Polyglycerol Modified Polysiloxane Surfactants :Their Adsorption and Aggregation Behavior in Aqueous Solution

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Abstract

A simple process to synthesize polyglycerol modified polysiloxane surfactants has been carried out applying a “grafting-to” approach. After formation of allyl polyglycerol ether (APGE) from diglycerol (DGY) and allyl glycidyl ether (AGE), polysiloxane modified by designed number of polyglycerol groups (PHMS-APGE) were obtained by connecting the APGE structure to different Si-H functionalized polyhydromethyl siloxane (PHMS). The synthesized APGE-PHMS were characterized by IR and ^1H NMR. Solubility measurements showed that the solubility of the as-prepared polymers increased in polar solvents with the increasing of the amount of hydrophilic APGE groups. Furthermore, the surface activity, surface adsorption, aggregation and spreading behaviors of APGE-PHMS were investigated utilizing surface tension measurements, dynamic light scattering (DLS), transmission electron microscopy (TEM) and contact angle measurements. The results showed that critical aggregation concentration (CAC) and the time needed to reach adsorption equilibrium on water surface decrease systematically with the increase in the number of APGE groups. These polymers in aqueous solutions could aggregate to form spherical assemblies. Moreover, the spreading behavior of these polymers on low energy surface was found to be influenced by the number of hydrophilic APGE groups.

Keywords: Polysiloxane; Polyglycerol; Adsorption behavior; Aggregation behavior

Graphic Abstract:

1 Introduction

Silicones have drawn people's attention for many years due to their unique properties. For instance they exhibit constant viscosity over a broad temperature range as well as an extremely high gas permeability and absolutely bio-inert. Thus, silicones are widely used in cosmetics, medicine, coatings, electronics and textiles, and so on[1]. Nevertheless, the hydrophobicity, which is the most significant feature of silicone, has always been a drawback for a great number of applications[2, 3]. Therefore, current attempts mostly focus on combination of silicones and hydrophilic materials in order to combine the unique silicone-specific properties with hydrophilicity. Stadler et al. focused on the attachment of various kinds of oligo- and polysaccharides[4-6]. Paul et al. synthesized hydrophilic silicone with glycerol side chains[2]. Further information on polymers combining silicone with various other hydrophilic groups, either in the form of random or block copolymers or with grafted[7], branched[8-10], star-shaped[11], or cross-linked[12-14] polymers, has been reported. Polyether modified polysiloxane is one of the most popular hydrophilic silicones. The specific properties of polyether modified polysiloxane have also been studied in a lot of publications[15-16]. However, the raw material of polyether may contain carcinogenic 1,4-dioxane, which is banned in some personal care products[17]. At the same time, the raw material for polyether, which depends on fossil fuels, is not sustainable.

Glycerol is water-soluble and renewable. Moreover, with the development of biodiesel, surplus glycerol has become an urgent issue. But little research has been

done on combination of silicone and hydrophilic polyglycerol. Here we report a two-step synthetic approach to graft polyglycerol groups to the polysiloxane backbone[18]. We further investigated their basic properties and application performances.

2 Experimental

2.1 Materials

Diglycerol (DGY, 81%) and allyl glycidyl ether (AGE, 99%) were purchased from TCI. Potassium hydroxide (KOH, 99%) was supplied by Tianjin Chemical Reagent Co., Ltd. (China). Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%) was provided by Nanjing Chemical Reagent Co., Ltd. (China). Isopropanol (IPA, 99.8%) and sulfuric acid (H_2SO_4 , 98%) were purchased from Beijing chemical Reagent Co., Ltd. (China). Other reagents, i.e., including octamethyl cyclotetrasiloxane (D_4), poly(methylhydrosiloxane) (Mw 3792) and hexamethyldisiloxane (MM) were of technical grade and obtained from Zhejiang Runhe Organosilicon New Material Co., Ltd. (China). Double distilled water was used for analyses and property measurements. All commercially available chemicals were used as received without any further purification.

