

Article

Wettability of a Polymethylmethacrylate Surface by Extended Anionic Surfactants: Effect of Branched Chains

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Abstract: The adsorption behaviors of extended anionic surfactants linear sodium dodecyl(polyoxyisopropene)₄ sulfate (L-C₁₂PO₄S), branched sodium dodecyl(polyoxyisopropene)₄ sulfate (G-C₁₂PO₄S), and branched sodium hexadecyl(polyoxyisopropene)₄ sulfate (G-C₁₆PO₄S) on polymethylmethacrylate (PMMA) surface have been studied. The effect of branched alkyl chain on the wettability of the PMMA surface has been explored. To obtain the adsorption parameters such as the adhesional tension and PMMA-solution interfacial tension, the surface tension and contact angles were measured. The experimental results demonstrate that the special properties of polyoxypropene (PO) groups improve the polar interactions and allow the extended surfactant molecules to gradually adsorb on the PMMA surface by polar heads. Therefore, the hydrophobic chains will point to water and the solid surface is modified to be hydrophobic. Besides, the adsorption amounts of the three extended anionic surfactants at the PMMA–liquid interface are all about 1/3 of those at the air–liquid interface before the critical micelle concentration (CMC). However, these extended surfactants will transform their original adsorption behavior after CMC. The surfactant molecules will interact with the PMMA surface with the hydrophilic heads towards water and are prone to form aggregations at the PMMA–liquid interface. Therefore, the PMMA surface will be more hydrophilic after CMC. In the three surfactants, the branched G-C₁₆PO₄S with two long alkyl chains exhibits the strongest hydrophobic modification capacity. The linear L-C₁₂PO₄S is more likely to densely adsorb at the PMMA–liquid interface than the branched surfactants, thus L-C₁₂PO₄S possesses the strongest hydrophilic modification ability and shows smaller contact angles on PMMA surface at high concentrations.

Keywords: extended anionic surfactant; branched chain; polymethylmethacrylate; contact angle; adsorption



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1. Introduction

Wetting phenomena on solid surfaces [1–3] have attracted considerable attention in the fields of adhesion, [4,5] oil exploitation, [6] flotation, [7] membrane distillation, [8] washing [9] and lubrication [10]. By adding surfactants, the wettability of solid surfaces can be regulated [11,12]. The surfactant molecules can adsorb onto the air–liquid interface and solid–liquid interface, thus changing the surface tension and the interfacial tension of solid–liquid, respectively [13,14]. Consequently, the contact angle is determined by the surface tension and the solid–liquid interfacial tension varies.

It is well known that polymethylmethacrylate (PMMA) is one of the most widely used acrylate plastics because of its excellent aging resistance and biocompatibility [15,16]. PMMA is a weakly polar polymer compound that contains -CH₃, -CO, and -OCH₃

groups [17]. Therefore, surfactants can interact with PMMA surfaces through a variety of adsorption methods. Numerous conventional surfactants' adsorption behaviors on the PMMA surface have been investigated and reported in the literature. Harkot et al. explored the adsorption behaviors of anionic surfactant (AOT) [18] and cationic surfactants (C_{12} (EDMAB), BDDAB) [19] on the PMMA surface. They found that the wettability of PMMA surfaces by the surfactants depends on the surfactants' concentration to a large extent. When these surfactants' concentration is around CMC, the contact angle and PMMA–solution interfacial tension reach the minimum value. As the surfactants' concentration continues to increase, the contact angle and interfacial tension change little. Zdziennicka et al. investigated the wettability of cationic surfactants (CTAB, CPyB), [20] nonionic surfactants (TX-100, TX-114) [21,22] and anionic surfactants (SDDS, SHS) [23] on the PMMA surface. It is found that the contact angles and the interfacial free energy of PMMA–liquid (γ_{SL}) of these conventional surfactants gradually decreased with the increase in surfactant concentration, which indicates that the surfactants will adsorb on PMMA surface by hydrophobic interactions. In recent years, research has been published about the adsorption behaviors of zwitterionic surfactants [24] and cationic gemini surfactants [25] on the PMMA surface. The group of Zhang discovered some surfactants with specific wetting properties because of the introduced polyoxyethylene (EO) units or branched hydrophobic chains in their structures [26–28]. These special surfactants will interact with the PMMA surface via polar groups at low concentration, resulting in a slightly hydrophobic PMMA surface. However, these surfactants will transform their original adsorption behavior to hydrophobic interactions after CMC, therefore γ_{SL} decreases with the increase in surfactant concentration.

The extended surfactant is a kind of novel surfactant, which contains a polyoxypropene (PO) chain inserted between the hydrophobic alkyl group and hydrophilic polar group [29]. Chen et al. [30,31] found that the extended surfactants' PO spacer results in an obvious rugby shape for the surfactant molecules at the air–liquid interface. This allows the extended surfactants to exhibit excellent interfacial properties for household cleaning. Owing to the polar and non-polar groups of extended surfactants, they may adsorb onto the PMMA surface through both polar interactions and hydrophobic interactions, resulting in a variety of modification behaviors on the PMMA surface by special structural extended surfactants.

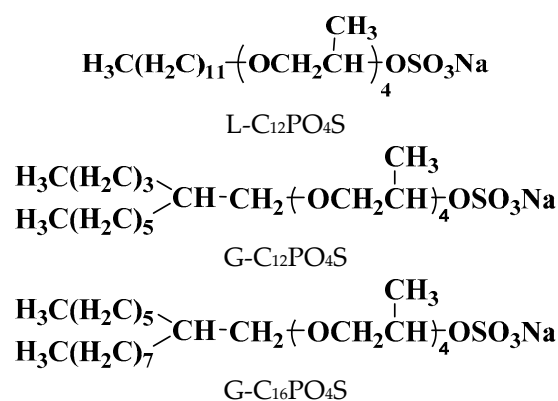
However, there are few reports involving the wettability of extended anionic surfactants on the PMMA surface. In particular, the effect of branched extended anionic surfactants on the wetting of the PMMA surface needs to be further explored. Wu et al. [28] explored the adsorption of branched betaine and cationic surfactants on the PMMA surface. It was reported that the branched C_{16} GPB, C_{16} GPC, and C_{16} G(EO)₃PC have a stronger hydrophilization capacity than similar surfactants with a linear structure. However, the branched structure inevitably increases the difficulty of forming aggregations; therefore, the adsorption amounts of branched C_{16} G(EO)₃PB on the PMMA surface are lower than the linear C_{16} (EO)₃PB. Zhang et al. [24] utilized two branched betaines (BCB, BSB) to detect their wettability properties on the PMMA surface. In their study, branched benzyl at hydrophobic chain of BCB improves the surfactants' molecular size, resulting in an increase in the turning concentration for the adsorption behavior. Gao et al. [25] investigated the adsorption behavior of branched cationic gemini surfactants (C3, C6) on the surface of quartz. The branched cationic gemini surfactants with enhanced steric hindrance will destroy the tight arrangement of the surfactant molecules at quartz. Therefore, gemini surfactant molecules could not form a bi-layer adsorption on a quartz surface after CMC.

