Synthesis and characterization of polymerizable epoxy resin surfactants

Yue Wang,[1] Zhipeng He,[1] Qiong Liu,[2] He Huang[1,2]

[1]Jiangsu Key Laboratory for the Design and Application of Advanced Functional Polymers, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China
[2]Zhangjiagang Institute of Industrial Technologies, Soochow University, Suzhou 215600, People's Republic of China
Correspondence to: H. Huang (E-mail: hehuang@suda.edu.cn)

ABSTRACT: Polymerizable epoxy resin (PER) surfactants have been prepared from the reaction of bisphenol A epoxy resin with acrylic acid, followed by the reaction with polyethylene glycol (PEG) with different molecular weights. The reaction procedures were monitored by chemical titrations, infrared spectroscopy, and NMR. The products show typical surface-active properties as but much higher water solubility than nonpolymerizable nonionic surfactant OP-10. With the increase of PEG's molecular weight, the HLB value, the water solubility, and the critical micellar concentration (CMC) of the PER surfactants, the cloud point of the PER surfactant solutions, as well as the solubilization capability of the PER surfactants to organic compounds increase under the experimental conditions. The copolymerization under UV radiation indicated that about 75–80 wt % of PER surfactants participated in the copolymerization with epoxy diacrylate (EdA), except for the PER surfactant with the lowest PEG molecular weight of 1 k. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42598.

INTRODUCTION

Polymerizable surfactant—also referred as a surfmer, polymerizable emulsifier, surface-active monomer, monomeric emulsifier, monomeric surfactant—has been paid a considerable attention in the past three decades. This is because polymerizable surfactant can be used not only to counteract negative effects caused by nonreactive surfactants, including foaming, destabilization of the latex particles or the dispersion, decrease of gloss and water resistance of the film formed, reduction of the wet adhesion characteristics of the binder, etc., but also to provide some positive features, such as reducing the total amount of surface-active matter necessary, making latexes redispersable, or functionalizing the latex particle surface.[1–3]

Polymerizable surfactants are commonly used in heterophase polymerizations, such as emulsion polymerization and dispersion polymerization, and a set of requirements have been found to be important for the optimal performance of the surfmers, including low CMC, allowing a certain degree of emulsification of the monomer mixture, providing smooth and reproducible nucleation stages, efficient enough in stabilizing the polymer particles, not reactive early in the process but able to chemically bound to the surface of the particles at the very end of the process, etc.[2] Some of the above requirements, such as low CMC,

not reactive early in the process, etc., may be not critical in the case when a UV-curing artificial latex, e.g., epoxy acrylate latex, will be produced.

Polymerizable surfactants are also amphiphilic organic compounds, containing both hydrophobic groups and hydrophilic groups. Though the hydrophilic groups can be nonionic, anionic, or cationic, the hydrophobic groups are usually short chain alkyl, such as undecyl, dodecyl, hexadecyl/cetyl, dioctyl, didodecyl, and so on.[4–19] Recently, Guo[20] reported the preparation of a self-emulsifying epoxy resin surfactant, using bisphenol A as the hydrophobic group. The hydrophilic groups include polyethylene glycol (PEG), alkylphenol polyoxyethylene ether. Acrylic acid was used to react with the epoxide group and induce C=C double bond. This is in fact a polymerizable epoxy resin (PER) surfactant. Nevertheless, its physiochemical properties and polymerizability were not mentioned. Chen et al.[21] synthesized a similar PER surfactant from methoxylated PEG at one end (MeO-PEG-OH), maleic anhydride (MA), and bisphenol A epoxy resin (E-44). However, this surfactant was used to emulsify E-44 to make water-borne epoxy resin, rather than epoxy diacrylate (EdA) emulsion. He et al.[22] also made a PER surfactant from the reaction of PEG and a polyether with two terminal epoxy groups and then with acrylic acid. Again, the

physiochemical properties and polymerizability of this surfactant was not a concern.

Compared to the normal short chain alkyl,[4–19] epoxy resins in the above studies[20–22] have relatively higher molecular weights. Correspondingly, the hydrophilic groups such as PEG and alkylphenol polyoxyethylene ether must also have higher molecular weights than those used in the normal surfactants or surfmers. However, no systematic study on the effect of the molecular weight of PEG on the physiochemical properties of the PER surfactants has been found yet.

In this work, a slightly different approach from the reported[20–22] was adopted to synthesize a series of PER surfactants. Bisphenol A epoxy resin (E-44) was first reacted with acrylic acid to form an epoxy monoacrylate (EmA), with the one remaining epoxide group reacting with PEG to obtain the final PER surfactant. The physicochemical properties of the corresponding PER surfactants are measured. Their polymerizability was further tested in the copolymerization with epoxy diacrylate under UV radiation. With this current approach, the synthesis of PER surfactants can be carried out at lower temperature (60–90°C) compared to the previous methods (90–120°C in Ref. 20, 110−120°C in Ref. 21, and 80−140°C in Ref. 22). Besides, fewer raw materials are required in the synthesis of PER surfactants. In addition to E44, PEG, and acrylic acid, there is no need to use other traditional surfactant such as alkylphenol polyoxyethylene ether,[20] organic solvent,[21] or other additives.[22] Furthermore, PER surfactant with higher activity than that obtained in Ref. 21 can be synthesized because the polymerizable C=C bond in Ref. 21 is in the middle of the PER molecule and is induced from maleic anhydride. Such polymerizable macromolecular surfactants have been proved to be very useful in the production of UV-curing epoxy diacrylate (EdA) latexes or polyacrylamide hydrogels in our laboratories.[23–25]