2.2 Synthesis of Polyglycerol-modified Polysiloxane (APGE-PHMS)

2.2.1 Synthesis of Allyl Polyglycerol Ether (APGE) and Polyhydromethyl Siloxane (PHMS)

Under N_2 , 19.94 g (0.12 mol) of diglycerol was reacted with 11.42 g (0.10 mol) of allyl glycidyl ether in the presence of potassium hydroxide as catalyst and the mixture was stirred for 3 h at a reflux temperature of 90°C . Then the product was

neutralized by adding 5.00 g of cation exchange resin and stirring for further 20 minutes, followed by filtration at 70°C. The volatile matters in the filtrate were removed by stripping for 2 h at 60°C under a pressure of 5 mmHg. A light yellow liquid product (APGE) was obtained in 95% yield.

Polyhydromethyl siloxane (PHMS) were prepared with D₄, poly(methylhydrosiloxane) (Mw 3792) and hexamethyldisiloxane (MM) catalyzed by sulfuric acid. The method has already been reported in literature [18]. Thus, PHMS with 2, 4, 5, 6 and 8 Si–H bonds according to feed composition were obtained in 90% yield (Table 1).

Table 1 Composition of PHMS and their molecular weights

Sample number	Feed composition		Expected Mn (g/mol)	Composition (²⁹ Si-NMR)		M _n based on ²⁹ Si-NMR spectra (g/mol)
	m	n		m	n	
1	8	2	874	8.38	1.49	872
2	6	4	846	5.76	3.15	777
3	5	5	832	4.82	4.10	765
4	4	6	818	4.24	6.25	851
5	2	8	790	1.70	7.83	758

2.2.2 Synthesis of Polyglycerol-modified Polysiloxane (APGE-PHMS)

Polyglycerol-modified polysiloxane (APGE-PHMS) were synthesized by the hydrosilylation reaction from APGE and PHMS with different Si-H groups. Five sets of APGE-PHMS systems were synthesized and the number of APGE contents was

1 expected to be 2, 4, 5, 6 and 8 respectively. For example, APGE(5)-PHMS was
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3 synthesized as follow. In a 250 ml three-necked round bottom flask, 26.2 g (0.08 mol)
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5 APGE together with 14.9 g (0.08 mol, referring to the amount of Si-H-groups) PHMS
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7 (m=5, n=5) were dissolved in isopropanol. The mixture was heated to reflux under
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9 nitrogen atmosphere. The reaction was catalyzed by chloroplatinic acid. After 6 hours,
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11 IR spectra showed complete disappearance of the Si-H bond. After completion of the
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13 reaction, the product was stripped at 60°C under a pressure of 5 mmHg to remove the
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15 volatile matters. A light yellow liquid product (APGE-PHMS) was obtained in 90%
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2.3 Characterization of structures

FT-IR spectra were measured using a Bruker V70 Fourier transform spectrometer (Germany) with a KBr plate. ¹H NMR and ²⁹Si MNR spectras were conducted with Bruker-400 MHz spectroscopy (Germany) at room temperature.

2.4 Measurement of solubility

Solubility was measured by dissolving APGE-PHMS directly in different solvents of various polarities at a concentration of 100 mg/mL at room temperature. There is no recognized standard to judge the polarity of solvent. We usually determine the polarity of the solvent according to the solvent dielectric constant. Thus, we choose seven solvents (isooctane, ether, methylene chloride, isopropanol, acetonitrile, dimethylsulfoxide, water) covering dielectric constant from 2 to 80 to carry out the experiment.

2.5 Measurement of equilibrium surface tension

The equilibrium surface tension of APGE-PHMS solutions was measured using a Krüss K12 Processor Tensiometer (Germany) and determined by the Wilhelmy plate method. The APGE-PHMS solutions were prepared by direct dissolution of APGE-PHMS in double distilled water. The length and thickness of the platinum plate were 19.9 mm and 0.2 mm, respectively. The dipping distance was 2 mm. The surface tension of the double distilled water was confirmed as being in the range of 72.0 ± 0.3 mN/m at 25.0 ± 0.1 °C, prior to measurements. The surface tension of each concentration was measured three times with an average deviation less than 0.2 mN/m at intervals of 90 s after stirring.