Herein, different branched extended anionic surfactants (L- C_{12} PO₄S, G- C_{12} PO₄S, and G- C_{16} PO₄S) were utilized to evaluate their adsorption properties at air–liquid and solid–liquid interfaces by measuring their surface tension and contact angles, respectively. It is helpful to understand the influence of the surfactants' branch degree on the wettability of a medium energetic polymer surface.

2. Experimental

2.1. Materials

The linear sodium dodecyl(polyoxyisopropene)₄ sulfate (L-C₁₂PO₄S), branched sodium dodecyl(polyoxyisopropene)₄ sulfate (G-C₁₂PO₄S), and branched sodium hexadecyl(polyoxyisopropene)₄ sulfate (G-C₁₆PO₄S) were provided by the Sasol corporation (South Africa). The molecular structures of the three surfactants are depicted in Scheme 1. Ultrapure water with 18.2 MΩ·cm resistivity was used for the experiments.



Scheme 1. The structures and abbreviations of the extended anionic surfactants.

2.2. Surface Tension Measurements

The surface tension values of the surfactant solutions were detected using an interfacial tension meter (DCAT21, Dataphysics Company, Germany) at 30 °C via the Wilhelmy plate technique [32]. Each concentration was measured three times. The measurement error of the surface tension is lower than 0.5 mN/m.

2.3. Contact Angle Measurements

Before the contact angle test, the PMMA surface was cleaned according to the literature [26]. The contact angles on PMMA surface were conducted by the LAUDA Scientific GmbH machine (Lauda-Königshofen, Germany) via the sessile drop method at 30 °C. Each concentration was measured at least five times with 2 μL droplets.

3. Results and Discussion

3.1. Surface Activity Parameters of the Extended Surfactants

The surface tensions of the three extended surfactants were measured at different concentrations, and the isotherms of equilibrium surface tensions as a function of concentration are plotted in Figure 1. The CMC value was obtained from the turning point in the curve. CMC is the most critical turning concentration of the surfactant solution, which implies the maximum monomer concentration in the solution. Besides, the surface tension of the surfactant solution at the turning point is represented as γ_{CMC} . As shown in the surface tension curves (Figure 1), the CMC values of L-C₁₂PO₄S, G-C₁₂PO₄S, and G-C₁₆PO₄S are 9.9×10^{-5} , 3.0×10^{-4} , and 1.5×10^{-5} mol L⁻¹, respectively. It can be seen that the CMC value of G-C₁₂PO₄S is higher than that of L-C₁₂PO₄S. This phenomenon can be attributed to the fact that branched chains will enhance the water-solubility of surfactants. Besides, branched G-C₁₂PO₄S has larger steric hindrance for forming micelles, which will increase the CMC value as well. As for the branched surfactants (G-C₁₂PO₄S and G-C₁₆PO₄S), G-C₁₆PO₄S with enhanced oleophilicity possesses smaller CMC.

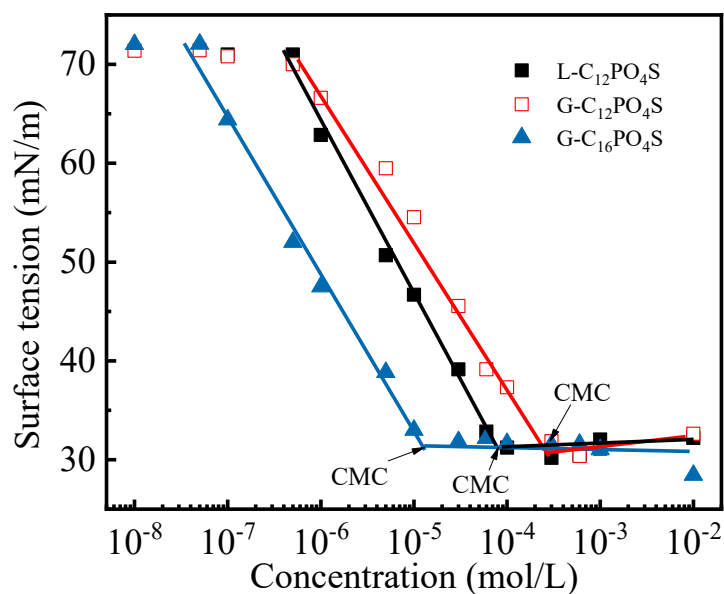


Figure 1. Surface tension (γ_{LV}) versus the concentration for the extended surfactants.

The saturated adsorption amount (Γ_{max}) and saturated adsorption area (A_{min1}) can be calculated by Gibbs equations as follows

$$\Gamma_{max} = - \left(\frac{1}{2.303nRT} \right) \left(\frac{d\gamma}{d \log C} \right) \quad (1)$$

$$A_{min} = \frac{10^{14}}{N_A \Gamma_{max}} \quad (2)$$

The values of Γ_{max1} and A_{min1} are calculated and listed in Table 1. Overall, there are few differences in the surface tension at the CMC (γ_{CMC}) for the three surfactants. However, the Γ_{max1} of the branched G-C₁₂PO₄S is relatively low, resulting in a slightly higher γ_{CMC} . As the alkyl chain gets longer, the hydrophobicity enhances while the steric hindrance rises. As a result, the A_{min1} of the branched surfactants (G-C₁₂PO₄S and G-C₁₆PO₄S) are both approximately 1.33 nm².

Table 1. The critical micelle concentration (CMC), γ_{CMC} , and saturated adsorption amount (Γ_{max1}) and area (A_{min1}) of the surfactants.