EXPERIMENTAL

Materials

Bisphenol-A-type epoxy resin E-44 with epoxide equivalent 0.44 mol/100 g and epoxy diacrylate (EdA) were supplied by Sinopec Group (China). Acrylic acid (AA), tetra methyl ammonium chloride (TMAC), 4-methoxyphenol, polyethylene glycol (M_n = 1k/2k/4k/6k g·mol^{-1}, PEG 1k/2k/4k/6k), methanol (MeOH), methyl methacrylate (MMA), toluene, 2-hydroxyl-2-methylpropiophenone (1173), isopropanol, Tween 80, and Span 80 were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used as received without any further purification.

Synthesis of Polymerizable Epoxy Resin (PER) Surfactants

The PER surfactants were synthesized as follows. First, 0.1 mol E-44 and 0.01 g 4-methoxyphenol were added to a three-necked flask and stirred for 15 min at 60°C. The mixed solution of AA (0.1 or 0.11 mol) and TMAC was added dropwise into the flask and then heated to 90°C. The reaction was finished until the acid number fell to below 3 mg KOH·g^{-1}. After that, the reaction mixture was cooled to 80°C, and then 0.1 mol PEG (dried under high vacuum at 110°C) was added into the flask and the reaction was continued for 1.0 h (the completion of the reaction was monitored by titration of epoxide values) to get the PER surfactants. The crude products were purified by precipitation

in a large amount of methanol and dried under high vacuum at 30°C.

^{1}H NMR of first-step products (δ, ppm, d-CDCl$_3$): 1.61 (s, 8.16H, CH$_3$), 2.70 (q, 1H, CH$_2$), 2.85 (t, 1H, CH$_2$), 3.11 (s, 3H, CH$_3$), 3.30 (m, 1H, CH), 3.88 (q, 2.72H, CH$_2$), 3.99 (m, 2.72H, CH$_2$), 4.08 (t, 2H, CH$_2$), 4.19 (m, 1.36H, CH), 4.32 (m, 1.36H, OH), 5.82 (d, 1H, CH$_2$), 6.13 (q, 1H, CH), 6.39 (d, 1H, CH$_2$), 6.78 (q, 5.44H, C$_6$H$_4$), 7.10 (q, 5.44H, C$_6$H$_4$).

Copolymerization with Epoxy Diacrylate (EdA)

To investigate the copolymerization of PER surfactants with epoxy diacrylate (EdA), water-borne EdA emulsions were prepared by phase inversion technique under high speed of stirring at ambient temperature (25°C).[26] The solid content of the EdA emulsions were 40 wt % with 7.4 wt % of PER surfactant. Subsequently, a certain quantity of above emulsion with photo initiator 1173 was cast onto glass plates with a thickness of 6 μm and irradiated under 365 nm UV light (2000 W, the distance between the samples and the lamp was 10 cm) for 20 s. Then the glass plates covered by cured films were immersed into methanol or water for 24 h and dried to a constant weight at 100°C. The mass loss ratio was calculated by the following formula:

$$\text{Mass loss ratio } (\%) = \frac{W_2 - W_0}{W_1 - W_0} \times 100\% \qquad (1)$$

where, W_0 is the weight of the glass plate, W_1 and W_2 are the total weight of cured film and glass plate before and after immersion in water or methanol, respectively.