2.6 Measurement of dynamic surface tension

The dynamic surface tension was measured by a Krüss BP100 bubble-pressure Tensiometer (Germany). The solutions were also prepared by dissolving APGE-PHMS directly in double distilled water. This measurement was conducted with effective surface ages ranging from 10 to 200,000 ms.

2.7 Measurement of aggregation behavior

The aggregation behavior of APGE-PHMS solutions was monitored by dynamic light scattering (DLS) with a Zeta Plus Particle Size Analyzer (Brookhaven, USA) and the scattering angle was set at 90°. All of the solutions were filtered with a 0.45 μm (mixed cellulose acetate) membrane filter.

The structures of APGE-PHMS aggregates in solutions were also observed with a JEM-1011 (JEOL Co., Japan) transmission electron microscopy (TEM) by negative

1 staining. A droplet of the surfactant solution was added onto a carbon-coated grid and
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3 allowed to equilibrate for 2 min. The removal of excess liquid was performed by
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5 blotting carefully with a filter paper. When the grid was partially dried, a drop of
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7 staining solution (2% phosphotungstic acid) was added onto the grid. Again, the
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9 removal of excess liquid was performed after 2 min, and the grid was dried at room
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11 temperature.
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16 **2.8 Measurement of spreading ability**

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18 The spreading ability of prepared surfactant solutions over hydrophobic
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20 substrates was measured using drop shape analyzer DAS-100 (Krüss Company,
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22 Germany). Paraffin film was chosen as solid substrates showing different solid–air
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24 interfacial energies in terms of contact angles for water ($106 \pm 2^\circ$) on paraffin. The
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26 hydrophobic film was placed on an aclinic stage in front of a microscope, which was
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28 connected to a CCD camera. To ensure minimal relative error, every measurement
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30 was repeated at least three times. The contact angles were the mean values obtained in
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32 each experiment.
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42 **3 Results and discussion**

43 **3.1 Synthesis of polyglycerol-modified polysiloxane (APGE-PHMS)**

44
45 Polyglycerol-modified polysiloxane were synthesized via the hydrosilylation
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47 reaction which grafts polyglycerol groups to the polysiloxane backbone. The synthesis
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49 included a two-step method as shown in Scheme 1. The first step was to produce the
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51 polyglycerol containing end group structure of C=C and polysiloxane containing
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53 designed number of Si–H bonds. In this simple procedure, allyl polyglycerol ether
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was obtained, in which the C=C bond could be attached to PHMS with Si-H bond. In the second step, five sets of polyglycerol-modified polysiloxane were prepared using APGE and polysiloxane with designed Si-H contents, which was catalyzed by chloroplatinic acid[18].

Scheme 1. Synthetic route of APGE-PHMS

^1H NMR spectra of APGE shows complete disappearance of the typical peak of epoxy group at 2.3-3.1 ppm and the double bond signals of allyl glycidyl ether at 5.2-5.9 ppm appear, confirming the complete reaction of epoxy ring opening (seen in Fig.1). The result of ^1H NMR suggested that APGE was obtained successfully.

Fig.1 ^1H -NMR spectra of (1) DGY, (2) AGE and (3) APGE

Meanwhile, the ^{29}Si -NMR spectrum for PHMS ($m=5$, $n=5$) is shown in Fig.2 as an example. ^{29}Si -NMR spectrum confirmed that the five sets of PHMS (Table 1) were basically synthesized as expected. Three typical signals were observed. The characteristic peak of $\text{Si}(\text{CH}_3)_3$ could be found at 9.0 ppm. The peak at -37.5 ppm is corresponding to $\text{Si}-\text{H}$. Meanwhile, the peak of $\text{Si}(\text{CH}_3)_2$ is observed at -20.0 ppm[20].

