactants by the addition polymerization of TDI to poly (ethylene glycol) and/or castor oil and ethylene glycol. He found that the curve of the surface tension versus the molar concentration was just like that of classical low-molecular-weight surfactants. In other words, the surface tension was stable after the CMC was reached. The same results also occurred in the work of Shi et al.[19] and Riess et al.[20]. The reason, that the surface tension could still be reduced slightly after the CMC was reached in our work, may be that the arrangements of polyurethane surfactants on the surface were not as tight as those of traditional low-molecular-weight surfactants. As the concentration of the polyurethane surfactant increased, the chains of the macromolecules could be condensed further. This increased the arrangement density of the hydrophobic part on the surface and resulted in the decrease of the surface tension. The curve of the surface tension versus the concentration obtained by Adler et al.[21] is similar to what we obtained. Figure 9 shows that the sample had good surface activity and very low CMC values, which could reduce the surface tension to as low as 35 mN/m. The ability to reduce the surface tension increased with an increase in the hydrophobic segment. That is, while the ratio of the hydrophobic segment increased, more hydrophobic chains were oriented on the surface with their hydrophilic parts dissolved in the aqueous solution. Consequently, the surface tension was reduced.

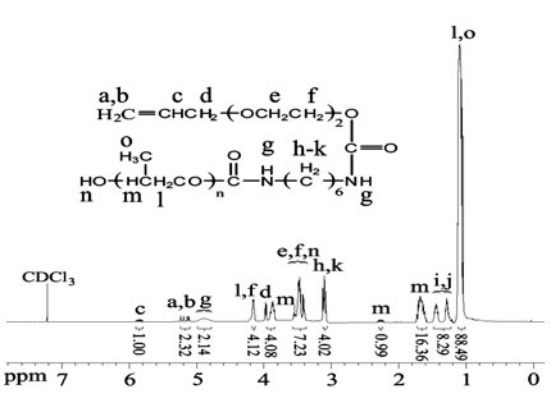

FIG. 7. ^{1}H-NMR spectrum of PUS.

UV spectroscopy has been widely used to determine the CMC and investigate the aggregate behaviors of surfactants[22–24]. The results of UV spectra in the various concentrations show a redshift occurred, after some sample reached a certain concentration, and increasing the concentration made the redshift greater. This indicated that an interaction between the macromolecular chains had to exist, and after the CMC, the polyurethane surfactant could accumulate to form micelle aggregates between molecules. The CMC data given by the UV solution were approximately in agreement with what we obtained with a surface tensiometer.

Effect of Salt on the Surface Tension

It is widely accepted that the addition of electrolytes has an effect on the surface tension[25–27]. As revealed by Figure 10, the addition of salt led to a slight decrease in the surface tension of PUS. This was due to the fact that the addition of salt increased the ionic strength of the aqueous solution. The hydrophilic parts of the polyurethane surfactants consisted of polyoxyethylene,

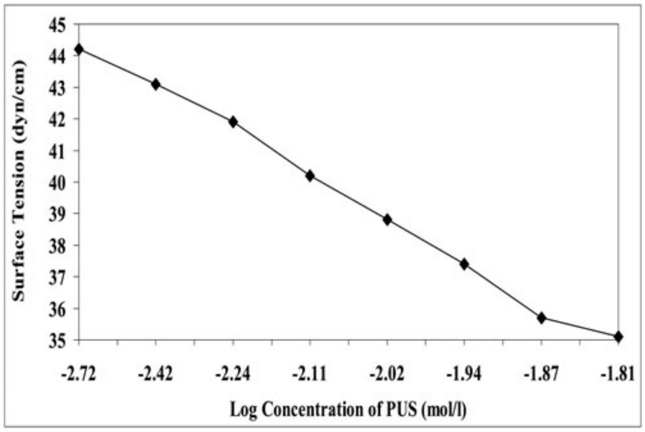

FIG. 9. Surface tension against molar concentration of PU-based copolymeric surfactant.

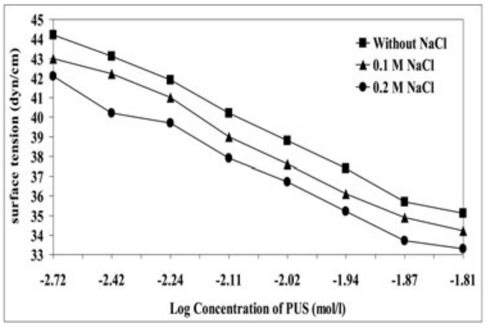

FIG. 10. Surface tension against molar concentration of PU-based copolymeric surfactants at different NaCl concentration aqueous solution.

