

## Synthesis and properties of polyvinyl acetate emulsion copolymers by three novel non-ionic functional polyurethane surfactants

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(Received 9 October 2013 • accepted 3 February 2014)

**Abstract**—Functional polyurethane surfactants (tri-block) were synthesized by addition polymerization of hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI) and 2, 4-toluene diisocyanate (TDI) with poly (propylene oxide) (PPO) and monoallyl-end-capped poly (ethylene oxide) (PEO). The chemical structure of the polyurethane surfactants (PUS) was confirmed by Fourier transform infrared, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. Then, a series of polyvinyl acetate (PVAc) latexes were successfully synthesized by the emulsion copolymerization in the presence of different PUS. The particle size, amount of coagulum and surface tension were evaluated. These polymeric surfactants were found to have excellent surface activity. The lowest surface tension of polyurethane surfactant aqueous solutions could be reduced to 41.5 dyn/cm for IPDI. All the polyurethane surfactants synthesized had low critical micelle concentrations and could reduce the surface tension even at very low concentration levels ( $10^{-3}$ - $10^{-2}$  molL<sup>-1</sup>).

Keywords: Polymeric Surfactants, Surface Tension, Polyurethane, Emulsion Copolymers

### INTRODUCTION

Polymeric surfactants containing both hydrophobic and hydrophilic segments have attracted considerable interest because of their unique solution properties as a result of their amphiphilic molecular structure. They are very versatile products and have found applications in emulsion polymerization [1,2], enhanced oil recovery [3], biomedical materials [4], Langmuir-Blodgett films [5], biomimeticism [6], etc. Thus, extensive studies in academic and industrial laboratories have focused on the development of functional polymeric surfactants, especially those containing unsaturated bonds. Such functional surfactants can be used as emulsifiers in emulsion polymerization and can copolymerize with a latex, thus providing it with excellent stability against high electrolyte concentrations, freeze-thaw cycling, and high shear rates [7-9]. Much attention has also been paid to the development of hydrophobically associating polymers [10,11], which are of great interest for their unique rheological behavior. 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 the solution of this problem.

However, compared with low-molecular-weight surfactants, polymeric surfactants usually have low surface activity due to their high molecular weight. The widely used nonionic surfactant Pluronic F68 (EO<sub>78</sub>-PO<sub>30</sub>-EO<sub>78</sub>,  $M_n=8,400$  g mol<sup>-1</sup>) is a difunctional block copolymer terminated with primary hydroxyl groups, which can reduce the surface tension (0.1 wt% aqueous) to 50 dyn/cm at 25 °C. Ogino et al. [12] pointed out that polymeric surfactants with high molecular weights generally are unable to reduce surface tension to 50 dyn/cm. To improve the surface activity of polymeric surfac-

tants, some intensive research has been carried out [13-15], but the results have not been satisfactory.

Another distinguishing feature of surfactants is their ability to enhance the solubility of compounds that usually have very low solubility in a pure solvent. This function is ascribed to the core of the micelle, which is incompatible with the solvent, providing a suitable microenvironment for solubilization. Consequently, the extent of dissolution of a product in solutions containing surfactant micelles is dramatically enhanced. The phenomenon of solubilization has been studied extensively in aqueous and nonaqueous solutions with conventional low-molecular-weight surfactants [16,17]. However, there have been only few studies of the solubilization tendencies of low-molecular-weight polymers in block copolymer micelles.

Thus, it is desirable to synthesize polymeric surfactants that have high surface activity and contain polymerizable functional groups. In the work reported here, based on the fact that polycondensation and polyaddition reactions are generally much easier and cheaper for the preparation of block copolymers of low molecular weight (e.g. from 1,000 to 50,000 g mol<sup>-1</sup>), we synthesized a novel series of polyurethane surfactants that contain functional polymerizable double bonds. The polyurethane surfactants synthesized could reduce surface tension to as low as 41.5 dyn/cm. As discussed above, these functional polyurethane surfactants may find potential applications in emulsion polymerization and, because of the hydrophobic part, in the synthesis of hydrophobically associating water-soluble polymers.