Fig.2 ^{29}Si -NMR spectra of PHMS

The final products APGE-PHMS were characterized by FT-IR and ^1H -NMR. FT-IR and ^1H -NMR spectra of APGE(5)-PHMS is shown in Fig. 3 for example. The reaction process was monitored by IR spectroscopy (Fig.3), from which the gradual

disappearance of the peak of Si-H bond at about 2155 cm^{-1} could be observed [20]. Complete conversion could easily be confirmed by ^1H NMR spectroscopy (Fig.4), where the characteristic absorption of neither Si-H at 4.8 ppm nor C=C of APGE at 5.2-5.9 ppm could be found in the spectroscopy. Meanwhile, a peak at about 0.5 ppm corresponding to Si-CH₂ arose, which also suggested the termination of hydrosilylation reaction [2]. Both the analysis of FT-IR and ^1H -NMR confirm that APGE-PHMS were successfully obtained.

Fig.3 Overlapped FT-IR spectra of (1) APGE, (2) PHMS and (3) APGE-PHMS

Fig.4 ¹H-NMR spectra of (1) PHMS, (2) APGE and (3) APGE-PHMS

3.2 Solubility

The most prominent feature of polysiloxane is their hydrophobicity. Because of the shielding effect of the organic moieties connected to silicone, polysiloxane present insolubility in water or polar organic solvents. Grafting polar groups of APGE to the polysiloxane molecular chains could change polarity and consequently improve solubility in polar solvents. So we take the method of dissolving APGE-PHMS in different solvents of various polarities to quantify their hydrophobicity. The number of APGE groups per mole APGE-PHMS can be used as horizontal ordinate.

Fig.5 shows the result of the experiment of solubility. As we can see, unlike polysiloxane, APGE-PHMS are soluble not only in nonpolar solvents but also polar solvents. The structure of APGE-PHMS can be described as brush-like, with the grafts forming the hydrophilic bristles of the brush.[2] These bristles are able to increase the hydrophilicity of polymer backbone, forming a hydrophilic surface of APGE-PHMS. The density of this hydrophilic surface depends on the number of APGE groups in the polymer. So the more number of APGE groups leads to an increasing solubility in polar solvents. Therefore, APGE-PHMS of various solubilities can specifically be designed.

Fig.5 The solubility of the five sets of APGE-PHMS in various solvents of different polarity

3.3 Surface Activity

The equilibrium surface tension is the most common way to evaluate the surface activity of surfactants. The surface tension of APGE(2)-PHMS was not measured because of its poor solubility in water at room temperature. In the following research, system 1 was not tested for the same reason. Inspection of the data in Fig. 6 shows that APGE-PHMS reduce the surface tension of water at low concentration, indicating that these APGE-PHMS molecules adsorb strongly at the air/water surface and they are highly effective surfactants. The critical aggregation concentration (CAC) and the surface tension at CAC (γ_{CAC}) were also obtained from the breakpoint of equilibrium surface tension-concentration curve. The values of CAC and γ_{CAC} of the four sets were summarized in Table 2. One may discover that the four polymers show two breakpoints in their surface tension curves. The result is in agreement with other siloxane surfactants. This may be attributed to the formation of pre-micellar aggregations before true micelles are formed. Meanwhile, the APGE-PHMS could

reduce the surface tension of water to 21 mN/m approximately, which is lower than ordinary hydrocarbon surfactants. The reason of this consequence may be that the methyl groups in polysiloxanes backbone packing at the air/solution interface have an intrinsically lower surface energy than methylene groups of ordinary hydrocarbon surfactants. On the other hand, with an increase in the number of APGE groups in the molecules, the CAC decreases gradually, which is not consistent with the result of other surfactants. Similar observation was shown by Han Fu[22]. The result indicates that CAC may be affected not only by the number, but also by the position of APGE in the molecule.