Abrr.	CMC /(10 ⁻⁵ mol L ⁻¹)	γ_{CMC} /(mN m ⁻¹)	10 ¹⁰ Γ_{max1} /(mol cm ⁻²)	A_{min1} /(nm ²)
L-C ₁₂ PO ₄ S	9.9	30.1	1.47	1.13
G-C ₁₂ PO ₄ S	30.0	31.4	1.25	1.33
G-C ₁₆ PO ₄ S	1.5	30.7	1.24	1.34
C ₁₂ P ₄ S ³³	42.0	40.0	1.00	1.66
C ₁₂ P ₈ S ³³	7.8	35.5	1.08	1.54
C ₁₂ P ₁₂ S ³³	4.3	33.7	1.01	1.64
PP ₃ S ²⁹	5.9	34.4	1.66	1.00
PP ₆ S ²⁹	3.0	34.1	1.29	1.29
PP ₉ S ²⁹	1.6	33.7	1.17	1.41
PP ₁₂ S ²⁹	1.2	36.9	0.97	1.71

Moreover, some reported [29,33] parameters of extended anionic surfactants with similar structures are also listed in Table 1. From the CMC values of the extended surfactants sodium dodecyl polypropylene oxide sulfate (C₁₂P_nS) and sodium nonylphenoxy polypropyleneoxide sulfates (PP_nS), it can be seen that their CMC values decrease with the

increase in the PO units. This can be attributed to the increasing lipophilicity as the PO chain gets longer. By comparing, it is observable that the surface activity parameters of L-C₁₂PO₄S, G-C₁₂PO₄S, and G-C₁₆PO₄S are reasonable.

3.2. Contact Angles of the Extended Surfactants at PMMA Surface

Figure 2 shows the contact angles (θ) of the three extended surfactant solutions on PMMA surface. It can be seen from Figure 2 that the contact angles of the surfactants vary little over a wide range of concentrations (1×10^{-8} – 3×10^{-5} mol L⁻¹) with a value of 72°. When the concentration of the surfactant solutions approaches 6×10^{-5} mol L⁻¹, the contact angles begin to decrease significantly. At high concentration of 1×10^{-2} mol L⁻¹, the contact angle of linear L-C₁₂PO₄S (21.9°) is smaller than that of branched G-C₁₂PO₄S (28.5°), but higher than that of G-C₁₆PO₄S (12.8°). It also must be pointed out that the θ values all decrease obviously after CMC for extended surfactants.

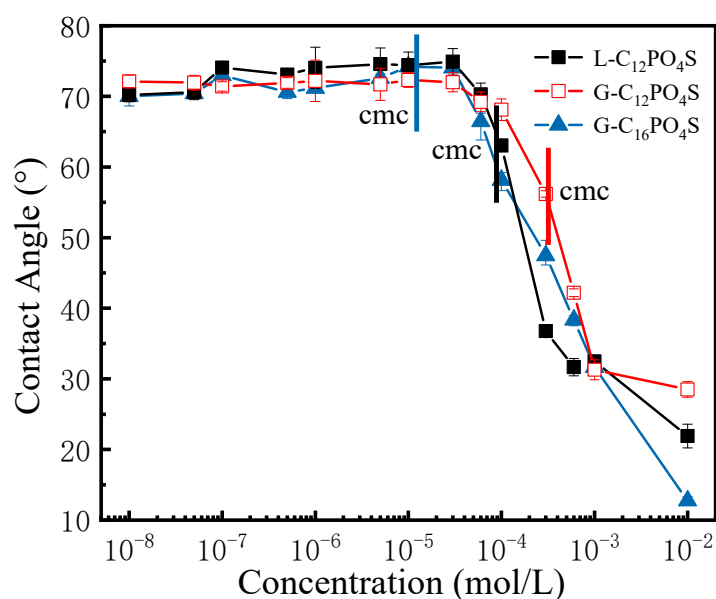


Figure 2. Effect of concentration on contact angles (θ) of the extended surfactant solutions on polymethylmethacrylate (PMMA) surface.

Significantly, the variation in contact angles for these extended anionic surfactants at PMMA surface is quite different from those of conventional surfactants. According to the literature, the contact angle of the cationic surfactant CTAB solution at PMMA surface will decrease dramatically to approximately 51.0° at the CMC, and then change slowly with the increase in bulk concentration [34,35]. The contact angles of anionic surfactant SDS [35] and nonionic surfactant TX-100 [36] decrease to 47.2° and 47.4°, respectively, at the CMC, whereas our previous studies found that the contact angles of special structural surfactants with branched hydrophobic chains or EO groups change noticeably after CMC on the PMMA [24,26,28], quartz [25,32,37], and PTFE [13,38,39] surfaces. For the extended surfactants in this study, the contact angle values also change after CMC, which means that the adsorption of extended surfactant molecules at the solid–liquid interface continues when the adsorption at the liquid surface reaches saturation.

Comparing Figures 1 and 2, surface tensions decrease significantly when contact angles remain constant at a low concentration range. Therefore, the contact angle is not enough to illustrate the adsorption behaviors of surfactants on solid surfaces. The relevant mechanism will be discussed in detail later.

3.3. Adhesional Tension of the Extended Surfactants at PMMA–Liquid Interface

The surfactants' adhesional tension that reveals their adhesion capacity on the solid–liquid interface is defined as the difference between the interfacial free energy of solid–air (γ_{SV}) and the interfacial free energy of solid–liquid (γ_{SL}). Based on Young's equation, the contact angle is related to γ_{SV} , γ_{SL} , and γ_{LV} (interfacial free energy of solid–liquid, surface tension). Therefore, the value of the adhesional tension is $\gamma_{LV}\cos\theta$ (Equation (3)).

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta \quad (3)$$

To quantify the surfactants' adsorption amounts at the interfaces, Young's equation is combined with the Gibbs adsorption equation, and the obtained equation is as follows

$$\frac{d(\gamma_{LV}\cos\theta)}{d\gamma_{LV}} = \frac{\Gamma_{SV} - \Gamma_{SL}}{\Gamma_{LV}} \quad (4)$$

where Γ_{SV} , Γ_{SL} , and Γ_{LV} represent the surfactants' adsorption amounts at solid–air, solid–liquid, and air–liquid interfaces, respectively. Assuming that $\Gamma_{SV} \approx 0$, the value of Γ_{SL}/Γ_{LV} can be obtained from the slope of the $\gamma_{LV}\cos\theta$ – γ_{LV} curve.