### EXPERIMENTAL

#### 1. Materials and Equipment

The monomer, vinyl acetate (VAc, Aldrich), was freed from the inhibitor by shaking with 10% aqueous NaOH, washing with distilled water and drying over Na<sub>2</sub>SO<sub>4</sub>. It was then distilled under reduced pressure before use and stored at -15 °C to avoid thermal polymerization. The initiators, ammonium peroxodisulfate (APS),

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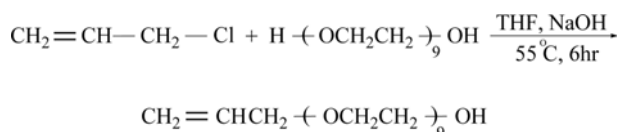
decanol, hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), 2, 4-toluene diisocyanate (TDI), polyethylene oxide (PEO), allyl chloride and tetrahydrofuran (THF) were supplied by Merck, Hohenbrunn, Germany, and were used as received. Polypropylene oxide 1000 (PPO-1000, Korea Polyol Ltd., 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. The other chemicals were of analytical grade and used without further purification.

## 2. Methods

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 4,000–400  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$  using an MCT detector with co-addition of 64 scans. NMR Spectra were recorded on a Bruker AV600 NMR Spectrometer ( $^1\text{H}$ , 600 MHz,  $^{13}\text{C}$ , 150 MHz). Chemical shifts were reported in ppm and referenced to residual solvent resonances ( $^1\text{H}$ ,  $^{13}\text{C}$ ) 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 Å with an Edwards S 150 B sputter coater. Laser light scattering was carried out using a Mastersizer-2000 of Malvern Instruments (Worcestershire, UK). The surface tension was measured using German du Nouy surface tension equipment. The measured temperature was established at  $(25 \pm 0.1)^\circ\text{C}$ . 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. UV-visible spectra were obtained using a U-2010 spectrophotometer (Hitachi, Japan) at room temperature. The amounts of coagulum were measured by collecting coagulum on reaction vessel wall and stirrer, and by filtering the latex (mesh 300). It is presented as weight of coagulum per total weight of monomer added.

## 3. Synthesis of Monoallyl-end-capped Poly (Ethylene Oxide) (MPEO)

(4.0 g, 0.1 mol of) NaOH and the solvent (THF) were introduced into a 100 mL three-necked round bottomed flask. Then (7.6 g, 0.1 mol of) allyl chloride and (40 g, 0.1 mol of) polyethylene oxide 400 (PEO-400) were added dropwise with rapid stirring at 50–55 °C. After the completion of the addition, stirring was continued for 6 hr 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 92.5% and a purity of 82.5% (Agilent 7890A gas chromatography). The structure of the compound was con-



Scheme 1. Synthesis of monoallyl-end-capped poly (ethylene oxide).

July, 2014

firmed by FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. The reaction process is outlined in Scheme 1.

