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SHORT COMMUNICATION

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Function and performance of silicone copolymer (VI). Synthesis and novel solution behavior of water-soluble polysiloxanes with different hydrophiles

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Abstract Silicone surfactants containing different pendant hydrophilic groups such as diethanol tertiary amine (SHE, nonionic), diethanol methyl quaternary amine (cationic) and triethyl quaternary amine (cationic) have been synthesized and characterized by ^{1}H and ^{13}C NMR and gel permeation chromatography. The solution behavior of these novel surfactants has also been investigated by surface tension measurement and a fluorescence method. It has been observed that the surface tension of these surfactants decreases as a function of time at a very low polymer concentration (1×10^{-4} wt%). At higher concentration (0.1 wt%), the equilibrium surface tensions reached very low values compared to that of typical polymer surfactants, for example, poly(ethylene oxide–propylene oxide) block copolymer (EPE0.8). In addition, the low I_1/I_3 values of these silicone surfactants indicate the formation of polymer aggregates in aqueous solution, and an extremely low I_1/I_3 value of SHE (1.06) compared to other polymeric surfactants (EPE0.8) and conventional surfactants [poly(ethylene glycol *n*-nonyl phenyl ethers), cetyltrimethylammonium bromide, and sodium dodecyl sulfate] indicates its stronger hydrophobicity.

Key words Silicone surfactant · Synthesize · Surface tension · Fluorescence · Polymer aggregates

Introduction

Hydrophobic groups with different hydrophobicity significantly influence the character of a surfactant. The efficiency of lowering the surface tensions or of forming close-packed aggregates in aqueous solution increases with the increase of hydrophobicity of the hydrophobic group present in the surfactants. Generally, long-chain hydrocarbons or polymer skeletons are used as hydrophobic groups for surfactants. However, polysiloxane has been used as hydrophobic groups for a wide range of applications [1, 2] and shows higher hydrophobicity than the usual long-chain hydrocarbons or polymer skeletons. Thus, it is interesting to study the surface-active properties of surfactants containing a polysiloxane backbone, called silicone surfactants, which have attracted diverse attention both for academic and industrial purposes, like surface modifiers, personal care, wetting of hydrocarbon surfaces, lubricants and foam controllers, etc. [3, 4].

The surface-active properties of a silicone surfactant are also highly influenced by the type and the content of the hydrophilic groups. Some types of nonionic [5–8], anionic [9, 10], cationic [11] and zwitterionic [12] groups have been used as the hydrophilic groups of silicone surfactants. In this study, a high-yield reaction of allyl glycidyl ether (AGE) with poly(methylhydrogensiloxane) copolymer was carried out, and then three types of amines (diethanolamine, diethanol methyl amine and triethylamine) were used to produce three silicone surfactants with different types of hydrophilic groups: diethanol tertiary amine (SHE), diethanol methyl quaternary amine (SQHE), triethyl quaternary amine (SQE). It is interesting that the aqueous solutions of these silicone surfactants show very low and time-dependent surface tension. Also, the hydrophobicity of the polymer aggregates of SHE in aqueous solution is even higher than that of conventional poly(ethylene oxide–propylene oxide) block copolymer (EPE0.8) and surfactants.

Experimental

Materials

Poly(methylhydrogensiloxane) (DC1107), octamethylcyclotetrasiloxane (D_4) and hexamethyldisiloxane (DC200) were obtained from Dow Corning Co. and were used without further purification. Sulfuric acid (Merck), AGE (Acros), diethanolamine (Lancaster), triethylamine (Merck), dimethyl sulfate (Merck), sodium hydrogen carbonate (Tedia), anhydrous sodium dihydrogenphosphate (Tedia), anhydrous disodium hydrogen phosphate (Merck) and pyrene (Merck) were also used as received. All the solvents used in this study were purified by standard methods.