Characterization

Infrared spectra were obtained on a Nicolet 6700 FT-IR Fourier transform infrared (FTIR) spectrometer using a minimum of 64 co-added scans at a resolution of 2 cm^{-1}. ^{1}H NMR spectra in deuterated chloroform were recorded using a 400 MHz Inova NMR spectrometer. The HLB values were determined by water number method[27] in mixed solvents of isopropanol/toluene (volume ratio 100/15) with Tween 80/Span80 (HLB value 15/4.3) as the standard surfactants. The cloud points were obtained by determination of the temperature while 1 wt % diluted surfactant aqueous solution turned from pellucid to visibly turbid in a heating water bath,[28] and the mean value of three tests was accepted. If the cloud point was higher than 90°C, 5 wt % NaCl was added additionally. Surface tension of a surfmer's aqueous solution was measured on Dynamic Contact Angle Test (Data Physics Instruments, DCAT21) and recorded three times to ensure a reproducibility for each solution. Critical micellar concentrations (CMCs) were determined from the surface tension curve under different surfactant concentrations. The light transmittance of the surfactant's aqueous solutions was monitored as a function of concentration at a fixed wavelength of 500 nm by means of a Hitachi U-3900/3900H UV/vis spectrophotometer using water as reference. For solubilization studies, PER surfactant's aqueous solutions of concentration 0.01 g·mL^{-1} were prepared. Different amounts of solubilizate (toluene or MMA) were added to this solution and the suspensions were standing overnight. Then, the light transmittance of these suspensions was recorded by UV/vis spectrophotometer at a fixed wavelength of 500 nm.[29]
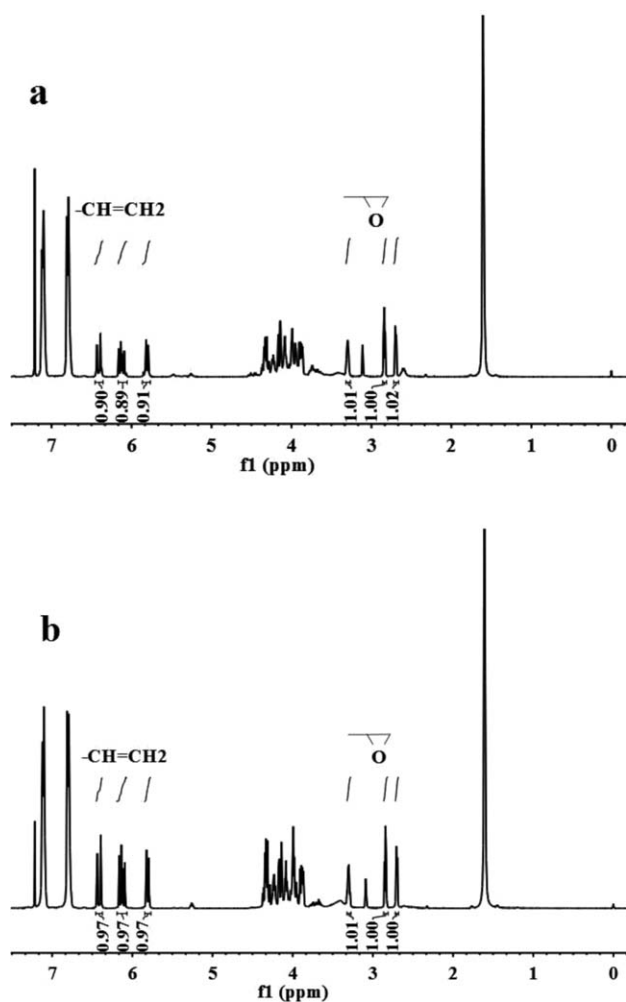
Figure 1. ^{1}H NMR spectra of the first-step products under different molar ratio of E-44/AA: (a) 1/1 and (b) 1/1.1.

The determination of epoxide value was referred to Ref. 30.

The acid number was determined by the following procedure. A certain amount of samples was weighed (accurate to 0.0001 g) and filled into a conical flask with a ground glass stopper with 10 mL acetone and 3–5 drops of phenolphthalein indicator. The mixture was titrated by 0.05 mol·L^{-1} KOH aqueous solution to a pink color which did not fade within 30 s. Each set of data was measured three times and the average value was taken as the end result. The acid number was calculated by

$$Acid\ number = \frac{N \times V}{W} \times 56.1 \qquad (2)$$

where, N (mol·L^{-1}) denotes the concentration of KOH aqueous solution, V is the volume (mL) of the KOH aqueous solution consumed by the acetone solution with dissolved sample, and W is the mass (g) of the sample.

RESULTS AND DISCUSSION

Preparation of PER Surfactant

The synthesis of the PER surfactants includes two steps. The first step is the formation of epoxy monoacrylate (EmA) from the reaction between E-44 and acrylic acid (AA). The reaction

Table I. The Epoxide Value for the Reactions with Different Molar Ratio of E-44/AA

	Molar ratio of E-44/AA	
Epoxide value (mol/100 g)	1/1	1/1.1
Initial[a]	0.392	0.415
Initial theoretical[b]	0.390	0.385
Final[a]	0.224	0.216
Excess percentage[c]	14.28%	4.10%

[a] Epoxide value of E-44/AA mixture before reaction obtained by titration method.
[b] Calculated theoretical epoxide value of E-44/AA mixture before reaction.
[c] Obtained from $\frac{Final - {}^{1}/_{2}\,Initial}{{}^{1}/_{2}\,Initial} \times 100\%$.

was carried out at 90°C. At such a high temperature, some AA may be lost due to evaporation even with water cooling setup. So, in contrast to the molar ratio of E-44/AA = 1/1, a lower molar ratio of 1/1.1 was also explored and ^{1}H NMR and titration methods were employed to monitor the reaction.

The ^{1}H NMR result (Figure 1) indicates that about 89.1% and 96.7% AA has been reacted with E-44 at the molar ratio of E-44/AA = 1/1 and 1/1.1, respectively. This is quite consistent with the result from titration method shown in Table I, in which the excess amount of epoxide group is 14.28% and 4.10%, respectively, when the molar ratio of E-44/AA = 1/1 and 1/1.1. Apparently, slightly excess AA at the beginning of the reaction is helpful with the synthesis of ideal product.

The infrared spectrum of the first-step product with the molar ratio of E-44/AA = 1/1.1 is shown in Figure 2, together with that of E-44.