## 4. Synthesis of Tri-block Polyurethane Surfactants (Samples I (IPDI), II (TDI) and III (HMDI))

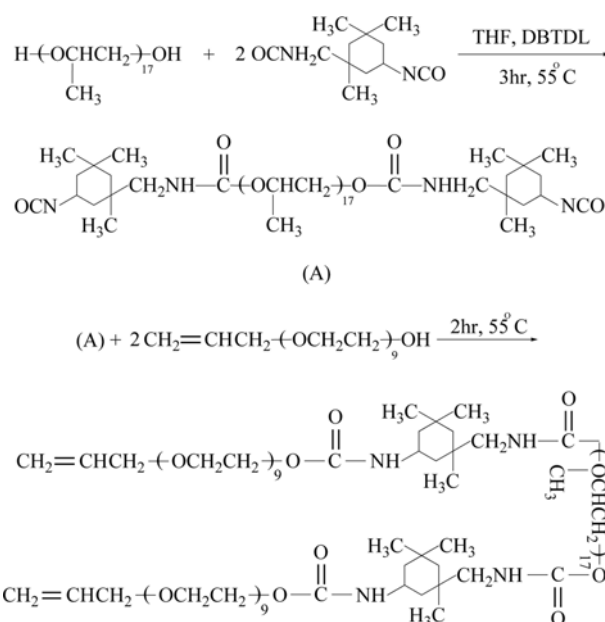
The calculated amount of PPO was put into a 500 mL four-necked flask equipped with a thermometer and a mechanical stirrer. While stirring, a calculated amount of IPDI, TDI and HMDI was added dropwise into the flask, each one through addition polymerization. After addition of dibutyltin dilaurate as a catalyst, the reaction was carried out at  $80.0 \pm 1.0^\circ\text{C}$  for 2 hr. Then monoallyl-end-capped polyethylene oxide (MPEO) was added and allowed to react for another 2 hr at  $80.0 \pm 1.0^\circ\text{C}$ . After the reaction mixture was cooled to room temperature, water was added with stirring. The recipes for the preparation of nonionic polyurethane surfactants and the reaction process for sample I (IPDI) are listed in Table 1 and Scheme 2, respectively.

## 5. Semi-continuous Emulsion Copolymerization Using Polyurethane Surfactants

Semi-continuous emulsion copolymerization of vinyl acetate (VAc), with polyurethane surfactants was 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. Before emulsion copolymerization start-up, the reaction vessel was first charged with the desired amounts of water, polyurethane surfactant (samples I, II, III),  $\text{NaHCO}_3$  and initiator solution ( $2.8 \times 10^{-3} \text{ mol L}^{-1}$ ), respectively. During polymeriza-

Table 1. Recipe for the synthesis of PUS

Ingredients	Charge (mol)
PPO (M.W.: 1000)	0.10
HMDI, IPDI, TDI	0.10
MPEO	0.10
TEA	0.01
D.D.W	4.45



Scheme 2. Synthesis of tri-block polyurethane surfactant.

**Table 2. Recipe for the semi-continuous emulsion polymerization of PVAc**

Ingredients	Charge (g)
VAc	40.00
Demineralized water	59.50
Antifoam, EFKA-2526	0.10
PUS (samples I, II and III)	0.20
NaHCO <sub>3</sub>	0.10
Initiator: (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.11

tion, the reaction mixture was stirred at 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 hr). The polymerization was performed with feeding rate of 1.0 mL/min under N<sub>2</sub> atmosphere to investigate the effect of surfactants concentration on monomer conversion. A typical recipe for the preparation of a product is given in Table 2. To determine the conversion percentage during the polymerization process, it was necessary to withdraw samples at various intervals from the reaction vessel. These samples were relatively small so that the overall composition in the reactor was not seriously affected; once a sample was removed and put in a watch glass, polymerization was 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 [18]. A small amount of coagulum was obtained from the polymerization with the polymeric surfactants, and this shows that they can be used in an emulsion polymerization rightly.

## 6. 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).

## 7. Water Absorption

Dried films (30 mm×30 mm; original weight designated as W<sub>0</sub>) were immersed in water for 24 hr at 25 °C. After the residual water was wiped from the films using filter paper, the weight (W<sub>1</sub>) was measured immediately [19]. It was calculated as follows: water absorption,

$$R(\%) = ((W_1 - W_0)/W_0) \times 100 \quad (1)$$

## RESULTS AND DISCUSSION

### 1. Spectral Analysis of MPEO and Tri-block Polyurethane Surfactants (Samples I, II, III)

The structure of MPEO was confirmed by FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies. FT-IR (KBr, cm<sup>-1</sup>): 3412 (OH), 2871 (CH), 1645 (C=C), 1100 (C-O-C). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz, δ ppm): 5.80 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 5.10 and 5.20 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 4.90 (CH<sub>2</sub>CH<sub>2</sub>OH), 3.90 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 3.40-3.60 [(OCH<sub>2</sub>CH<sub>2</sub>O) and (OCH<sub>2</sub>CH<sub>2</sub>OH)], 3.20 (OCH<sub>2</sub>CH<sub>2</sub>OH). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, δ

ppm): 135 (C=C-C-O), 117 (C=C-C-O), 72 (C=C-C-O), 70 (O-CC-O), 69 (O-CCOH), 61 (O-CCOH). Purity: 82.5%. Elemental analysis calculated for C<sub>21</sub>H<sub>42</sub>O<sub>10</sub> (%): C 55.49, H 9.31, and O 35.2. Found: C 56.60, H 9.40, and O 36.61.