Methods

Synthesis and characterization

Synthesis of poly(dimethylsiloxane–methylhydrogensiloxane) copolymer Siloxanes DC1107 (120.0 g), D4 (70.0 g) and DC200 (10.0 g) were placed in a 500-ml four-necked reactor fitted with a stirrer and a nitrogen gas inlet. After raising the temperature to 45 °C, concentrated sulfuric acid (10.0 g) was added and the reaction mixture was stirred under nitrogen for 48 h. Sodium hydrogen carbonate was then added to neutralize the acid in the reaction mixture. The solid was separated by centrifugation to obtain a viscous transparent liquid product, poly(dimethylsiloxane–methylhydrogensiloxane) (SH) copolymer. The yield was determined as 96%.

Synthesis of poly(dimethylsiloxane–(methyl(3-(glycidoxyl) propyl)-siloxane) copolymer SH copolymer was charged into a 500-ml flask with an excess of AGE (1.05 Eq Si–H) and 250 g toluene. After raising the temperature to 75 °C, 1 wt% Pt catalyst was added to the flask along with a low stream of nitrogen and the mixture was stirred until the absorption peak of the Si–H (around 2165 cm^{-1}) in the Fourier transform (FT)-IR spectra disappeared. The excess AGE and the solvent were then removed under reduced pressure. The product was a viscous pale-yellow liquid. The yield was 98%.

Synthesis of SHE Into a 500-ml flask, poly(dimethylsiloxane-(methyl(3-(glycidoxyl)propyl)siloxane) (SG) copolymer (50.0 g), diethanolamine (26.3 g) and ethanol (350 ml) were added sequentially. The reaction was carried out at 70 °C for 10 h. The solvent was removed under reduced pressure. The reaction mixture was dissolved again in about 250 ml chloroform to extract the excess of diethanolamine using deionized water several times. After removing the chloroform, the residue was dissolved in anhydrous ethanol and was dried by addition of anhydrous magnesium sulfate. The solvent was then distilled off under reduced pressure to obtain the SHE copolymer. Finally, the product was dried at 60 °C for 48 h in a vacuum oven. The yield was 87%.

Synthesis of SQHE Into a 250-ml flask, SHE copolymer (20.7 g) and methanol (120 ml) were charged and the solution was stirred at room temperature. A mixture of dimethyl sulfate (14.2 g) and methanol (30 ml) was added dropwise over a period of 2 h. After completion of the addition, the mixture was stirred for 8 h. After removing the solvent, the residue was then purified by reprecipitation with methanol/diethyl ether several times. The SQHE copolymer was then dried at 60 °C under vacuum for 48 h. The yield was 82%.

Synthesis of SQE SG copolymer (20 g), triethylamine (11.2 g) and ethanol (150 ml) were charged in a 250-ml flask. The solution was then heated to 60 °C for 8 h with continuous stirring. The solvent and unreacted triethylamine were evaporated under reduced pressure to obtain the SQE copolymer as a residue. The product was then dried at 60 °C for 48 h under vacuum. The yield was 90%.

Characterization of silicone surfactants

All the copolymers were dissolved in D_2O or $CDCl_3$ and were characterized by ^1H NMR and ^{13}C NMR spectra (Bruker AMX-400). The number-average molecular weight of the SG copolymer was determined by gel permeation chromatography (GPC) [Waters 510 high-pressure liquid chromatography (HPLC) pump with a Waters 410 differential refractometer]. Two GPC columns (TSK-GEL G5000-HXL, G3000-HXL: 7.8-mm inner diameter × 30 cm, Tosoh) were combined in series for the measurements. Polystyrene and tetrahydrofuran (HPLC grade) were used as standard and mobile phases (flow rate: 1 ml/min) respectively.

Fluorescence measurements

All fluorescence measurements were conducted by using a fluorescence spectrophotometer (model F-4010, Hitachi, Japan). The intensity ratio of the emission spectrum of pyrene at 374 and 385 nm, which is defined as I_1/I_3, was measured as a function of concentration. All the solutions for the fluorescence measurements were put in a buffer solution to maintain the pH at 7. For reference, I_1/I_3 values for pyrene in water and *n*-hexane were measured to be 1.86 and 0.58, respectively.

Surface tension measurements

The surface tension values were measured by using a commercial ring tensiometer (model TE1C, Lauda, Germany) as a function of concentration and the equilibrium surface tensions were then obtained from the long-time asymptotes at 25 °C.