Fig.6 Equilibrium surface tension with concentration for APGE-PHMS at 298K: ■, APGE(4)-PHMS ●, APGE(5)-PHMS ▲, APGE(6)-PHMS ▼, APGE(8)-PHMS

At equilibrium, by calculating the surface excess concentration Γ_{CAC} , the area/molecule A_{CAC} , the adsorption efficiency Π_{CAC} , the standard free energy of aggregation ΔG_{mic}^0 and adsorption ΔG_{ads}^0 as estimated from five equations below (1-5), the packing characteristics of the groups at the interface can be inferred.

$$\Gamma_{CAC} = (-1/nRT)/(d\gamma/d\ln C) \quad (1)$$

$$A_{CAC} = 10^{16}/(N_A \Gamma_{CAC}) \quad (2)$$

$$\Delta G_{mic}^0 = nRT \ln(CAC/55.5) \quad (3)$$

$$\Delta G_{ads}^0 = nRT \ln(C_{II}/55.5) - 6.022 \Pi_{CAC} A_{CAC} \quad (4)$$

$$\Pi_{CAC} = \gamma_0 - \gamma_{CAC} \quad (5)$$

where, $n=2$, R is gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is absolute temperature in K , γ is surface tension in mN/m , C is concentration in mol/L , Γ_{CAC} is expressed in mol/m^2 obtained from the linear portion of the surface tension versus $\log C$ graph. Meanwhile, N_A is Avogadro's number, from the surface excess concentration, the area/molecule at the interface A_{CAC} is calculated, γ_0 is the surface tension of water, γ_{CAC} is the surface tension at CAC , C_{II} is the molar concentration of the surfactant in the aqueous phase at a surface pressure Π in mN/m .

The surface areas per molecule of the four systems are about $50 \text{ \AA}^2$, which agrees with the result of other silicone surfactants. In general, for both the known ionic and nonionic surfactants present, the value of the surface area per molecule appears to be determined by the area packed by the hydrated hydrophilic groups. Thus, it was expected that increasing the number of APGE will increase the area per molecule of the surfactant at the interface, but the result was not in agreement with our expectation. This may be due to that increasing the number of APGE could enhance intermolecular interactions and therefore expose polysiloxane chain more to water. Furthermore, exposing polysiloxane chain more to water may influence the formation of aggregates. This may just explain that the CAC decreases with an increase in the numbers of APGE groups. Meanwhile, as we can see, the standard free energy of micellization (ΔG_{mic}^0) and adsorption (ΔG_{ads}^0) are negative, showing the tendencies to form micelles

in solution and adsorb at the air/water interface. In this case, ΔG_{ads}^0 is more negative than the corresponding ΔG_{mic}^0 , indicating that adsorption is the predominant event as oppose to aggregation. However, the variation of standard free energy of micellization (ΔG_{mic}^0) and adsorption (ΔG_{ads}^0) along with the variation of APGE is not completely straightforward. This may be attributed to the complexity of their molecular structure.

Table 2 Parameters of aggregation and adsorption at the air/water interface of the APGE-PHMS at 25 °C

Sample	CAC (mol/L)	γ_{CAC} (mN/m)	$10^6 \Gamma_{\text{CAC}}$ (mol/m ²)	A_{CAC} (Å ²)	Π_{CAC} (mN/m)	ΔG_{mic}^0 (KJ/mol)	ΔG_{ads}^0 (KJ/mol)
APGE(4) -PHMS	7.41×10^{-5}	28.80	3.50	46.00	43.30	-67.03	-79.02
APGE(5) -PHMS	5.25×10^{-5}	25.73	2.84	56.62	46.37	-68.73	-84.54
APGE(6) -PHMS	4.07×10^{-5}	23.68	3.46	46.46	48.42	-70.00	-83.54
APGE(8) -PHMS	2.40×10^{-5}	21.76	3.36	47.78	50.34	-72.61	-87.09

3.4 Dynamic Adsorption Property

Dynamic surface tension measurements performed by the maximum bubble-pressure technique are well suited for researching the adsorption property of surfactant at the air/water interface. Fig.7 shows the curves of the surface tension as a function of the surface age for APGE-PHMS. Obviously, with increasing of the number of APGE, the final surface tension as well as the time required to reach adsorption equilibrium decrease regularly. The consequence is consistent with the

result of the equilibrium surface tension approximately. This suggests that APGE-PHMS with more APGE groups diffuse faster and absorb quicker at air/water interface from the interior of the solution. In general, the “motion ability” of diffusion and adsorption is caused by the hydrophobic chains. This may be also due to that increasing the number of APGE could improve intermolecular interactions and therefore the polysiloxane chain would be exposed more to water[23-24].