#### 1-1. Sample I

FT-IR (KBr, cm<sup>-1</sup>): 3342 (CO-NH), 2872 (CH), 1725 (C=O), 1604 (C=C), 1102 (C-O-C). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz, δ ppm): 8.00 (NH(COO)(C)), 7.50 (NH(COO)(CH)), 5.80 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 5.10 and 5.20 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 3.90 (OCH<sub>2</sub>CH<sub>2</sub>O-CO), 3.80 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 3.3-3.6 [(OCH<sub>2</sub>CH<sub>2</sub>O), and (OCH<sub>2</sub>CH(CH<sub>3</sub>)(O))], 2.8-3 (OOCNHCH<sub>2</sub>CH), 1.60 and 1.80 [(CCH<sub>2</sub>CH), and (CCH<sub>2</sub>C)], 1.00 [(CH<sub>3</sub>CH(O)(CH<sub>2</sub>)) and (CH<sub>3</sub>C(NH)(CH<sub>2</sub>))], 0.80 (CH<sub>3</sub>CCH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, δ ppm): 156 ((O)(NH)C=O), 135 (C=C-C-O), 117 (C=C-C-O), 73 and 75 ((O)(CH<sub>3</sub>)CC-O), 72 (C=C-C-O), 70 (O-CC-O), 62 (O-CC-O-C=O), 51 (C(NH)(CH<sub>3</sub>)), 48 (CH(NH)), 44 (OOCNHCC), 45 (C(CH<sub>3</sub>)(CH<sub>3</sub>)), 36 (C(C)(CH)), 32 (C(CH<sub>3</sub>)(CH<sub>3</sub>)), 25 (CH<sub>3</sub>C(NH)(CH<sub>2</sub>)), 17 (CH<sub>3</sub>CH(O)(CH<sub>2</sub>)). Purity: 87%. Elemental analysis calculated for C<sub>116</sub>H<sub>222</sub>N<sub>4</sub>O<sub>42</sub> (%): C 59.41, H 9.54, N 2.39, and O 28.66. Found: C 59.71, H 9.56, N 2.65, and O 29.12.

#### 1-2. Sample II

FT-IR (KBr, cm<sup>-1</sup>): 3295 (CO-NH), 2870 (CH), 1725 (C=O), 1638 (phenyl), 1101 (C-O-C). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz, δ ppm): 8.9 (NH(phenyl)(COO)), 6.7, 7.1 and 7.8 (phenyl-H), 5.9 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 5.2 and 5.3 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 4 (OCH<sub>2</sub>CH<sub>2</sub>O-CO), 3.4-3.7 [(OCH<sub>2</sub>CH<sub>2</sub>O) and (OCH<sub>2</sub>CH(CH<sub>3</sub>)(O))], 2.1 (phenyl-CH<sub>3</sub>), 1.1 and 1.3 (CH<sub>3</sub>CH(O)(CH<sub>2</sub>)). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, δ ppm): 152 and 153 (NH(phenyl)(COO)), 114, 117 and 135 (phenyl), 129 and 133 (phenyl-NH), 127 (phenyl-CH<sub>3</sub>), 133 (C=C-C-O), 117 (C=C-C-O), 68, 73 and 75 ((O)(CH<sub>3</sub>)CC-O), 69 and 71 (O-CC-O), 62 (O-CC-O-C=O), 17 [(O)(CH<sub>3</sub>)CC-O) and phenyl-CH<sub>3</sub>]. Purity: 86%. Elemental analysis calculated for C<sub>111</sub>H<sub>200</sub>N<sub>4</sub>O<sub>42</sub> (%): C 58.92, H 8.91, N 2.48, and O 29.7. Found: C 59.17, H 8.93, N 2.78, and O 30.03.