Results and discussion

Synthesis and characterization

The syntheses of silicone surfactants with hydrophiles containing SHE, SQHE or SQE the preparation of polysiloxane copolymers, SH, containing about 60 mol% of hydrogensilane units. This step involves the acid-catalyzed equilibration of D_4 and linear DC1107 with DC200 as a chain-end terminator. The SH copolymer was then converted into epoxysiloxanes by a hydrosilylation reaction using a Pt catalyst as shown in Eq. (2). The completion of the hydrosilylation reaction was monitored by observing the disappearance of the absorption peak at 2160 cm^{-1} (Si–H stretching) in the FT-IR spectrum and the Si–H resonance ($\delta = 4.7$ ppm) in the ^1H NMR spectrum, and the concomitant disappearance of proton resonance peaks of the allyl group of AGE at $\delta = 5.5$ and 6.0 ppm. In the ^{1}H NMR spectrum of the SG copolymer (Fig. 1), the resonance peaks at $\delta = 0.5$, 1.5 and 3.4 ppm represent the protons of the newly formed silylpropyl group, and the peaks at $\delta = 2.5$, 2.7 and 3.1 ppm correspond to the protons of the epoxide group. These results clearly demonstrate the successful hydosilylation reaction.

The number-average molecular weight (M_n, determined by GPC) of the SG copolymer is 6800 g/mol, as shown in Table 1. From the definition of epoxy equivalent weight (EEW), the weight of an epoxy compound containing 1 mol epoxy group, the ratio of the number of dimethylsiloxane units to that of epoxysiloxane units (m:n) can be calculated from the following equations:

$$n = \frac{M_n \text{ of SG}}{\text{EEW of SG}} ,$$

$$m = \frac{M_n - (n \times 158)}{74} ,$$

where 158 and 74 are the unit weights of dimethylsiloxane and epoxysiloxane, respectively. Thus, the mole percent of epoxy content ($n/m + n \times 100\%$) for the SG copolymer is 64.7%.

The silicone surfactants were then prepared by a ring-opening reaction of the epoxide groups in the SG copolymer with diethanol amine and trimethylamine to give SHE (nonionic surfactant with two hydroxyethyl group) and SQE (cationic surfactant with three ethyl groups). SQHE (cationic surfactant with two hydroxyethyl groups and a methyl group) was obtained by reacting SHE with dimethyl sulfoxide. Representative ^{1}H NMR and ^{13}C NMR spectra of SHE are shown in Fig. 2a and b, respectively. The peaks at $\delta = 2.7$ and 3.7 ppm in Fig. 2a correspond to the protons of the newly formed hydroxyethyl groups and to the methylene protons connected to nitrogen, respectively. The peak at $\delta = 3.9$ ppm corresponds to the methine proton next to the hydroxyl group which is formed by the ring-opening reaction of the epoxide ring in the SG copolymer, and at the same time the resonance peaks of the protons at the epoxide ring disappear. In the ^{13}C NMR spectrum of SHE (Fig. 2b), the resonance peaks at $\delta = 56.5$ and 59.2 ppm are attributed to the carbons on the hydroxyethyl groups and the peak at $\delta = 58.1$ ppm is attributed to the methylene carbon bonded to nitrogen. The peak at $\delta = 67.7$ ppm corresponds to the methane carbon neighboring the hydroxyl group. The detailed peak assignments of the ^{1}H NMR and ^{13}C NMR spectra of these silicone surfactants are listed in Table 2. These characteristic spectral data evidently demonstrate the successful syntheses of the desired silicone surfactants (SHE, SQHE and SQE).