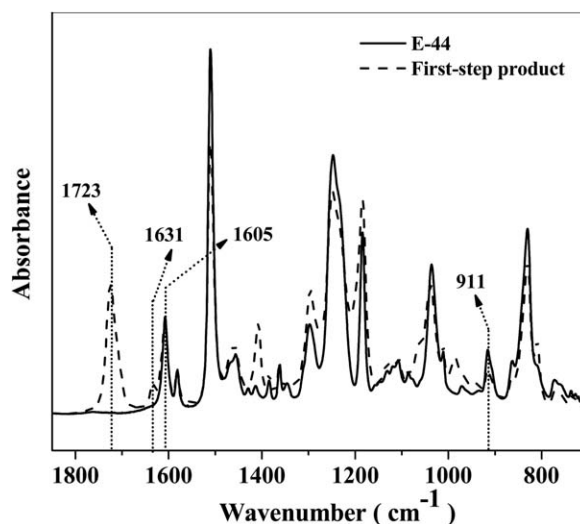It can be found that, compared to the IR spectrum of pure E44, two new bands appeared around 1631 and 1723 cm^{-1},

Figure 2. The FT-IR spectra of the first-step product with molar ratio of E-44/AA = 1/1.1 and raw material E-44 (normalized based on the 1605 cm^{-1} band).
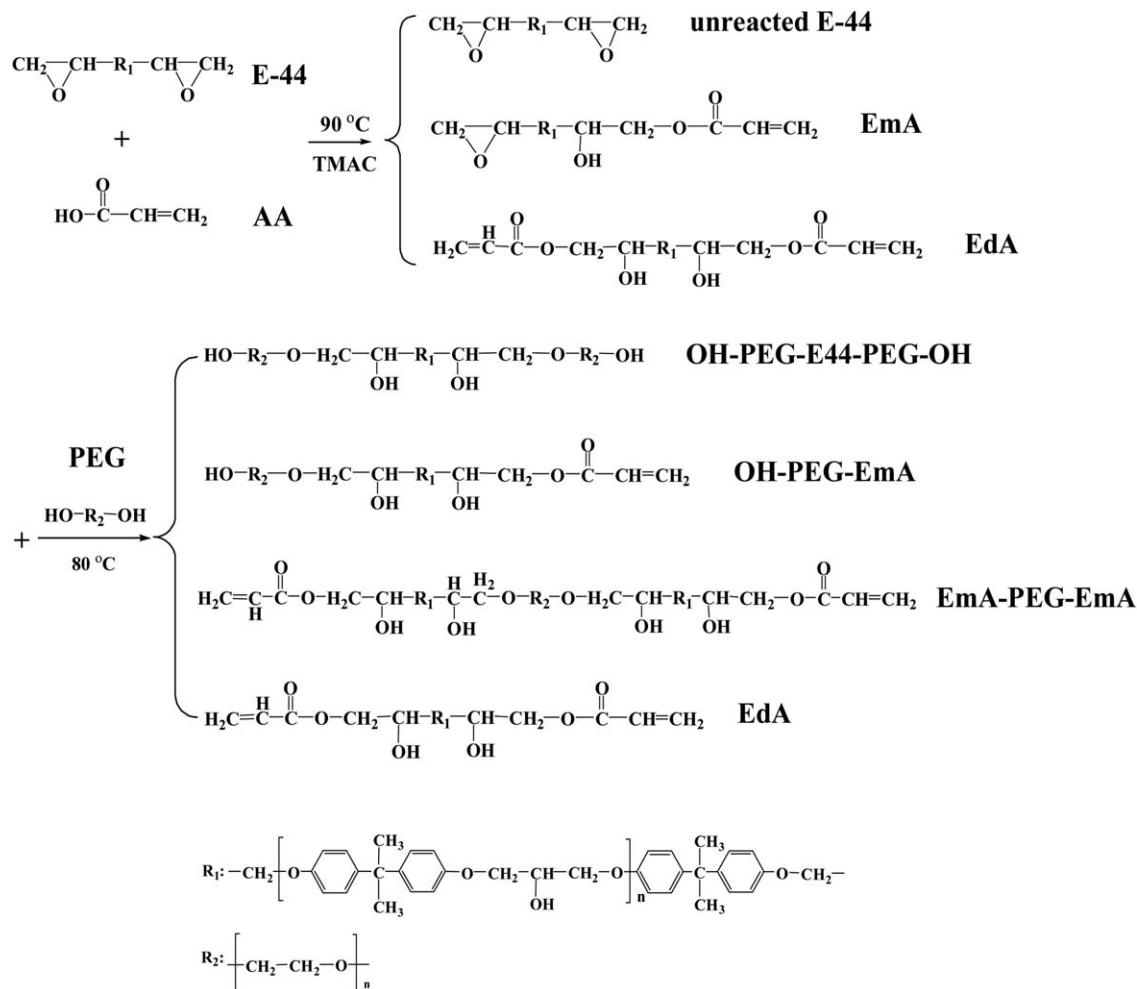
Figure 3. Synthetic procedures of preparing the PER surfactants.

corresponding to the C=C bond and C=O bond, respectively. In addition, the intensity of the 911 cm^{-1} band corresponding to the epoxide group decreased about 50%. All these indicate that about half of the epoxide group has been reacted with AA, in good agreement with the result from titration method. This result does not guarantee, however, that only one epoxide group of an E-44 molecule participated in the reaction. This suggests that, in addition to epoxy monoacrylate (EmA), the reaction product of the first step may also contain epoxy diacrylate (EdA) and even unreacted E-44 (Figure 3). It is hard to determine the exact percentage of epoxy monoacrylate (EmA) in the product at this step. Statistically, of course, EmA should be the predominant one. Molecular weight determination of the final product in the second step of the reaction revealed that the amount of EdA is about 10–18%, depending on the molecular weight of PEG, which confirmed our above assessment.