#### 1-3. Sample III

FT-IR (KBr, cm<sup>-1</sup>): 3333 (CO-NH), 2928 (CH), 1718 (C=O), 1648 (phenyl), 1135 (C-O-C). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz, δ ppm): 8.1 (NH(COO)(CH<sub>3</sub>)), 5.9 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 5.2 and 5.3 (CH<sub>2</sub>=CHCH<sub>2</sub>O), 3.9 and 4.1 [(CH<sub>2</sub>=CHCH<sub>2</sub>O) and (OCH<sub>2</sub>CH(CH<sub>3</sub>)(O))], 3.4-3.7 [(OCH<sub>2</sub>CH<sub>2</sub>O) and (OCH<sub>2</sub>CH(CH<sub>3</sub>)(O))], 3.1 (CH<sub>2</sub>CH<sub>2</sub>NHCOO), 1.3 and 1.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.1 (CH<sub>3</sub>CH(O)(CH<sub>2</sub>)). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz, δ ppm): 155 and 157 ((O)(NH)C=O), 135 (C=C-C-O), 117 (C=C-C-O), 68, 73 and 75 ((O)(CH<sub>3</sub>)CC-O), 71 (O-CC-O), 61 (O-CC-O-C=O), 40 ((OOC)(NH)CC), 26 (CCCCC), 17 ((O)(CH<sub>3</sub>)CC-O). Purity: 84%. Elemental analysis calculated for C<sub>109</sub>H<sub>212</sub>N<sub>4</sub>O<sub>42</sub> (%): C 58.16, H 9.49, N 2.49, and O 29.85. Found: C 58.44, H 9.52, and N 2.83, and O 30.23.

### 2. Effect of the PUS Concentration on the Surface Tension

According to Fig. 1, the surface tension decreased with an increase in the concentration of the polyurethane surfactants in an aqueous solution. This trend resembles what appears in conventional low-molecular-weight surfactants, 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 usually remains constant after the CMC is reached. Thus, this phenomenon is interesting. To the con-

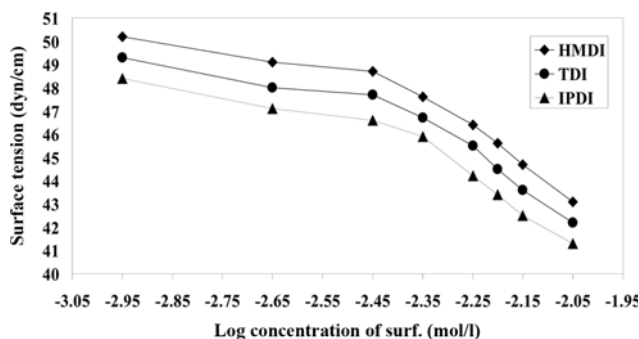


Fig. 1. Surface tension against molar concentration of PUS.

trary, Ismail [20] 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. [21] and Riess et al. [22]. 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 surfactants 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. [23] is similar to what we obtained. Fig. 1 shows that the samples had good surface activity and very low CMCs values, which could reduce the surface tension to as low as 43.5, 42.5 and 41.5 dyn/cm for HMDI, TDI and IPDI, respectively. 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.

UV spectroscopy has been widely used to determine the CMC and investigate the aggregate behaviors of surfactants [24-26]. The results of UV spectra in the various concentrations show a red shift occurred after some sample reached a certain concentration, and increasing the concentration made the red shift 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.