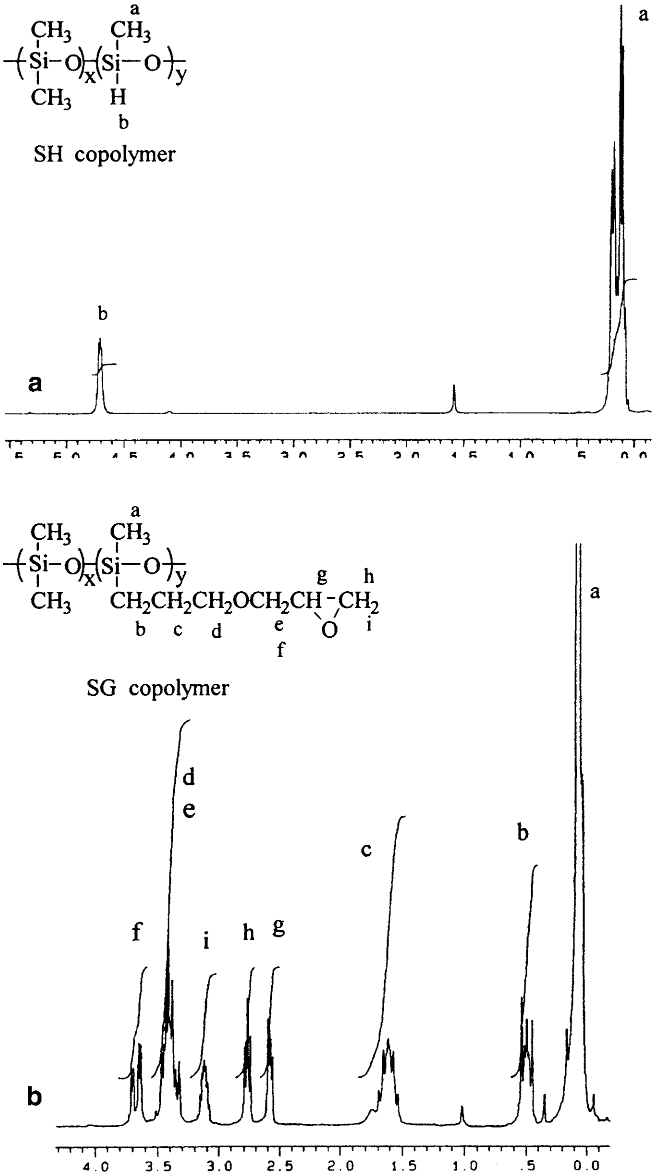

Fig. 1 ^{1}H NMR spectra of **a** poly(dimethylsiloxane-methylhydrogensiloxane) (*SH*) copolymer and **b** the corresponding poly(dimethylsiloxane–(methyl(3-(glycidoxyl)propyl)siloxane) (*SG*) polymer

Table 1 Description of poly(dimethylsiloxane-(methyl(3-(glycidoxyl)propyl)siloxane) (*SG*) copolymer. The average molecular weight was measured by gel permeation chromatography analysis. The epoxy equivalent weight was determined by the method described in our previous study [13]

Sample	$\overline{M_n}\left(\text{g/mol}^{-1}\right)$	Epoxy equivalent weight	Mole percent of epoxy content
SG copolymer	6800	208	64.7