The second step is the reaction between epoxy monoacrylate (EmA), unreacted epoxy resin, and PEG. The end of the reaction was recorded by the disappearance of epoxide group determined by titration method as well as infrared spectroscopy. At the end of the reaction, the epoxide value reaches 0 and the 911 cm^{-1} band (Figure 4) corresponding to the epoxide group disappeared.

It is of note that PEG (OH-PEG-OH) has two end hydroxyl groups, i.e., it may react with the product EmA and unreacted epoxy resin in the first step and the final product of the second
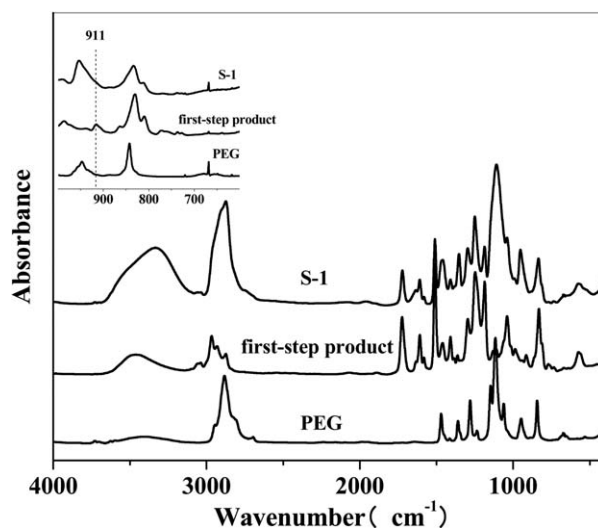

Figure 4. The FT-IR spectra of PEG, the first-step product and the final product S-1 (molar ratio of E-44/AA = 1/1.1).

Table II. HLB Values of PER Surfactants Synthesized

PER surfactant	(HLB)$_G$	HLB
S-1	13.1	12.0
S-2	15.8	14.5
S-4	17.7	15.8
S-6	18.4	16.0
SDS	5.17	
OP-10	14.5	

Note: S-1, S-2, S-4, and S-6 are PER surfactants made from PEG with the molecular weight of 1K, 2K, 4K, and 6K, respectively.

step may consist of OH-PEG-EmA, OH-PEG-E44-PEG-OH, EmA-PEG-EmA and EdA (Figure 3). The crude products were purified by precipitation in a large amount of methanol and dried under high vacuum at 30°C, i.e., EdA has been removed by this purification. Therefore, the final PER surfactant is a mixture of at least three components: OH-PEG-EmA, OH-PEG-E44-PEG-OH, and EmA-PEG-EmA. Apparently, it is impossible to separate the target product OH-PEG-EmA from the other two. Fortunately enough, the other two components are useful in the production of UV-curing EdA latexes, and they are also three-block copolymers which may behave as surfactants. With this, the physicochemical properties of the PER surfactants are to be investigated in the next section.

Physicochemical Properties of the PER Surfactants

Hydrophile–lipophile balance (HLB) value is an important parameter for a surfactant. Table II shows the HLB values of the synthesized PER surfactants calculated from the Griffin method[31] and measured from the Water number method.[27] It can be found that the HLB value measured from the Water number method is slightly lower than that calculated from the Griffin method. This is because only the OH-PEG-EmA PER surfactant was taken to calculate the HLB value using the Griffin method, while a real PER surfactant is at least a three-component mixture. It can also be seen from Table II that the HLB values of the PER surfactants increase with the molecular weight of PEG, which is as expected. In addition, all the PER surfactants, except for S-1, have better hydrophilicity than the common nonpolymerizable surfactant OP-10.

The measurement of the cloud points is important for nonionic surfactants. As expected, the cloud point of the PER surfactants increases with the increasing molecular weight of PEG (Table III). In addition, all the PER surfactants, except for S-1,

Table III. Cloud Points of per Surfactants Synthesized

PER surfactant	Cloud points (°C)	
	Aqueous solution	5 wt % NaCl aqueous solution
S-1	48 ± 0.5	32.5 ± 0.5
S-2	78 ± 0.5	61 ± 0.5
S-4	>90	78 ± 0.5
S-6	>90	81 ± 0.5

Table IV. Properties of PER Surfactant's Aqueous Solutions ($T = 25$°C)

PER surfactant	CMC (mg·mL^{-1})	γ_{CMC} (mN·m^{-1})	Γ_{CMC} (mol·m^{-2})
S-1	0.25	46.82	1.78
S-2	0.40	47.23	1.47
S-4	0.56	47.25	1.40
S-6	1.00	47.26	1.23

have a higher cloud point than the common nonpolymerizable surfactant OP-10 (70 ± 1°C). This suggests that the PER surfactants, including S-2, S-4, and S-6, can be used at higher temperatures than OP-10.