whose oxygen atom could interact with H_2O or H_3O^+ by a hydrogen bond and, consequently, was a little positive[28]. When the polyurethane surfactants were dissolved in water, the hydrophilic parts pointed to the water, whereas the hydrophobic parts aggregated on the surface (away from the water). As the salt was added, the repulsion between oriented hydrophobic heads and hydrophilic heads could be reduced. This resulted in a closer packaging of the surfactants on the surface and, therefore, reduced the surface tension. The effect of salt on the surface tension reduction, varied in terms of the concentration of the polyurethane surfactants. Figure 10 indicates that the effect of salt on the surface tension was more prominent at a lower concentration level. This may be attributed to the fact that macromolecular chains of the polyurethane surfactants at a lower concentration level, which could be condensed further when salt was added, were not arrayed as tightly as those at a higher concentration level.

Effect of the Temperature on the Surface Tension

The obtained result demonstrates the variation of the surface tension of PUS in aqueous solutions at 14, 20, and 25°C. The surface tension decreased with an increase in the temperature. This was due to the fact that more heat was absorbed as the temperature increased, and the heat allowed enough energy for the molecules of the polyurethane surfactants to surmount the attractive forces of the interior, and subsequently migrate to the surface. The enrichment of the polyurethane surfactants on the surface led to the decrease in the surface tension accordingly. Here we also can explain this phenomenon in terms of the Gibbs adsorption equation:

$$\Gamma = -\frac{d\gamma}{da} \times \frac{a}{RT} \qquad [1]$$

where Γ is the surface excess concentration, γ is the surface tension, α is the solution activity, R is the gas constant, and T is the absolute temperature. The Gibbs adsorption equation indicates that the adsorption amount will increase with an increase in the temperature. Thus, it gives an excellent explanation for what we have discussed.

Effect of the Rest Time on the Surface Tension

It has been found that time is needed for polyurethane surfactants to reach a constant surface tension, and that the time needed to obtain a constant value of the surface tension varies as the concentration of the polyurethane surfactant changes[29]. According to the experimental results, we think that it must take some time for macromolecules of polyurethane surfactants to migrate to the surface. As for polymeric surfactants, they usually have a high molecular weight, and there exist interaction and entanglement between the long macromolecular chains, when they dissolve in water. The rest time allows them to adjust their conformation sufficiently and results in a better arrangement on the surface. The time needed to achieve a constant value of the surface tension for surfactants at a higher concentration level is less than that at a lower concentration level.

Effect of PUS Concentration on Reaction Rate

Although emulsion copolymerization of VAc, BA and St has been well established [30,31], their copolymerization in presence of PUS has not been reported. Therefore, the role of this surfactant is not perfectly clear. It is possible that during the copolymerization process, this polymeric surfactant will make part of the copolymer chain. However, the extent of its incorporation in the polymer chain was not measured. Figure 11 shows the effect of PUS on the reaction rate versus time for BA, St and VAc, respectively, where the initial initiator and PUS concentration were fixed at $I_0 = 2.8 \times 10^{-3}$ molL^{-1}. It can be observed that the rate of reaction increased in the order VAc > St > BA. This result shows that the PUS is a better surfactant for VAc emulsion copolymerization in comparison with BA and St. According to the experimental results, we think that St is a hydrophobic monomer, due to benzene ring and consequently it's resonance effect with the electrons of double bond. So a disinclined reaction will be obtained between St and PUS. Also there is a long hydrophobic chain in the BA monomer and this is a cause for a low reaction rate of PBA.

On the other hand, the obtained results demonstrated that the reaction rate increased by increasing PUS concentrations.

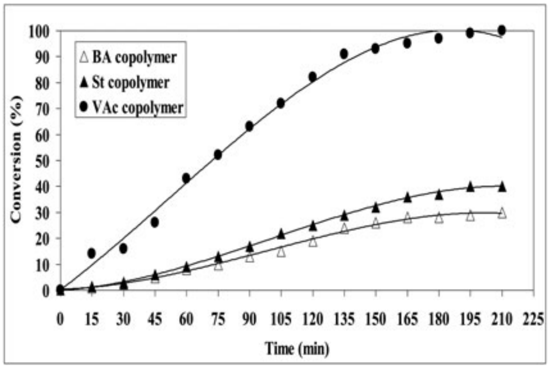

FIG. 11. The effect of PUS with constant concentration on monomer conversion vs. time for PBA (△), PSt (▲) and PVAc (●) at T = 80åC, $I_0 = 2.80 \times 10^{-3}$ molL^{-1}.

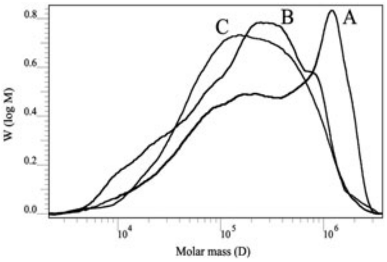

FIG. 12. Molecular weight measurements of (A) PSt, (B) PVAc and (C) PBA films.