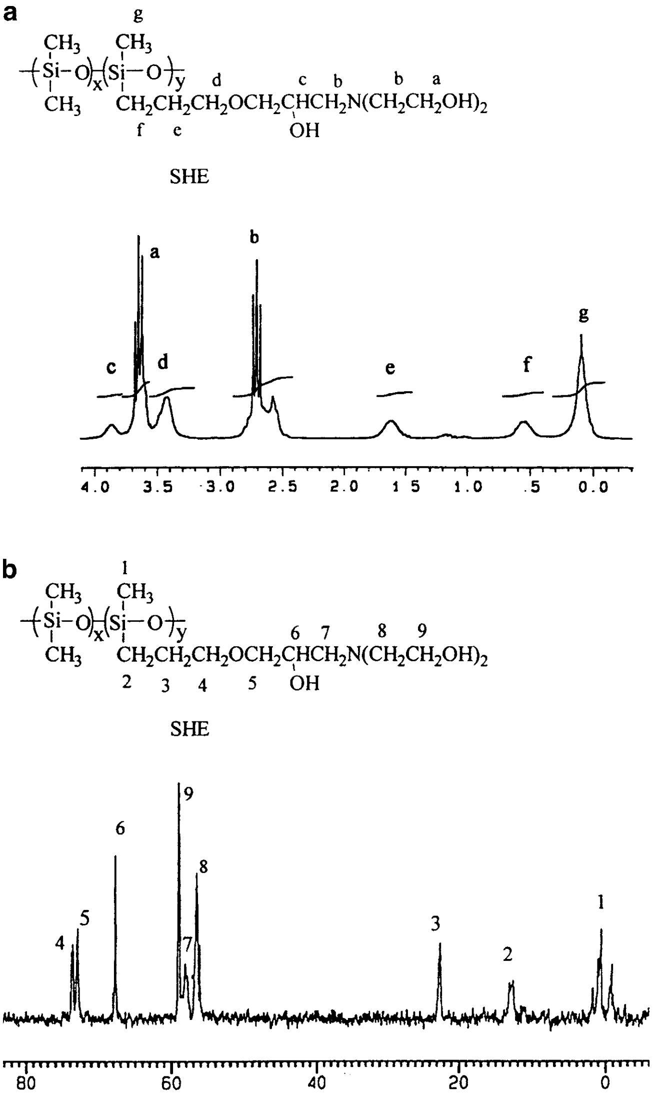

Fig. 2 **a** ^{1}H NMR spectrum of the diethanol tertiary amine (*SHE*) copolymer and **b** ^{13}C NMR spectrum of the SHE copolymer

Solution behavior of silicone surfactants

To determine the solution behavior of the silicone surfactants the dynamic surface tension and the I_1/I_3 values were measured for aqueous solutions of SQE, SHE and SQHE. The efficient reduction of surface tension as a function of time with addition of SQE, SHE and SQHE at very low concentration (1×10^{-4} wt%) is shown in Fig. 3. The phenomenon is very different from that observed for usual surfactants, for which the surface tension reaches a constant value within a few seconds. Since surface tension is inversely proportional to the surface excess concentration at the air–water interface, the continual decreasing of the surface tension of silicone surfactants means the continual increasing surface excess concentrations of those polymer solutions. Thus, it takes a longer time for the silicone

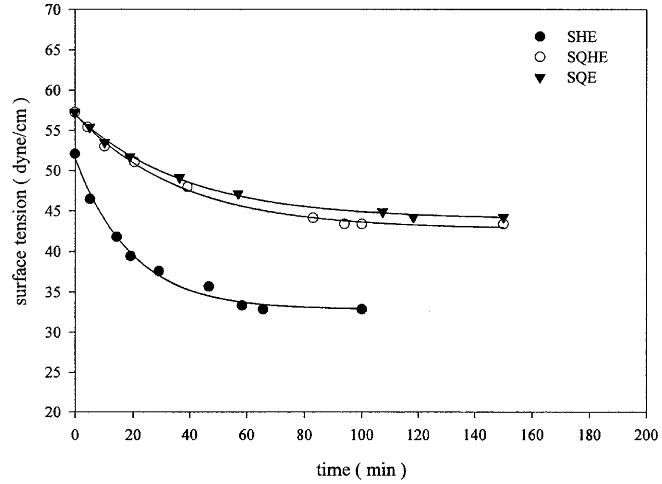

Fig. 3 Plot of surface tension versus time for aqueous solutions of SHE, diethanol methyl quaternary amine (*SQHE*) and triethyl quaternary amine (*SQE*) at a concentration of 1×10^{-4} wt%

Table 2 Peak assignments of ^{1}H NMR and ^{13}C NMR spectra for silicone surfactants: diethanol tertiary amine (*SHE*), triethyl quaternary amine (*SQE*) and diethanol methyl quaternary amine (*SQHE*)