### 3. Effect of Salt on the Surface Tension

It is widely accepted that the addition of electrolytes has an effect on the surface tension [27-29]. As revealed by Fig. 2, the addition of salt led to a slight decrease in the surface tension of polyurethane surfactants (PUS), because the addition of salt increased the ionic strength of the aqueous solution. The hydrophilic parts of the polyurethane surfactants consisted of polyoxyethylene, whose oxygen atom could interact with  $H_2O$  or  $H_3O^+$  by a hydrogen bond and, con-

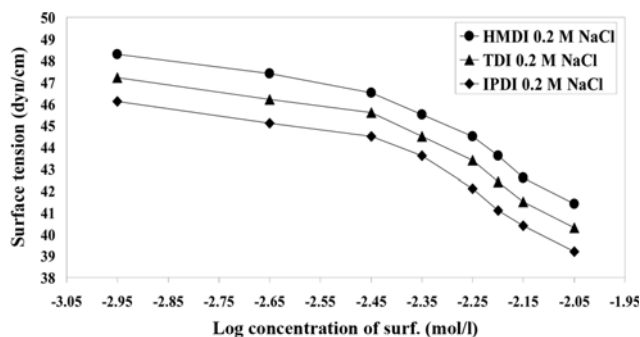


Fig. 2. Surface tension against molar concentration of PUS at different NaCl concentration aqueous solution.

sequently, was a little positive [30]. 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. Fig. 2 shows the effect of salt on the surface tension for HMDI, TDI and IPDI. This effect was more prominent at a lower concentration level and also IPDI shows the lowest level of surface tension among the others. 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.

### 4. 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 because 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:

$$\Gamma = - \frac{d\gamma}{da} \times \frac{\alpha}{RT} \quad (3)$$

where  $\Gamma$  is the surface excess concentration,  $\gamma$  is the surface tension,  $\alpha$  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.

### 5. 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 [31]. 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 molec-

ular 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.

### 6. Effect of PUS Concentration on Reaction Rate

Although emulsion copolymerization of VAc has been well established [32,33], its copolymerization in the presence of PUS has not been reported. Therefore, the role of these surfactants is not perfectly clear. It is possible that during the copolymerization process these polymeric surfactants will make part of the copolymer chain. However, the extent of their incorporation in the polymer chain was not measured. Fig. 3 shows the effect of PUS on the reaction rate versus time for VAc where the initial initiator and PUS concentrations were fixed at  $I_o = 2.8 \times 10^{-3} \text{ mol L}^{-1}$ . It can be observed that the rate of reaction of IPDI, TDI and HMDI containing PUS increased in the order IPDI > TDI > HMDI. This result shows that the IPDI containing PUS is a better surfactant for VAc emulsion copolymerization in comparison with TDI and HMDI containing PUS.

### 7. Molecular Weights of PVAc

The molecular weight is considered to be one of the most important parameters of PVAc. The mechanical property is significantly affected by the molecular weight of PVAc [34,35]. Fig. 4(a)-(c) shows

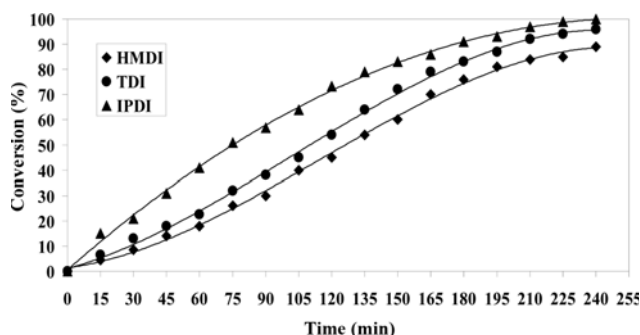


Fig. 3. The effect of PUS with constant concentration on monomer conversion vs. time for HMDI (◆), TDI (●) and IPDI (▲) at  $T=80^\circ\text{C}$ ,  $[I]_0=2.80 \times 10^{-3} \text{ mol L}^{-1}$ .