Figure 3 displays the dependence between the adhesional tension and surface tension of the three extended surfactants. Before CMC, the adhesional tension decreases with the increase in bulk concentration. When the bulk concentration exceeds CMC, the surface tension keeps a constant value, while the adhesional tension continues to increase. As a result, the curves exhibit a vertical upward trend. It is noticeable that the surface tension and adhesional tension of the surfactant solutions exhibit a good linear relationship before CMC, and the linear correlation coefficient (R^2) for L-C₁₂PO₄S, G-C₁₂PO₄S, and G-C₁₆PO₄S is respectively 0.996, 0.990, and 0.973. Interestingly, the slopes of the three extended surfactants are all about 0.3, which means the extended surfactants that adsorb at the air–liquid interface are all approximately three times higher than those at the PMMA–liquid interface.

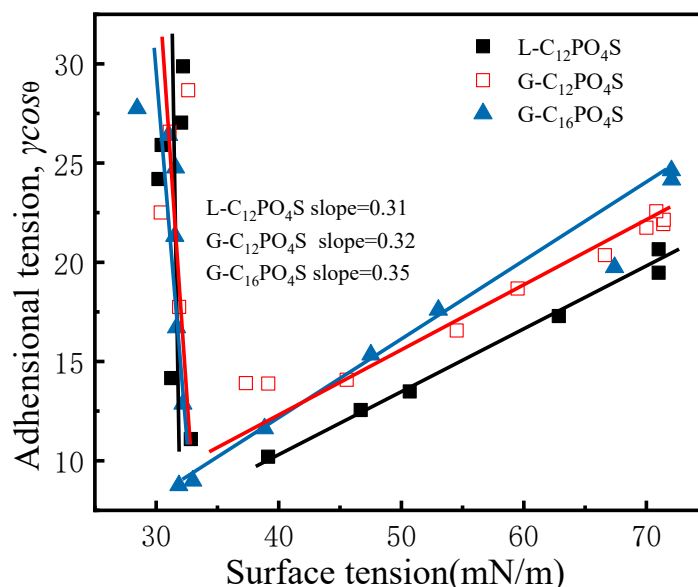


Figure 3. Dependence between the adhesional tension and surface tension of the extended surfactants.

For comparison, the slopes of the adhesional tension curves of some conventional and special structural surfactants are summarized in Table 2. Based on the value of Γ_{SL}/Γ_{LV} and the surfactants' saturated adsorption area ($A_{\min1}$) at the air–liquid interface, the saturated adsorption area ($A_{\min2}$) of the surfactant molecules on the PMMA surface before CMC is calculated and also listed in Table 2.

Table 2. The slopes (Γ_{SL}/Γ_{LV}) and the theoretical adsorption area (A_{min2}) of the conventional surfactants and several surfactants with specific structures before CMC.

Surfactants	Slopes	$A_{min2}/(nm^2)$
L-C ₁₂ PO ₄ S	0.31	3.65
G-C ₁₂ PO ₄ S	0.32	4.16
G-C ₁₆ PO ₄ S	0.35	3.83
CTAB ³⁴	−0.34	-
CPyB ³⁴	−0.34	-
C ₁₂ (EDMAB) ¹⁹	−0.30	-
BDDAB ¹⁹	−0.31	-
C ₁₆ PC ²⁷	0.045	-
C ₁₆ (EO) ₃ PC ²⁷	0.033	-
C ₁₆ PB ²⁷	0.136	-
C ₁₆ (EO) ₃ PB ²⁷	0.063	-
C ₁₆ GPC ²⁸	0.11	7.36
C ₁₆ G(EO) ₃ PC ²⁸	0.11	6.36
C ₁₆ GPB ²⁸	0.11	6.00
C ₁₆ G(EO) ₃ PB ²⁸	0.11	6.18
C ₃ ²⁶	0.13	8.69
C ₆ ²⁶	0.13	9.62
18C ⁴⁰	0.26	2.84
18S ⁴⁰	0.28	3.01
BCB ²⁴	0.30	2.00
BSB ²⁴	0.34	2.05

In general, the slopes of conventional surfactants such as nonionic surfactant TX-100, [21] anionic surfactant SDDS, [23] and cationic surfactants CTAB, [34] CPyB, [34] C₁₂(EDMAB) [19], and BDDAB¹⁹ are all negative, demonstrating that they adsorb at the PMMA-water interface via hydrophobic interactions. Meanwhile, the conventional surfactants exhibit slopes of about −0.3, which indicates that they are likely to tile at the PMMA-liquid interface with about 1/3 of the adsorption amounts at the air-liquid interface. Therefore, the adsorption amounts of both the conventional surfactants (slopes ≈ -0.3) and the extended surfactants (slopes ≈ 0.3) in this work at the air-liquid interface are approximately three times higher than those at the solid-liquid interface. However, the adsorption behavior between the conventional surfactants and the extended surfactants are quite different. However, it must be pointed out that the slope values of the extended surfactants in this work are all positive at a low concentration, which means that surfactant molecules adsorb on the PMMA surface by ionic heads with the hydrophobic tail towards the water.

Comparing the structures of the surfactants, it is worth noting that these specific surfactants with positive slopes have more than one hydrophilic group. As for the three extended surfactants in this work, they all have a PO chain and $-SO_4^-$ group. Besides, the C₁₆PC²⁷ and C₁₆GPC²⁸ surfactants have the -OH and $-N(CH_3)_3^+$ groups. The C₁₆PB²⁷ and C₁₆GPB²⁸ molecules have the -OH, $-N(CH_3)_3^+$ and $-COO^-$ groups. The C₁₆(EO)₃PC²⁷ and C₁₆G(EO)₃PC²⁸ molecules have the -OH, $-N(CH_3)_3^+$ and EO groups. The C₁₆(EO)₃PB²⁷ and C₁₆G(EO)₃PB²⁸ surfactants have the -OH, $-N(CH_3)_3^+$, EO and $-COO^-$ groups. Furthermore, the C₃²⁶ and C₆²⁶ surfactants all have two polar xylyl and two $-N(CH_3)_3^+$ groups. The 18C⁴⁰ molecule has $-N(CH_3)_3^+$ and $-COO^-$ groups, while the 18S⁴⁰ molecule has $-N(CH_3)_3^+$, -OH and $-SO_3^-$ groups. Moreover, the BCB²⁴ molecule has the polar xylyl, $-N(CH_3)_3^+$ and $-COO^-$ groups, while BSB²⁴ molecule has the polar xylyl, $-N(CH_3)_3^+$, -OH and $-SO_3^-$ groups.