Silicone surfactants	^{1}H NMR δ (ppm)	^{13}C NMR δ (ppm)
SHE	0.1–0.3(–Si–C$\underline{H}_3$), 0.4–0.8(–Si–C$\underline{H}_2$–), 1.4–1.8(–Si–CH$_2$C$\underline{H}_2$–), 2.4–2.8(–C$\underline{H}_2$N–), 3.3–3.6(–C$\underline{H}_2$–O–C$\underline{H}_2$–), 3.6–3.8(–NCH$_2$C$\underline{H}_2$OH), 3.8–3.9(–C$\underline{H}$(OH)-CH$_2$N)	0.1–0.3(–Si–$\underline{C}$H$_3$), 13.0(–Si-$\underline{C}$H$_2$–), 21.2(–Si–CH$_2\underline{C}$H$_2$–), 56.7(–N($\underline{C}$H$_2$–CH$_2$OH)$_2$), 57.4(–$\underline{C}$H$_2$N–), 58.7(–N(CH$_2$–$\underline{C}$H$_2$OH)$_2$), 66.8(–$\underline{C}$H(OH)–CH$_2$N), 72.3(–$\underline{C}$H$_2$–O–CH$_2$–), 73.5(–CH$_2$–O–$\underline{C}$H$_2$–),
SQE	0.1–0.3(–Si–C$\underline{H}_3$), 0.4–0.8(–Si–C$\underline{H}_2$–), 1.0–1.1(–N$^+$(CH$_2$C$\underline{H}_3$)$_3$), 1.4–1.8(–Si–CH$_2$C$\underline{H}_2$–), 3.0–3.2(–C$\underline{H}_2$N$^+$), 3.0–3.2(–N$^+$(C$\underline{H}_2$CH$_3$)$_3$), 3.3–3.5(–C$\underline{H}_2$–O–C$\underline{H}_2$–), 3.8–3.9(–C$\underline{H}$(OH)–CH$_2$N$^+$)	0.7(–Si–$\underline{C}$H$_3$), 9.4(–N$^+$(CH$_2\underline{C}$H$_3$)$_3$), 14.2(–Si–$\underline{C}$H$_2$–), 24.5(–Si–CH$_2\underline{C}$H$_2$–), 51.5(–N$^+$($\underline{C}$H$_2$CH$_3$)$_3$), 56.3(–$\underline{C}$H$_2$N$^+$), 66.7(–$\underline{C}$H(OH)–CH$_2$N$^+$), 74.2(–$\underline{C}$H$_2$–O–CH$_2$–), 76.3(–CH$_2$–O–$\underline{C}$H$_2$–)
SQHE	0.1–0.2(–Si–C$\underline{H}_3$), 0.4–0.6(–Si–C$\underline{H}_2$–), 1.5–1.7(–Si–CH$_2$C$\underline{H}_2$–), 2.9–3.2 (–N$^+$C$\underline{H}_3$), 3.2–3.4(–C$\underline{H}_2$N$^+$), 3.5–3.7(–C$\underline{H}_2$–O–C$\underline{H}_2$–), 3.7–4.0 (–N$^+$CH$_2$C$\underline{H}_2$OH), 4.0–4.1(–C$\underline{H}$(OH)–CH$_2$N$^+$)	−0.1(–Si–$\underline{C}$H$_3$), 14.6(–Si–$\underline{C}$H$_2$–), 24.5(–Si–CH$_2\underline{C}$H$_2$–), 57.8(–N$^+$($\underline{C}$H$_2$CH$_2$OH)$_2$), 58.7(–$\underline{C}$H$_2$N$^+$), 62.8 (–N$^+$CH$_2\underline{C}$H$_2$OH), 66.6(–$\underline{C}$H(OH)–CH$_2$N$^+$), 74.6(–$\underline{C}$H$_2$–O–CH$_2$–), 76.5(–CH$_2$–O–$\underline{C}$H$_2$–)

surfactant to reach equilibrium at the air–water interface at this lower concentration.

Moreover, it is amazing to find that the time-dependant surface tension plots of these silicone surfactants can be fitted very well with the following three-parameter exponential decay equation:

$$\gamma = \gamma_o + A\exp(-t/k), \qquad (1)$$

where γ_o, k and A are the fitting constant of the plots, and their values are summarized in Table 3.

From the exponential decay relationship between surface tension and time, it can be concluded that the constant k in Eq. (1) is a translation time constant, which can be used as a criterion of the rate of the silicone surfactant to move to the air–water interface. The lower the value of k, the faster the silicone surfactant moves to the air–water interface. Additionally, the constant γ_o can be treated as the initial surface tension of silicone surfactant that moves to the air–water interface very fast at nearly $t = 0$. The constant A is a characteristic constant for various surfactants. Therefore, from Table 3, the order of the values of γ_o has been found to be SQE ≈ SQHE > SHE, indicating that at the initial condition, the surface concentration of SHE is higher than that of SQHE and SQE. The order of the values of k is also the same as that of γ_o (SQE ≈ SQHE > SHE); this means that the transfer rate for SHE molecules from the bulk solution to the air–water interface is faster than for SQHE and SQE. These results are consistent with the chemical structures of the silicone surfactants, where SHE (nonionic) is more hydrophobic than the other two (cationic).