Though the PER surfactants are not to be used in conventional emulsion polymerization of monomers in this study, their CMCs (Table IV) are determined by surface tension measurements, shown in Figure 5.

The CMCs of these PER surfactants increase slightly with the molecular weight of PEG. This is because the solubility of the PER surfactants in water should increase with increasing molecular weight of PEG (more on this later). Besides, all the final surface tensions of the PER surfactant solutions are around 47 mN·m^{-1}, 26 mN·m^{-1} lower than that of the pure water (72.97 mN·m^{-1}, 25°C).

Based on the surface tension result in Figure 5, surface excess can be calculated using the Gibbs adsorption isotherm equation:[32]

$$\Gamma = \frac{-1}{RT} \frac{d\gamma}{d\ln a} \tag{3}$$

Where, Γ is the surface excess, γ is the surface tension (mN·m^{-1}), R is the gas constant, 8.314 J·(mol·K)$^{-1}$, T is the temperature (K), a is equivalent to the concentration of dilute PER surfactants aqueous solution (g·mL^{-1}) when the CMCs range from 1 to 10 mmol·dm^{-3}.[33]
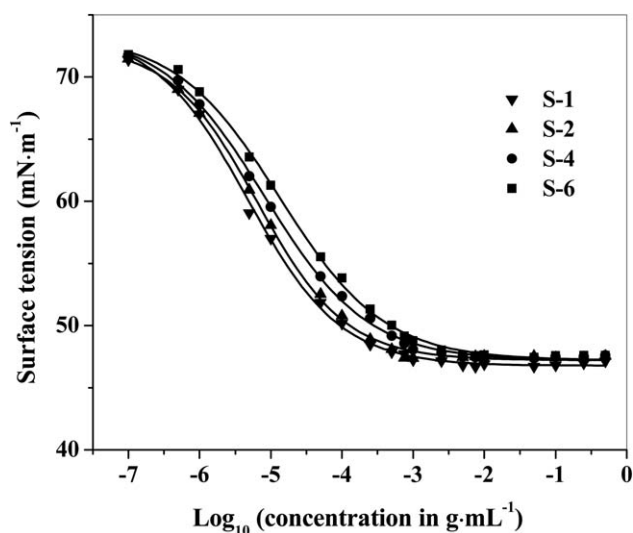
Figure 5. Surface tension dependence of the PER surfactant's aqueous solutions on concentration, $T = 25$°C.

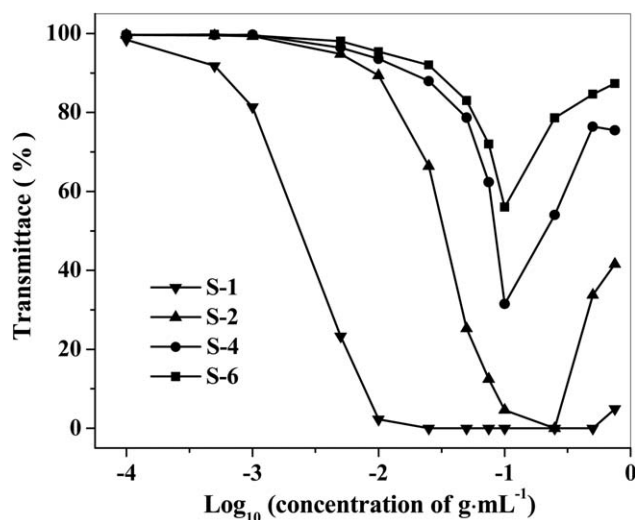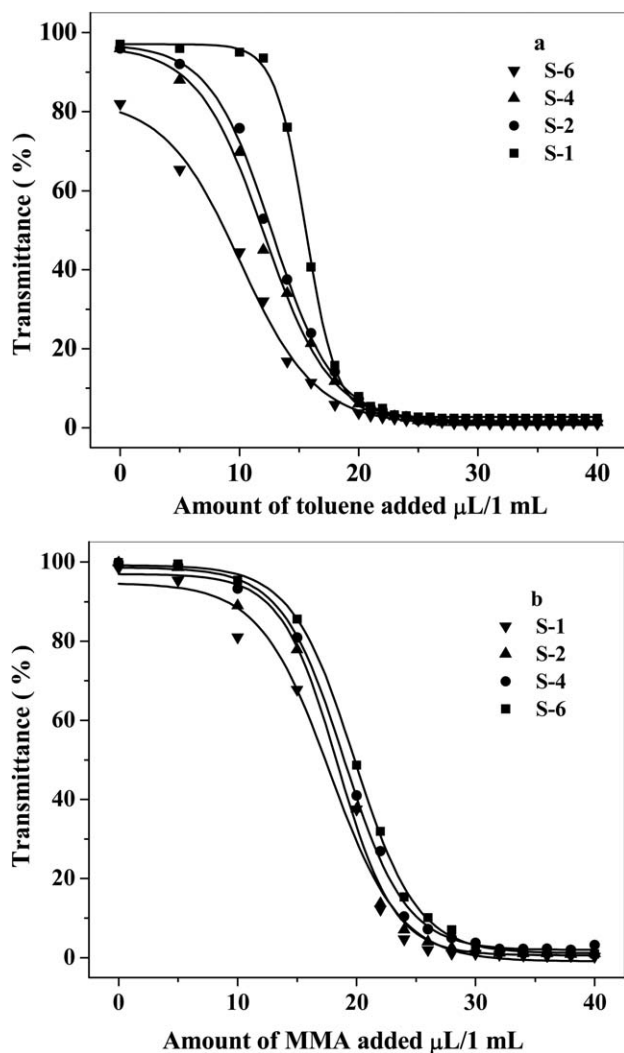**Figure 6.** Light transmittance of PER surfactant's aqueous solutions with concentration, $T = 25°C$.