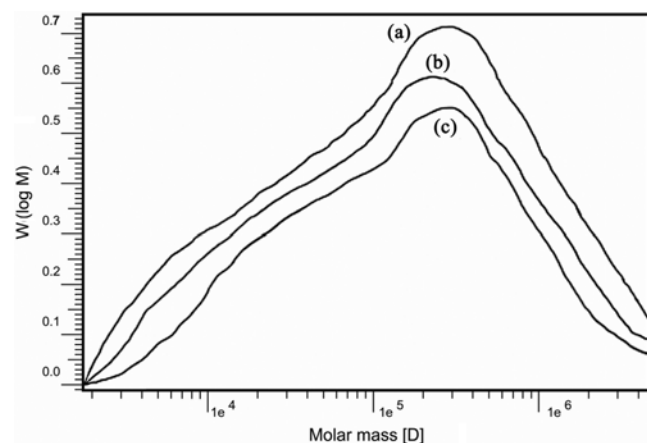


Fig. 4. Molecular weight measurements of PVAc latexes by (a) IPDI, (b) TDI and (c) HMDI containing PUS at  $T=80^\circ\text{C}$ ,  $[I]_0=2.80 \times 10^{-3} \text{ mol L}^{-1}$ .

the molecular weight of PVAc by IPDI, TDI and HMDI containing PUS, respectively. According to this figure the molecular weight of PVAc emulsion copolymers increased by IPDI, TDI and HMDI containing PUS in the order IPDI > TDI > HMDI. The IPDI exhibited the highest molecular weight among all of the samples and the HMDI samples exhibited lower molecular weight than the others.

### 8. Morphology of Latex Particles of PVAc

The particle morphology of the PVAc is illustrated in Fig. 5(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 except (c) micrograph. 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  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}$ -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.

### 9. Particle Size and Coagulum Percentage of the Emulsions

The particle sizes of the PVAc emulsions were measured by laser light scattering and are given in Fig. 6(a)-(c) for IPDI, TDI and HMDI, respectively.

The geometric mean diameter ( $d_g$ ) was calculated according to Eq. (4) [38].

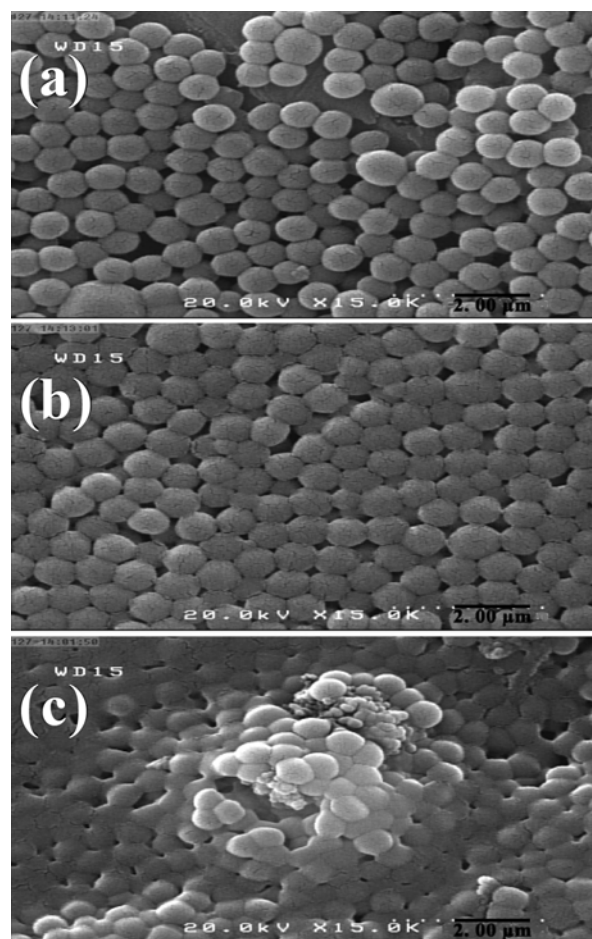


Fig. 5. SEM micrographs of PVAc latexes by (a) IPDI, (b) TDI and (c) HMDI containing PUS at  $T=80^\circ\text{C}$ ,  $[I]_0=2.80 \times 10^{-3} \text{ mol L}^{-1}$ .