The equilibrium surface tensions (γ_{eq}) of SHE, SQE and SQHE reach values of 25.2, 26 and 36.6 dynes/cm, respectively, at 1 wt% (Table 4). Comparing the values of γ_{eq} with regular water-soluble polymers, EPE0.8 ($\gamma = 47$ dynes/cm) or a typical surfactant, sodium dodecyl sulfate (SDS, $\gamma = 39$ dynes/cm), it has been observed that the surface tensions of aqueous SHE, SQE and SQHE solutions are very low. That means that SHE, SQE and SQHE can efficiently reduce the cohesion of the water molecules at the air–water interface compared to conventional water-soluble polymers or surfactants.

The intensity ratio (I_1/I_3) of the emission of pyrene at 374 and 385 nm is proportional to the micropolarity of the surroundings of pyrene. The greater the I_1/I_3 value, the greater the micropolarity of the solution around pyrene, for example, $I_1/I_3 = 1.86$ for water ($\varepsilon = 80$) and 0.58 for n-hexane ($\varepsilon = 3$). A plot of I_1/I_3 as a function of concentration can therefore be used to detect the formation of micelles of surfactants or aggregates of polymers [16–20]. Also, the value of I_1/I_3 can be used to monitor the micropolarity of the hydrophobic inner core of polymer aggregates.

Table 3 Fitting constants for the time-dependant surface tension plots of silicone surfactants according to Eq. (1)

Sample	k	γ_o	A
SHE	19.4	32.8	18.8
SQHE	36.0	42.7	14.5
SQE	37.9	44.0	13.0

Table 4 Surface tension (γ_{eq}), aggregate-forming concentration (*AFC*) at which polymer aggregates start to form and I_1/I_3 for SHE60, SQE60, SQHE60, poly(ethylene oxide–propylene oxide) block copolymer (*EPE0.8*), sodium dodecyl sulfate (*SDS*), cetyltrimethylammonium bromide (*CTAB*) and poly(ethylene glycol *n*-nonyl phenyl ethers) (C_9PhE_{10})

Sample	γ_{eq} (dyne/cm) 1 wt%	AFC 1×10^{-3} wt%	I_1/I_3[a] 1 wt%	Reference
SHE60	26.7	50	1.06	–
SQE60	25.2	5	1.30	–
SQHE60	36.6	50	1.53	–
EPE0.8	47.0	2	1.53	[14]
SDS	39	–	1.22	[15]
CTAB	37	–	1.40	[16]
C_9PhE_{10}	34	–	1.41	[15]

[a] I_1/I_3 value obtained at 1 wt%

In Fig. 4, the I_1/I_3 values of pyrene in polymer solutions of SQHE, SQE and SHE are shown as a function of polymer concentration. When the polymer concentrations are below 5×10^{-4} wt%, the I_1/I_3 values remain at 1.9, which is close to that of pure water, indicating no aggregate formation at these concentra-