Fig.7 Variation in the dynamic surface tension as a function of surface age for APGE-PHMS (500mg/L) at 298K: ■, APGE(4)-PHMS ●, APGE(5)-PHMS ▲, APGE(6)-PHMS ▼, APGE(8)-PHMS

3.5 Aggregate Property

In order to visualize the morphology and size of the aggregates for APGE-PHMS solutions above CAC, negative-staining TEM and DLS measurements were carried out.

Spherical assemblies were exhibited in the negative-stained TEM images (Fig. 8). This consequence suggested the presence of aggregates of APGE-PHMS, the diameters of which ranged from 200 to 1000 nm. From the TEM result, one may find

that these aggregates are much larger in size than the small spherical micelles, which have diameters typically less than 10 nm. The formation of larger complex aggregates is due to the further aggregation of simple assemblies, which is induced by hydrogen bonding or van der Waals interactions among the hydrophilic shells[25-26].

Fig.8 Negative-stained TEM images of aggregates formed in APGE-PHMS (500mg/L): a, APGE(4)-PHMS b, APGE(5)-PHMS c, APGE(6)-PHMS d, APGE(8)-PHMS

In order to obtain bulk information on average aggregates size and further confirm the presence of aggregates, DLS was performed[22]. The DLS data of the four systems were shown in Fig.10a-d. Obviously, the size of aggregates observed by DLS was in consistent with the data obtained from TEM. One may discover that with an increase in number of hydrophilic APGE groups, the diameter decreases. This might be attributed to an improved difficulty in association of molecules which leads to the diameter decrease[27-29].

Fig.9 The intensity-weighted size distributions of APGE-PHMS (500mg/L): a, APGE(4)-PHMS b, APGE(5)-PHMS c, APGE(6)-PHMS d, APGE(8)-PHMS

3.6 Spreading Property

Contact angle is a widely adopted method to study the spreading ability of aqueous drops. The spreading ability of APGE-PHMS with different number of hydrophilic APGE groups was tested via contact angle as a function of time over hydrophobic substrate (paraffin films). It was found that the contact angle of APGE-PHMS with any number of APGE groups generally decreased gradually from an initial value (θ_0 , $t=0$), which was the contact angle of droplet while it just deposited on the substrate, to a certain equilibrium value (θ_{eq}). Fig. 10 shows that with increase in number of hydrophilic APGE groups, θ_0 and θ_{eq} decrease, which could be explained by the efficient adsorption kinetics of molecules on a liquid/air interface[30-32].

Fig.10 Evolution of dynamic contact angle of droplets of aqueous APGE-PHMS (500mg/L): ■, APGE(4)-PHMS ●, APGE(5)-PHMS ▲, APGE(6)-PHMS ▼, APGE(8)-PHMS

4 Conclusions

Polyglycerol-modified polysiloxane were synthesized via the hydrosilylation reaction by grafting polyglycerol groups to the polysiloxane backbone using a two-step method. A series of APGE-PHMS systems with 2, 4, 5, 6 and 8 APGE groups were obtained. Furthermore, solubility, surface activity, adsorption, aggregation and spreading properties of these products were investigated. Measurement on solubility of APGE-PHMS indicated a positive correlation between the number of hydrophilic groups (APGE) and the polarity of suitable solvents. Therefore, , polarity and thus solubility could be modulated by grafting different number of polar polyglycerol groups. Second, the equilibrium surface tension of APGE-PHMS could reach 21 mN/m, which agreed with other silicone surfactants. The system with more APGE groups possessed lower CAC, which might be due to the intermolecular interactions. Third, from dynamic surface tension experiments, we found that the time needed to reach adsorption equilibrium decreased systematically

with the increase in the hydrophilic groups. Forth, the aggregates of these polymers formed in aqueous solutions could be assigned as spherical assemblies from TEM and DLS analysis. Finally, it was found from contact angle measurements that systems with more APGE groups exhibited better spreading ability. Therefore, given their excellent performance, further investigation of APGE-PHMS will be done in the future work.

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