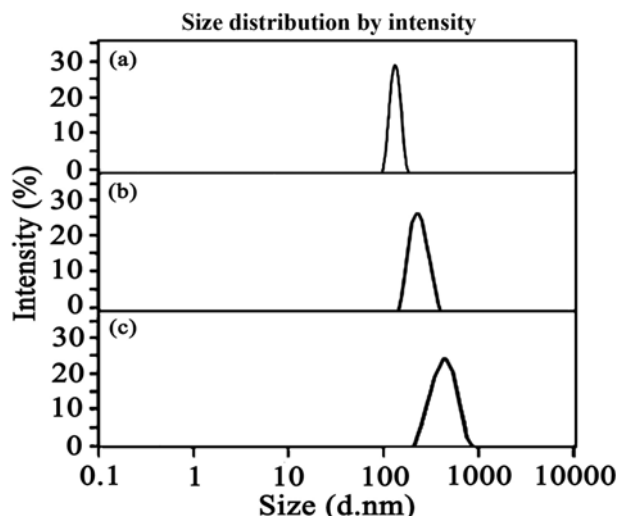


Fig. 6. Particle size of the PVAc latexes with (a) IPDI, (b) TDI and (c) HMDI containing PUS at  $T=80\text{ }^{\circ}\text{C}$ ,  $[I]_0=2.80\times 10^{-3}\text{ molL}^{-1}$ .

$$d_g = \exp \left( \frac{\sum (n_i \ln d_i)}{N} \right) \quad (4)$$

where  $n_i$  is the number of particles in group  $i$ , with a midpoint of size  $d_i$ , and  $N=\sum n_i$ , means the total number of particles. According to experimental results and Eq. (4), it can be obtained that the  $d_g$  were 108 nm, 117 nm, and 124 nm for IPDI, TDI and HMDI, respectively. Particle nucleation is assumed to occur predominantly in the aqueous phase for emulsion polymerizations. Thus the particles are formed over the entire period of the polymerization process, and the particle growth occurs by coalescence of smaller size particles or low molecular weight oligomers with larger size particles. In the case of more hydrophobic monomer adsorption of emulsifier onto the particle surface results in small size latex particles. When the average particle size decreases for constant solid contents of latexes, the total surface area of polymer particles increases. This means that the increase in the latex viscosity corresponds to an increase in the total surface area, and because emulsifier concentration is proportional to the total surface area, an increase in the latex viscosity with an increase in the emulsifier concentration is reasonable. The abundance of particle size is the reason that small particles enter larger particles, which leads to a compartmentalization effect. Because of this effect there is an increase in latex fluidity and a decrease in the latex viscosity.

Although there existed C=C double bond at the end of the molecular chain, during the emulsion polymerization, they were used not only as polymer surfactant to stabilize the latexes, but also as cross-linker and they would be copolymerized to form network polymers, leading to insoluble polymers. It should be pointed out that the emulsion polymerizations were carried out with only 0.2 wt% of copolymeric surfactants and the coagulum percentages were 0.6-1. Therefore, the latex system would be in the stability limit and also there was not any difficulty for measurements of molecular weights, due to solubility of the poly (vinyl acetate) in THF.

## CONCLUSIONS

By addition polymerization of IPDI, TDI and HMDI with PPO

and monoallyl-end-capped poly (ethylene oxide) (PEO), we synthesized a novel series of nonionic polyurethane surfactants containing reactive double bonds. The chemical structure of the polyurethane surfactants was confirmed using FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopes. With all polymeric surfactants, a monodispersity latex was obtained with very little coagulum, and all the surfactants exhibited good surface activity; for example, IPDI containing PUS could reduce surface tension to as low as 41.5 dyn/cm. The surface tension of these polyurethane surfactants in aqueous solution changed with concentration. An increase in the temperature was favorable for the enhancement of the surface activity, and the addition of salt reduced the surface tension. We also found that time was needed for the polyurethane surfactant to reach a constant value of the surface tension. These polymeric surfactants may find potential applications in emulsion polymerization as a promising alternative to conventional low-molecular-weight surfactants. At the same time, because of the hydrophobic part, they could be used in the synthesis of hydrophobically associating water-soluble polymers. Further studies in this direction are in progress.

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