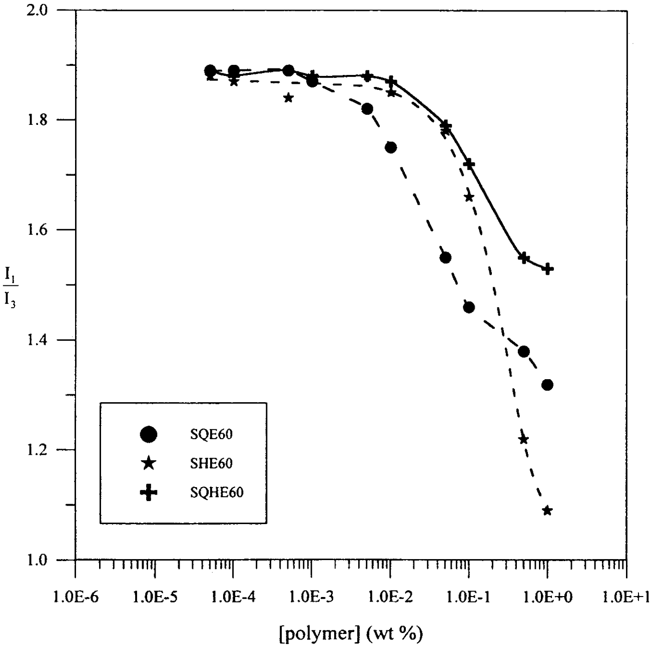

Fig. 4 Plot of I_1/I_3 versus the polymer concentration for aqueous solutions of SHE, SQHE and SQE

tions. In the region of 5×10^{-3}–1 wt%, the I_1/I_3 values decrease gradually with increasing polymer concentration. The decrease in I_1/I_3 indicates that the micropolarity in the polymer aggregates becomes less accompanied by the closer packing of the inner core. This demonstrates the phenomenon of forming polymer aggregates. The concentrations at which polymer aggregates start to form (AFC) are 5×10^{-3}, 5×10^{-2} and 5×10^{-2} wt% for SQE, SHE and SQHE, respectively.

The I_1/I_3 values for SHE, SQE and SQHE at 1 wt% concentration are 1.06, 1.30 and 1.53, respectively, and are much lower than that of water ($I_1/I_3 = 1.86$), as shown in Table 4. The low values of I_1/I_3 of these silicone copolymers strongly indicate the existence of polymer aggregates in aqueous solution. These values are also remarkably less than that of EPE ($I_1/I_3 = 1.53$). It means that aggregates of the silicone copolymers have significantly higher hydrophobicity in the inner core of the polymer aggregates compared to that of regular water-soluble polymer EPE. The aggregates formed by polymer surfactants are always less closely packed than the micelle of conventional surfactants monitored by I_1/I_3 values, indicating that the inner core of the former is less hydrophobic than that of the later [15, 16]. However, the I_1/I_3 value of SHE is even lower than that of the regular nonionic surfactant poly(ethylene glycol *n*-nonyl phenyl ethers) ($I_1/I_3 = 1.41$), cationic surfactant cetyltrimethylammonium bromide ($I_1/I_3 = 1.40$) and anionic surfactant SDS ($I_1/I_3 = 1.22$). This illustrates that the hydrophobicity of SHE is even stronger than that of usual surfactants; however, the I_1/I_3 values of SQHE and SQE are still higher than that of SDS.

It is interesting to observe that the order of the I_1/I_3 values (SHE < SQE < SQHE) is the same as that of γ_{eq} at 1 wt%. The smaller I_1/I_3 value for SHE due to its higher hydrophobicity in the inner core compared to SQE and SQHE indicates the aggregates of SHE to more shrunken and closely packed. The lower γ_{eq} of SHE means polymer chains of SHE are more closely packed at the air–water interface, resulting in a higher surface excess concentration. These two parallel results demonstrate well the correlation between γ_{eq} and the I_1/I_3 value and the consistency of the characteristic of silicone polymer chains at the air–water interface with that in the bulk phase.

Conclusions

A successful synthesis method of water-soluble silicone surfactants by ring opening of epoxypolysiloxanes (SG copolymer) with different aminio compounds has been established. Their behavior in solution leads to the conclusion that the surface tension decreases as a function of time and can be fitted very well with an exponential three-parameter (k, γ_o, A) decay function at low concentration (1×10^{-4} wt%). The order for k and γ_o has been found to be SQE $\approx$ SQHE > SHE, which implies that SHE is more hydrophobic than the other two. At higher polymer concentration (1 wt%), the γ_{eq} values of the silicone surfactants are very low compared to polymer surfactants or regular surfactants. Further, the plot of I_1/I_3 versus polymer concentrations and the resulting low I_1/I_3 values at 1 wt% show the formation of polymer aggregates. SHE has more excess concentration at the air–water interface and has more hydrophobic inner cores in the bulk phase.

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