Figure 7. Solubilization of PER surfactants' aqueous solutions to (a) toluene and (b) methyl methacrylate determined by UV–vis, $T = 25°C$.

It can be seen (Table IV) that Γ decreases with increasing the chain length of PEG in a PER surfactant, i.e., the concentration difference of a PER surfactant at the air/water interface and inside the water decreases when the molecular weight of PEG increases. Again, this must be the result that the solubility of the PER surfactant in water should increase with increasing molecular weight of PEG. This assessment can be easily verified by the water solubility result of the PER surfactants measured with UV–vis spectroscopy, i.e., the light transmittances of the PER surfactant's solutions increase with the chain length of PEG in the PER surfactant at all concentrations (Figure 6).

From Figure 6, it can also be found that the light transmittance of a PER surfactant's solution decreases with the increasing concentration of the PER surfactant at a relatively low concentration. This is straightforward and common to any surfactant because of the formation of more micelles with increasing concentration of the surfactant. It is interesting to notice, however, that the light transmittance of a PER surfactant's solution starts to increase again after a certain concentration. This specific concentration may be referred to as the *phase inversion point*, after which the continuous phase (water) may start to become the disperse phase, and the micelle structure may change at the same time. An investigation on the details of such a transition is still undergoing.

Solubilization is another characteristic for a typical surfactant. Figure 7 shows the solubilization result of the PER surfactants for toluene and methyl methacrylate.

The maximum amount of solubilized toluene and methyl methacrylate are calculated by Eq. (4):

$$A_m = \frac{A}{V \times c} \times 100\% \qquad (4)$$

where, A_m (mL·g^{-1}) is the maximum solubilization capacity of PER surfactant, A (mL) is the maximum volume of solubilized toluene or methyl methacrylate by a PER surfactant, V (= 1 mL) and c (= 0.01 g·mL^{-1}) are the volume and concentration of a PER surfactant aqueous solution, respectively.

The result is shown in Table V. Also listed in Table V are the maximum amounts of solubilized toluene in SDS and OP-10 solutions. It is evident that the solubilization capability of the PER surfactants slightly increases with the molecular weight of PEG. This slight increase in solubilization capacity of PER

Table V. The Maximum Solubilization Capacity of per Surfactant's Aqueous Solutions to toluene and Methyl Methacrylate, $T = 25°C$

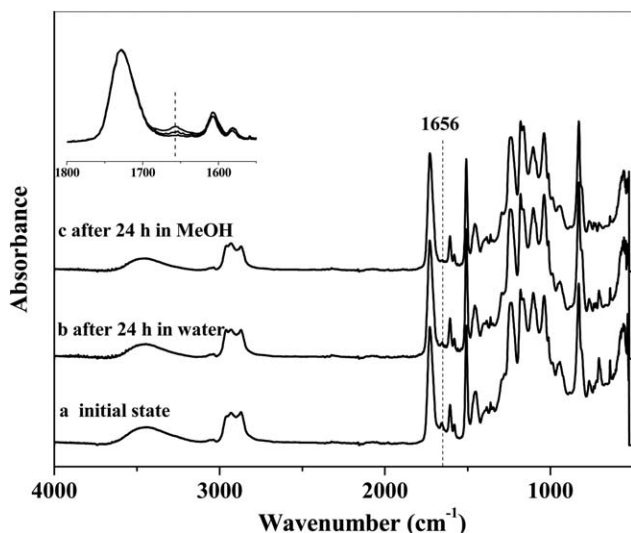| PER surfactant	A_m (mL·g^{-1})	
	Toluene	MMA
S-1	1.12	1.88
S-2	1.31	1.93
S-4	1.37	1.99
S-6	1.60	2.08
SDS	1.20	
OP-10	1.35	

Figure 8. The FT-IR spectra of cured films (a) untreated, (b) immersed in water for 24 h, and (c) immersed in MeOH for 24 h. Inset: FT-IR spectra normalized based on the 1731 cm^{-1} band.

surfactants is due to the increasing PEG chain length from S-1 to S-6. Under the experimental condition, the PER surfactant's concentration of 0.01 g·mL^{-1} is much higher than CMCs, which guarantees the formation of micelles. Therefore, though larger amount of PER surfactants are soluble in water with the increase of PEG molecular weight, the higher hydrophilicity of the PER surfactant to water will, on the other hand, be able to bring more solubilizate (toluene or MMA) into water. Besides, all the PER surfactants, except for S-1, have higher or similar solubilization capability than SDS and OP-10.