Multi-hydrophilic groups can undoubtedly increase the polar interactions with the PMMA surface. Therefore, these surfactants can adsorb on the PMMA surface by polar interactions that more easily rely on their special structures (hydroxyl, EO, or PO groups). Since the hydroxyl group can form hydrogen bonds, EO group has a good hydrophilic

effect, and PO group owns a partly hydrophilic and partly lipophilic nature; these special structural surfactants can easily interact with PMMA surfaces.

The size of hydrophilic part controls the positive value of the slope. As for $C_{16}(EO)_3PC$ and $C_{16}(EO)_3PB$ in Table 2, their $-(OCH_2CH_2)_n$ groups increase the steric hindrance and reduce their adsorption capacity [27]. This is the reason why their slopes are only 0.033~0.063. Comparing the two linear betaines $C_{16}PB^{27}$ and $18C^{40}$, the slope of $C_{16}PB$ is only 0.136 due to its ether hydroxypropyl. Among them, the PO group has a stronger interaction with the PMMA surface due to its partially hydrophilic and partially lipophilic nature [31], so the extended surfactants in this work have the maximum slope values compared with other surfactants with special structures.

3.4. Interfacial Tension of the PMMA–Liquid Interface

The variation of solid–liquid interfacial tension reveals the adsorption behavior of extended surfactant molecules on a solid surface. The surface free energy of PMMA is about 39.5 mN m^{-1} , [27] and the interfacial tension at PMMA-liquid interface (γ_{SL}) can be calculated by using Young’s equation, and the obtained results are plotted in Figure 4. The saturated adsorption area before CMC (A_{min3}) and after CMC (A_{min4}) are calculated by Gibbs equation and listed in Table 3.

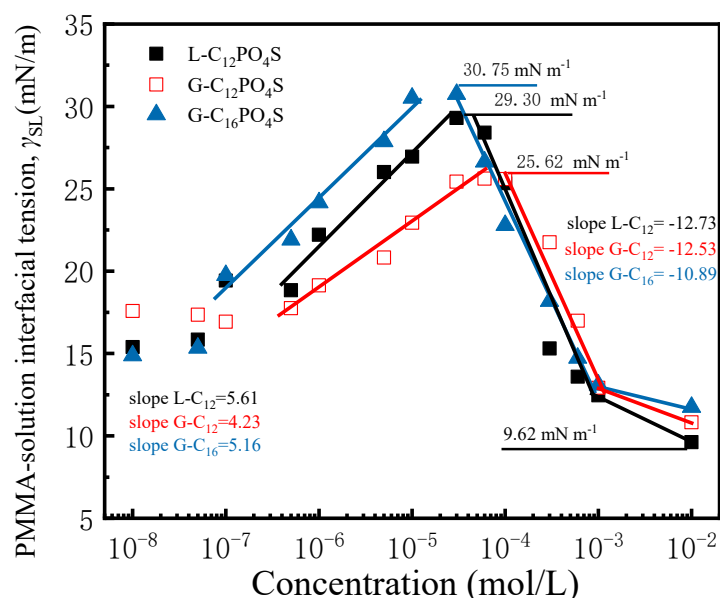


Figure 4. The PMMA–solution interfacial tension as a function of surfactant concentration.

Table 3. The surface activity parameters of the extended surfactants at PMMA.

Abbr.	$10^{10}\Gamma_{max3}/(\text{mol}/\text{cm}^2)$ (<CMC)	$A_{min3}/(\text{nm}^2)$ (<CMC)	$10^{10}\Gamma_{max4}/(\text{mol}/\text{cm}^2)$ (>CMC)	$A_{min4}/(\text{nm}^2)$ (>CMC)
L- $C_{12}PO_4S$	0.48	3.44	1.10	1.51
G- $C_{12}PO_4S$	0.36	4.56	1.08	1.54
G- $C_{16}PO_4S$	0.44	3.74	0.94	1.77

As seen in Figure 4, the adsorption of the three extended surfactants on PMMA surface has two stages. At a low concentration, γ_{SL} increases gradually with the increase in the bulk concentration. At a high concentration, γ_{SL} decreases sharply as the bulk concentration increases. A linear relationship exists between the concentration and γ_{SL} in the two stages. There is a maximal γ_{SL} in the PMMA–solution interfacial tension curve for each surfactant, and the values of γ_{SL} vary with the structure of extended surfactants.

In the first stage, the extended surfactants interact with PMMA surface by polar groups, so γ_{SL} gradually increases. As a consequence, the hydrophobic tails that point

to water strengthen the hydrophobic modification of the PMMA surface. Because of the electrostatic repulsion among the surfactant molecules, the adsorption amount on the solid surface at this stage is low (Table 3). Though the ionic group SO_4^- is followed by the PO group, the steric hindrance of the PO group does not work due to the small adsorption amount of the surfactants. On account of the higher steric hindrance, the branched G-C₁₂PO₄S has a smaller Γ_{max} ($3.6 \times 10^{-11} \text{ mol cm}^{-2}$) and a larger A_{min} (4.56 nm^2) than L-C₁₂PO₄S. Besides, the longer alkyl chain results in a stronger hydrophobic interaction. Accordingly, G-C₁₆PO₄S has a larger adsorption amount and smaller adsorption area than G-C₁₂PO₄S. Furthermore, the values of $A_{\text{min}3}$ calculated by the Gibbs equation are consistent with the theoretical $A_{\text{min}2}$ obtained by adhesional tension, which implies the reliability of the results.