Molecular Weights of PVAc, PBA, and PSt

The molecular weight is considered to be one of the most important parameters of polyurethane. The mechanical property is significantly affected by the molecular weight of polyurethane[32,33]. The polyurethane molecular weight depends on the polyol, chain extender, and diisocyanate content[34,35]. Figure 12(A–C) shows the molecular weight of PSt, PVAc, and PBA, respectively. According to this Figure it can be observed that the molecular weight increases in the order PSt > PVAc > PBA. The PSt exhibited the highest molecular weight among all of the samples, and the PVAc samples exhibited lower molecular weight than the others.

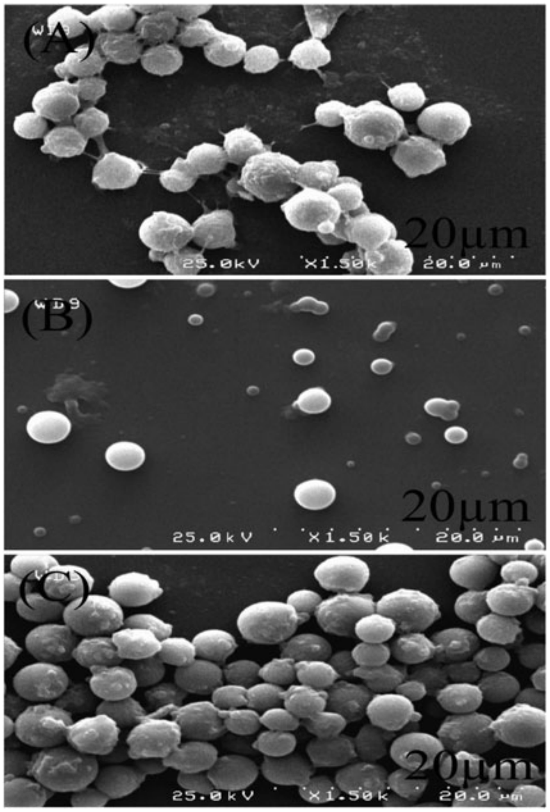

FIG. 13. SEM micrographs of (A) PVAc, (B) PBA and (C) PSt at T = 80åC, $[I]_o = 2.80 \times 10^{-3}$ $molL^{-1}$.

Morphologies of Latex Particles of PVAc, PBA, and PSt

The particle morphologies of the PVAc, PBA, and PSt has been illustrated in Figure 13(A–C). Comparing all the micrographs, we can conclude that the morphology of the copolymer particles is all spherical and it is almost homogeneous in the particles. Double bond containing PUS is often used for copolymerization with acrylic monomers[36,37]. It is commonly held that they can easily copolymerize with those monomers, because there exists a $CH_2{=}C\ (CH_3)\ COO–$ group with a similar structure. However, most copolymerization is carried out in an organic solvent. In our study, the free-radical copolymerization of PUS with other monomers was conducted in an aqueous system.

CONCLUSIONS

By the polycondensation of HMDI with PPO and DGME, we synthesized a novel of diblock non-ionic polyurethane surfactant that contained reactive double bond. This polymeric surfactant had good surface activity. The surface tension of this polyurethane surfactant in aqueous solution changed as the concentration changed. An increase in the temperature was favorable for the enhancement of the surface activity, and the addition of salt led to the reduction of the surface tension. In this experiment, we also found that time was needed for the polyurethane surfactant to reach a constant value of the surface tension. This polymeric surfactant has potential application in emulsion polymerization as promising alternative to conventional low-molecular-weight surfactant. At the same time, it can incorporate with hydrophilic chains as the hydrophobic part in the synthesis of hydrophobically associating water-soluble polymers. Further studies in this direction are currently in progress.