Copolymerization of PER Surfactant with Epoxy(di)acrylate

A water-borne EdA emulsion with a solid content of 40 wt % was prepared by phase inversion technique.[26] The amount of the PER surfactant (S-2) is 18.6 wt % of EdA. Figure 8 shows the iTR FT-IR spectra of the initially UV-curved film, UV-curved films immersed in water, and methanol for 24 h.
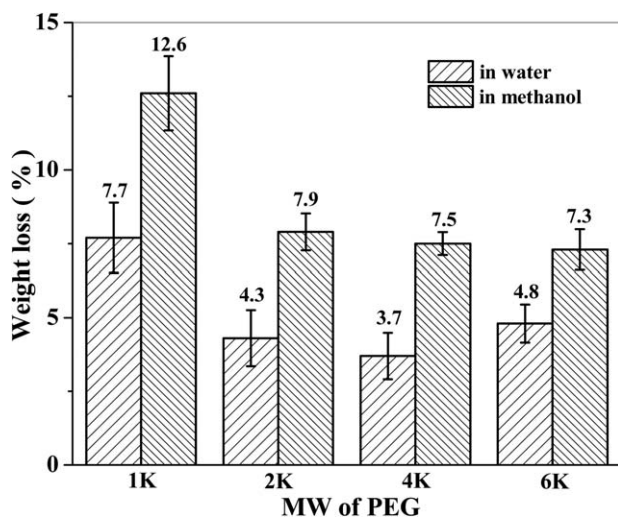

Figure 9. The weight losses of UV-cured films immersed in water and methanol for 24 h.

Table VI. The Conversion of per Surfactants in the Copolymerization with EdA

PER surfactant	Conversion (%)
S-1	58.6
S-2	77.4
S-4	80.1
S-6	74.2

From Figure 8, the C=C double bond at 1656 cm^{-1} is still visible after UV curving, indicating that not all the EdA or PER surfactant have been polymerized. After immersion in water for 24 h, the band intensity at 1656 cm^{-1} decreased, indicating that the unpolymerized PER surfactant has been removed from the film. If the film was immersed in methanol for 24 h, no C=C double bond can be visible any more, demonstrating that all the unpolymerized EdA or PER surfactant have been removed from the film.

The weight losses of the UV-cured films after immersion in water and methanol are presented in Figure 9.

Apparently, the weight loss of a UV-cured film immersed in water is less than that in methanol, because methanol may remove both EdA and PER surfactants, while water can only remove PER surfactant. Besides, the weight loss of the film using S-1 as the PER surfactant is the largest both in water and methanol, indicating the lowest copolymerization extent of both EdA and S-1.

The copolymerization extent or conversion of a PER surfactant (Table VI) with EdA may now be calculated from the following equation:

$$\text{Conversion} = \frac{a_0 - a}{a_0} \times 100\% \qquad (5)$$

where, a_0 is the percentage of a PER surfactant in the UV-cured film, a is the weight loss (%) of the UV-cured film after immersion in water for 24 h.

It is now more straightforward to see (Table VI) that the conversion of S-1 in the copolymerization with EdA is the lowest, while that of S-2, S-4, and S-6 has no significant difference.

It was noticed that the water-borne EdA emulsion using S-1 as surfactant has the lowest stability, compared to the emulsions prepared from S-2, S-4, and S-6. This poor stability is apparently due to the low emulsifying capability of the S-1 to EdA and gives rise to the largest separation of S-1 from EdA. So, more homopolymerization of S-1 in the aqueous phase will take place and the polymerization of EdA will be affected due to the lowest micelle concentration formed from S-1. Therefore, it can be concluded that the low conversion of S-1 in the copolymerization with EdA is a result of the poor stability of the water-borne EdA emulsion using S-1 as surfactant.

CONCLUSIONS

A series of polymerizable epoxy resin (PER) surfactants with highly reactive C=C double bonds have been synthesized from

bisphenol A epoxy resin (E-44), acrylic acid (AA), and polyethylene glycol (PEG) with various molecular weights. The results of chemical titration and ^{1}H NMR indicated that slightly excess AA at the first step of the reaction is helpful with the synthesis of targeted final products. The HLB value and cloud point of the PER surfactants increase with the increase of PEG's molecular weight and are slightly higher than the nonpolymerizable nonionic surfactant OP-10, except for S-1 with the lowest PEG molecular weight of 1 K. The critical micellar concentration (CMC) and solubilization capability of PER surfactants to toluene and methyl methacrylate also increase with the increase of PEG's chain length. The light transmittance measurement shows that the water solubility of the PER surfactants increases but the phase inversion point of their water solutions starts at a lower concentration with the increase of PEG's molecular weight. The polymerizability of PER surfactants in the copolymerization with epoxy diacrylate (EdA) under UV radiation was further evaluated and it was found that about 75–80 wt % of PER surfactants participated in the copolymerization, except for S-1.

ACKNOWLEDGMENTS

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