In the second stage, the hydrophobic tails of the surfactants interact with the PMMA surface, while the hydrophilic heads point to the solution. Consequently, the solid surface is modified to be hydrophilic, and γ_{SL} decreases significantly when the bulk concentration increases. Combined with the previous research, the change trends of γ_{SL} have three cases as the surfactant concentrations increase: (1) γ_{SL} rises firstly and then keeps a stable value; (2) γ_{SL} rises firstly and then declines, and the slopes of the two stages are almost equal; (3) γ_{SL} rises firstly and then declines, and the slope of the second stage is 2–3 times higher than the first stage. Zhang et al. [24] studied the wettability of benzyl-substituted alkyl sulfobetaine (BSB) on PMMA surface. It is found that the γ_{SL} values increase as the bulk concentration increases and then γ_{SL} reaches a plateau value around CMC, which indicates that BSB molecules adsorb on PMMA surface only by polar interaction. Therefore, the hydrophobic adsorption stage does not occur. Hu et al. [40] investigated the adsorption of alkyl carboxylbetaine (18C) and alkyl sulfobetaine (18S) on the PMMA surface. They found that the γ_{SL} rises firstly and then declines, and the slope of the decreasing stage is almost the same as the increasing stage. The saturated adsorption areas of surfactants (18C, 18S) on the PMMA–liquid interface before CMC ($A_{\text{min}3}$) are, respectively, 2.78 and 3.06 nm^2 , which is very close to the $A_{\text{min}4}$ after CMC (2.99 nm^2 and 4.57 nm^2). This implies that the hydrophobic chains of the surfactants are towards the water at the beginning, but the surfactants may form the bilayer adsorption film with the hydrophilic heads towards the water as the bulk concentration increases. Lv et al. [26] found a similar bilayer adsorption phenomenon on the wettability of xylyl-substituted biquaternary ammonium salt Gemini surfactants (C3, C6) on PMMA surface. In this work, it is obvious that the slopes of γ_{SL} after CMC are much larger than the slopes at a low concentration, which demonstrates that the adsorption amount of the surfactants on the PMMA surface remarkably increase. Therefore, the adsorbed surfactants are more likely to form aggregations on the solid surface than bilayer adsorption.

At the turning point of adsorption behavior, the maximum value of γ_{SL} represents the maximum hydrophobic modification capability of the extended surfactants. It is visually observable that branched G-C₁₆PO₄S whose γ_{SL} reaches 30.75 $\text{mN}\cdot\text{m}^{-1}$ possesses the strongest hydrophobic modification ability. Furthermore, the minimum value of γ_{SL} at high concentration can manifest the maximum hydrophilic modification ability of the surfactants. It can be seen that γ_{SL} of linear L-C₁₂PO₄S reaches 9.62 $\text{mN}\cdot\text{m}^{-1}$, suggesting that L-C₁₂PO₄S has the strongest hydrophilic modification capability.

The maximum hydrophobic and hydrophilic modification abilities of the special structural surfactants in the literature are summarized in Table 4. In order to avoid the influence of the initial values of γ_{SL} for different PMMA sheets in the literature, the maximum hydrophobic modification capacity ($\Delta\gamma_{\text{SL}}$) is represented by the difference between the maximum γ_{SL} and the initial γ_{SL} for pure water, whereas the maximum hydrophilic modification capacity corresponds to the minimum γ_{SL} at high concentrations. It is observable that L-C₁₂PO₄S, G-C₁₆PO₄S, BCB, and BSB possess strong hydrophobic modification ability with $\Delta\gamma_{\text{SL}}$ of more than 10 $\text{mN}\cdot\text{m}^{-1}$. Comparing their structures, the strong hydrophobic modification ability can be attributed to the strong polar interactions and the small steric hindrance. On one hand, the stronger the polar interactions, the more

surfactants will adsorb at the PMMA surface. On the other hand, less steric hindrance leads to relatively higher adsorption amounts, thus manifesting strong hydrophobic modification ability. The branched C₁₆GPB, C₁₆GPC, and C₁₆G(EO)₃PC have a higher hydrophilic modification ability on the PMMA surface compared to the linear surfactants with similar structures. However, the branched structure increases the difficulty of forming aggregations on the PMMA surface, thus the hydrophilic modification ability of C₁₆G(EO)₃PB is lower than that of the linear C₁₆(EO)₃PB.

Table 4. The maximum hydrophobic modification and the maximum hydrophilic modification of the special surfactants on PMMA surface in the literature.

Surfactants	$\Delta\gamma_{SL}$	The Minimum γ_{SL}
L-C ₁₂ PO ₄ S	13.91	9.62
G-C ₁₂ PO ₄ S	8.69	10.83
G-C ₁₆ PO ₄ S	15.87	11.75
C ₁₆ PC ²⁷	1.1	21.75
C ₁₆ (EO) ₃ PC ²⁷	4.25	26.8
C ₁₆ PB ²⁷	5.4	27.2
C ₁₆ (EO) ₃ PB ²⁷	4.1	9.75
C ₁₆ GPC ²⁸	2.7	18.8
C ₁₆ G(EO) ₃ PC ²⁸	4.4	18
C ₁₆ GPB ²⁸	5	18
C ₁₆ G(EO) ₃ PB ²⁸	4.9	17.5
C ₃ ²⁶	2.8	29.8
C ₆ ²⁶	3	28.1
18C ⁴⁰	9	21
18S ⁴⁰	9.2	24
BCB ²⁴	11.8	22.5
BSB ²⁴	13	27.8

3.5. Adhesion Work of the Extended Surfactants on PMMA Surface

The work of adhesion (W_A) of the surfactant solutions on the solid surface, which can represent the work required to separate a unit area of liquid from the solid surface, can be computed by Equation (5). Moreover, combined with Young's equation, W_A can be obtained as shown in Equation (6).

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (5)$$

$$W_A = \gamma_{LV}(\cos \theta + 1) \quad (6)$$

According to the equation, the adhesion work is the sum of adhesional tension ($\gamma_{LV}\cos \theta$) and surface tension (γ_{LV}).

The work of adhesion (W_A) for the extended surfactants at the PMMA surface has been calculated and plotted in Figure 5. We can see from Figure 5 that W_A of the surfactant solutions is almost constant at low concentrations because the γ_{LV} and γ_{SL} change little. As the concentration increases, W_A decreases, which is caused by the decrease in both γ_{LV} and adhesional tension. When the concentration exceeds the CMC value, the adsorption of surfactants at the air–liquid interface is saturated and the γ_{LV} is constant. However, the surfactants continue to adsorb at the PMMA–liquid interface and, accordingly, the γ_{SL} decreases, which leads to an increasing trend of W_A .

3.6. Adsorption Mechanism of the Extended Surfactants on PMMA Surface

The mechanisms responsible for the adsorption behaviors and wettability of the extended anionic surfactants were detected by analyzing their structural dependence results in Figure 6, and the corresponding possible adsorption behaviors are schematically plotted in Figure 7.