REFERENCES

1. Riess, G. *Colloid. Surf. A*. **1999**, *153*, 99–110.
2. Rouzes, C.; Durand, A.; Leonard, M.; Dellacherie, E. *J. Colloid. Interface. Sci*. **2002**, *253*, 217–223.
3. Babadagli, T. *Colloid. Surf. A*. **2003**, *223*, 157–175.
4. Eeckman, F.; Moës, A.; Amighi, K. *Int. J. Pharm*., **2004**, *273*, 109–119.
5. Kim, I.; Rabolt, J.F.; Stroeve, P. *Colloid. Surf. A*. **2000**, *171*, 167–174.
6. Hartgerink, J.D.; Beniash, E.; Stupp, S.I. *Science*. **2001**, *294*, 1684–1688.
7. Ogino, K.; Onoe, Y.; Abe, M.; Ono, H.; Bessho, K. *Langmuir*. **1990**, *6*, 1330–1331.
8. Baines, F.L.; Armes, S.P.; Billingham, N.C.; Tuzar, Z. *Macromolecules*. **1996**, *29*, 8151–8159.
9. Vamvakaki, M.; Unali, G.F.; Bultul, V.; Boucher, S.; Robinson, K.L.; Billingham, N.C.; Armes, S.P. *Macromolecules*. **2001**, *34*, 6839–6841.
10. Dai, S.; Ravi, P.; Leong, C.Y.; Tam, K.C.; Gan, L.H. *Langmuir*. **2004**, *20*, 1597–1604.
11. Liu, J.; Chew, C.H.; Gan, J.M. *J. Macromol. Sci. Chem*. **1996**, *33*, 337–352.
12. Liu, J.; Chew, C.H.; Gan, L.M.; Teo, W.K.; Gan, L.H. *Langmuir*, **1997**, *13*, 4988–4994.
13. Wang, X.; Sudol, E.D.; El-Aasser, M.S. *Langmuir*, **2001**, *17*, 6865–6870.
14. Hill, A.; Candau, F.; Selb, J. *Macromolecules*, **1993**, *26*, 4521–4532.
15. Wang, Y.Y.; Dai, Y.H.; Zhang, L. *Macromolecules*, **2004**, *37*, 2930–2937.
16. Shaffie, A.; Moustafa, A.B.; Mohamed, E.S.; Badran, A.S. *J. Polym. Sci. A Polym. Chem*. **1997**, *35*, 3141–3149.

17. Lambourne, R. Paint and Surface Coatings Theory and Practice. Horwood, E. (ed.) In *Market Cross House*, Chichester: West Sussex, **1987**, Ch. 9, pp. 359–363.
18. Ismail, E. A. *J. Appl. Polym. Sci.* **1998**, *68*, 1531–1536.
19. Shi, Y.C.; Wu, Y.S.; Zhang, L. *Polym. Mater. Sci. Eng.* **2003**, *19*, 69–71.
20. Riess, G.; Hurtrez; Bahadur, G. New York, **1985**.
21. Adler, H.J.; Jahny, K.; Vogt-Birnbrich, B. *Prog. Org. Coat.*, **2001**, *43*, 251–257.
22. Beyaz, A.; Oh, W.S.; Reddy, V.P. *Colloid. Surf. B.* **2004**, *35*, 119–124.
23. Krishnana, R.S.G.; Thennarasub, S.; Mandala, A.B. *Chem. Phys.* **2003**, *291*, 195–205.
24. Willemen, H.M.; Vermonden, T.; Koudijs, A.; Marcelis, A.T.M.; Sudhölter, E.J.R. *Colloid. Surf. A.* **2003**, *218*, 59–64.
25. Para, G.; Jarek, E.; Warszynski, P.; Adamczyk, Z. *Colloid. Surf. A.* **2003**, *222*, 213–222.
26. Aydogan, N.; Abbott, N.L. *Langmuir.* **2002**, *18*, 7826–7830.
27. Mukerjee, P.; Chan, C.C. *Langmuir.* **2002**, *18*, 5375–5381.
28. Zhao, G.X. *Physical Chemistry of Surfactant*; Beijing University Press: Beijing, **1991**, 32–47.
29. Dong, Y.; Jin, Y.; Wei, D.Q. *J. Appl. Polym. Sci.* **2006**, *100*, 2956–2962.
30. He, W.D.; Cao, C.T.; Pan, C.Y. *J. Appl. Polym. Sci.* **1996**, *61*, 383–388.
31. He, W.D.; Cao, C.T.; Pan, C.Y. *Polym. Int.* **1996**, *39*, 31–36.
32. Pérez-Limiñana, M.A.; Arán-Aís, F.; Torró-Palau, A.M.; Orgilés-Barceló, A.C.; Martín-Martínez, J.M. *J. Adhes. Adhes.* **2005**, *25*, 507–517.
33. Dieterich, D. *Prog. Org. Coat.* **1981**, *9*, 281–340.
34. Rahman, M.M.; Kim, H.D. *J. Adhes. Sci. Technol.* **2007**, *21*, 81–96.
35. Chattopadhyay, D.K.; Raju, K.V.S.N. *Prog. Polym. Sci.* **2007**, *32*, 352–418.
36. Dong, Y.; Jin, Y.; Wei, D. *Polym. Int.* **2007**, *56*, 14–21.
37. Mingyue, Zh.; Weihong, Q.; Hongzhu, L.; Yingli, S. *J. Appl. Polym. Sci.* **2008**, *107*, 624–628.