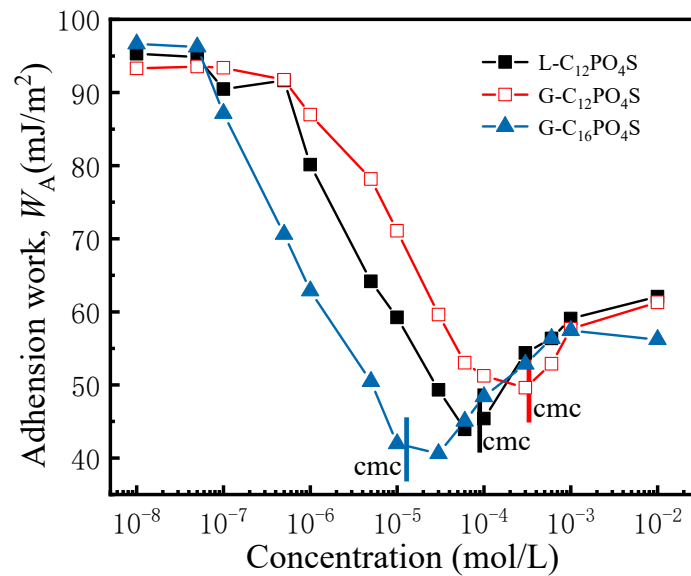


Figure 5. Effect of concentration on the adhesion work of the extended surfactants at the PMMA surface.

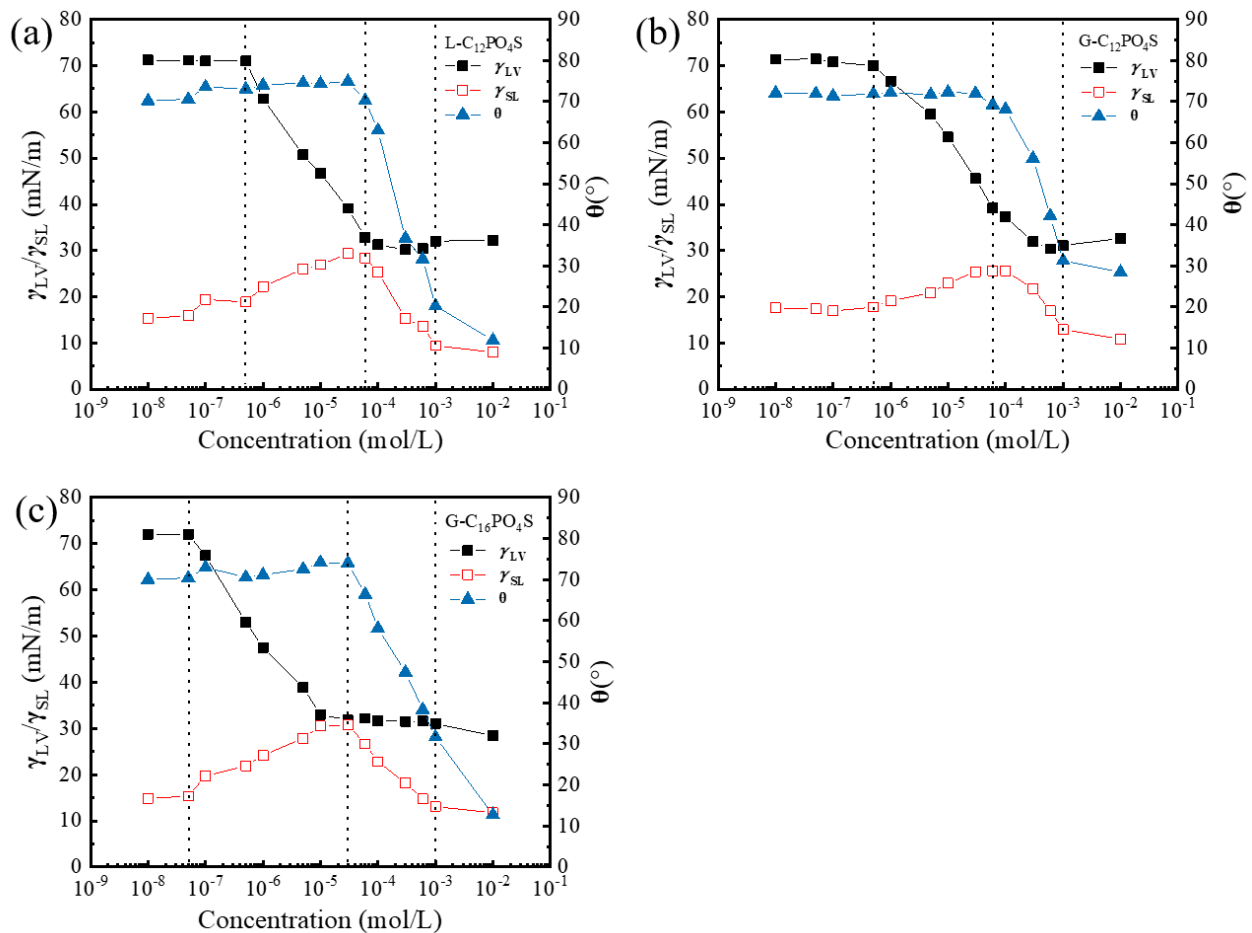


Figure 6. Concentration dependence of the adhesion data of extended surfactants L-C₁₂PO₄S (a), G-C₁₂PO₄S (b), and G-C₁₆PO₄S (c) on PMMA surface.

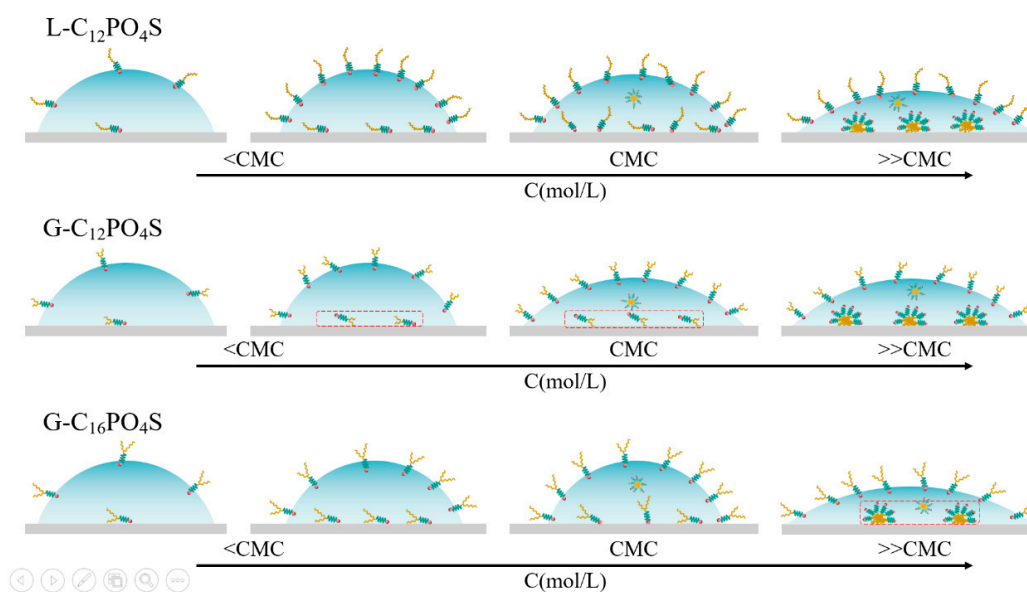


Figure 7. The possible adsorption behaviors of the surfactants on the PMMA surface.

Observing the curves in Figure 6, it can be found that the adsorption behaviors of the three extended surfactants on the PMMA surface can be divided into four stages. We take linear L-C₁₂PO₄S as an example to discuss the four stages of the surfactants' adsorption behavior.

In the first stage ($1 \times 10^{-8} \sim 5 \times 10^{-7} \text{ mol L}^{-1}$), the adsorption of surfactant molecules at both the solid–liquid interface and the air–liquid interface can be ignored, and the contact angles remain about 72° and the other adhesion data keep constant.

In the second stage ($5 \times 10^{-7} \sim 6 \times 10^{-5} \text{ mol L}^{-1}$), the adsorption amounts at both the air–liquid and solid–liquid interface increase as the bulk concentration increases, which results in a decreasing γ_{LV} and an increasing γ_{SL} . However, the contributions of γ_{LV} and γ_{SL} are offset, resulting in little change in the contact angles. At the same time, surfactants rely on ionic heads to adsorb at the solid–liquid interface, and the hydrophobic chains point toward the solution. The contact angles exhibit a slightly increasing tendency on account of the hydrophobized PMMA surface.

In the third stage ($6 \times 10^{-5} \sim 1 \times 10^{-3} \text{ mol L}^{-1}$), the surfactants' adsorption amounts at the air–liquid interface tend to be saturated and the γ_{LV} tends to reach a plateau value when approaching the CMC value. However, the γ_{SL} suddenly decreases, which triggers a sharp decline in the contact angles. The adsorption behavior starts to transform, and surfactant molecules are more inclined to adsorb on the PMMA surface through hydrophobic interactions. Since the adsorption amounts of surfactant molecules increase significantly at this stage, it is presumed that the adsorbed surfactants are forming aggregations at the solid–liquid interface, as we discussed above.

At the last stage ($1 \times 10^{-3} \sim 1 \times 10^{-2} \text{ mol L}^{-1}$), the adsorbed surfactant molecules at the solid–liquid interface also tend to be saturate; thus, the contact angles display a stable tendency.

Among the three surfactants, the γ_{SL} of L-C₁₂PO₄S and G-C₁₆PO₄S starts to decrease when the surfactant concentration exceeds CMC. Similarly, the contact angles of L-C₁₂PO₄S and G-C₁₆PO₄S start to decrease after CMC. Interestingly, the γ_{SL} of G-C₁₂PO₄S starts to decrease before CMC, indicating that its adsorption behavior changes before CMC. The branched chain of the G-C₁₂PO₄S molecules enhanced the hydrophobic effect, thus intensifying the adsorption of hydrophobic groups on the PMMA surface. On the other hand, a branched chain improves the water-solubility of G-C₁₂PO₄S and CMC value increases as a result. Therefore, the G-C₁₂PO₄S molecules begin adsorbing on PMMA surface before the saturated adsorption at the air–liquid interface. Meanwhile, the G-

C₁₂PO₄S molecules start to form aggregations like semi-micelles at the PMMA–liquid interface. As the branched chains get longer, however, the steric hindrance at PMMA surface increases. It becomes difficult to form aggregations at a solid surface, so the γ_{SL} of G-C₁₆PO₄S changes after CMC. Moreover, G-C₁₆PO₄S shows the highest γ_{SL} value at high concentrations, which can also be attributed to the steric hindrance to forming aggregations.

For the extended surfactants, the branched G-C₁₆PO₄S molecules with two long alkyl chains exhibit the strongest hydrophobic modification capacity. Due to its having the least steric hindrance and the highest adsorption amount, the linear L-C₁₂PO₄S is more likely to form aggregations at the PMMA–liquid interface. Therefore, L-C₁₂PO₄S manifests a stronger hydrophilic modification ability than branched G-C₁₂PO₄S and G-C₁₆PO₄S surfactants.

4. Conclusions

In this work, the adsorption mechanism and wetting properties of branched extended anionic surfactants (L-C₁₂PO₄S, G-C₁₂PO₄S, G-C₁₆PO₄S) on the PMMA surface were investigated. Based on the structural dependence of extended anionic surfactants on the wettability of PMMA surface, the following conclusions are obtained:

(1) Before CMC, the contact angles change little as the surfactants' concentration increases because the decrement of γ_{LV} exactly counterbalances the increment of γ_{SL} . The contact angles decrease significantly after CMC, which attributes to the rapidly decreasing γ_{SL} ;

(2) Before CMC, the adhesional tension decreases with the increase in bulk concentration, and a linear relationship exists between the adhesional tension and surface tension. After CMC, the adhesional tension exhibits a vertical upward trend in the $\gamma_{LV}\cos\theta-\gamma_{LV}$ curve. At low concentrations, the special property of PO groups allows the extended surfactants to adsorb on the PMMA surface by polar interactions; thus, the solid surface is modified to be hydrophobic. Besides this, the surfactants' adsorption amounts at the air–liquid interface are all approximately three times higher than those at the PMMA–liquid interface before CMC;

(3) There are two stages for the three extended surfactants in PMMA–solution interfacial tension. At low concentrations, γ_{SL} increases gradually with the increase in the bulk concentration. At high concentrations, γ_{SL} decreases significantly as the bulk concentration increases. In this stage, the surfactants are prone to forming aggregations and their hydrophobic tails will interact with the PMMA surface with their polar heads pointing to the water. Accordingly, the PMMA surface is modified to be hydrophilic;

(4) In the three extended surfactants, linear L-C₁₂PO₄S with the least steric hindrance shows the strongest hydrophilic modification ability. On the contrary, the branched G-C₁₆PO₄S molecules with two long alkyl chains exhibit the strongest hydrophobic modification capacity.

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Sample Availability: Samples of the L-C₁₂PO₄S, G-C₁₂PO₄S, and G-C₁₆PO₄S are available from the authors.

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