

Effect of Sequence Structure on Wetting Behaviors of Fluorinated Methacrylate Polymers Based on Perfluorohexylethyl Methacrylate and Stearyl Acrylate*

Zi-xu Gu, Jun Cheng, Ming-zu Zhang, Jin-lin He and Pei-hong Ni**

College of Chemistry, Chemical Engineering and Materials Science, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Soochow University, Suzhou 215123, China

Abstract Due to the non-crystalline properties of short chain perfluoroalkyl groups, using short chain perfluoroalkyl to stabilize low surface free energy polymers has been a challenging task. In this study, we prepare a series of random copolymers poly(perfluorohexylethyl methacrylate)-*co*-poly(stearyl acrylate) (P13FMA-*co*-PSA) and block copolymers poly(perfluorohexylethyl methacrylate)-*b*-poly(stearyl acrylate) (P13FMA-*b*-PSA), and systematically investigate the effects of the sequence structure and the content of 13FMA of the fluorinated copolymers on surface free energy and surface reorganization. Static/dynamic contact angle goniometry and water/oil repellency analyses demonstrate that the random polymer P13FMA-*co*-PSA could not achieve low surface free energy and low surface reorganization at the same time. In contrast, for the block copolymer P13FMA-*b*-PSA, both low surface free energy and low surface reorganization are acquired simultaneously. The results of X-ray photoelectron spectroscopy (XPS), dynamic contact angle goniometry and differential scanning calorimetry (DSC) reveal the above-mentioned properties. The consecutive 13FMA segments improve the surface fluorine density, while the consecutive SA chains enhance the crystallinity of the SA segments, and further hinder the surface reorganization of the perfluoroalkyl groups. Therefore, P13FMA-*b*-PSA exhibits a higher utilization efficiency of fluorine atoms and a better structural stability than P13FMA-*co*-PSA.

Keywords Surface free energy; Surface reorganization; Perfluorohexylethyl methacrylate (13FMA); Stearyl acrylate (SA); Water/oil repellency

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1966-x>.

INTRODUCTION

Fluoropolymers, especially poly(perfluoroalkyl acrylate), due to their low surface free energies (*ca.* 7.0 mN/m), non-adhesive properties, low friction coefficients and good film-forming properties^[1–4], have been extensively studied and applied as surface modifiers, such as the applications in imparting oil and water repellency to textiles, providing efficient moisture protection for printed circuit boards (PCBs), and maintaining the dispersion of different coloured inks for display applications^[5–13].

* This work was financially supported by the National Natural Science Foundation of China (Nos. 21374066 and 20474041), the Major Program of the Natural Science Project of Jiangsu Higher Education Institutions (No. 15KJA150007), the Natural Science Foundation of Jiangsu Province (No. BK20151263), the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions, and Soochow-Waterloo University Joint Project for Nanotechnology from Suzhou Industrial Park.

** Corresponding author: Pei-hong Ni (倪沛红), E-mail: phni@suda.edu.cn

Received March 8, 2017; Revised April 18, 2017; Accepted April 20, 2017

doi: 10.1007/s10118-017-1966-x

Perfluoroalkyl (meth)acrylates are usually copolymerized together with a range of non-fluorinated (meth)acrylates in order to achieve a required performance^[14–22]. It has been found that these non-fluorinated (meth)acrylates significantly influence two essential properties, *i.e.* surface free energy and surface reorganization. And these two properties are necessary for low surface free energy materials.

In our previous study^[23], we prepared two types of fluorinated copolymers poly(perfluorohexylethyl methacrylate)-*co*-poly[alkyl (meth)acrylate] through solution polymerization and miniemulsion polymerization, respectively. We focused on studying the effects of the groups at the α -position and the side-chain lengths of the alkyl (meth)acrylate moiety on the surface free energy and surface reorganization of the copolymer films. We found that the fluorinated copolymers without α -methyl groups in the alkyl acrylates have lower surface free energy than those with α -methyl groups. However, the copolymers without α -methyl groups have lower T_g , which resulted in higher surface reorganization. According to this result, the effects of alkyl (meth)acrylate comonomers on surface free energy and surface reorganization are always contradictory for low surface free energy materials. However, for most low surface free energy materials, they must simultaneously possess both low surface free energy and low surface reorganization.

n-Stearyl acrylate (SA), as a special case of the above study, could potentially achieve low surface free energy and low surface reorganization at the same time because of its long crystallized alkyl side chain^[24]. The properties of these copolymers, which are obtained by copolymerizing SA with fluorinated acrylate monomers, have been widely studied^[25–33]. In these studies, the fluorinated acrylate monomers form a stable semi-crystalline structure. It is worth noting that perfluorohexylethyl methacrylate (13FMA) is environmentally friendly^[34–37] and commercially widely used monomer, in which fluoroalkyl side chain cannot be crystallized^[2]. Thus, the properties of copolymers composed of SA and 13FMA may be different from those reported in previous works and need to be further studied.

In the present work, we first prepared a series of random copolymers (P13FMA-*co*-PSA) and block copolymers (P13FMA-*b*-PSA) by solution polymerization and atom transfer radical polymerization (ATRP), respectively. Subsequently, we systematically investigated the effects of sequence structure and 13FMA content on the surface free energy and surface reorganization properties for the different copolymer films, including those comprising P13FMA-*co*-PSA, P13FMA-*b*-PSA and a P13FMA/PSA blend. This work provides an approach for the preparation of fluorinated copolymer films with both low surface free energy and low surface reorganization simultaneously.

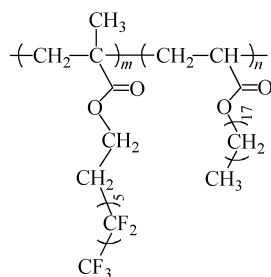
EXPERIMENTAL

Materials

Perfluorohexylethyl methacrylate (13FMA, Sigma-Aldrich) was distilled under reduced pressure in the presence of calcium hydride before use. Stearyl acrylate (SA, Sigma-Aldrich) was dissolved in benzotrifluoride (TFMB) and dried over calcium hydride, then through an activated alumina column before use. Ethyl 2-bromopropanoate (EtBr), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), cuprous bromide (CuBr), tetrahydrofuran (THF), benzotrifluoride (TFMB), dipropylene glycol (DPG), 2,2'-azobis(2-amidinopropane) dihydrochloride (AIBA), 2,2'-azobisisobutyronitrile (AIBN), dodecyl mercaptan (*n*-DM), stearyl trimethyl ammonium chloride (STAC), and polyoxyethylene (20) oleyl ether (POE) were purchased from Sigma-Aldrich and used as received. Deionized water was used for all experiments.

Preparation of Copolymers

The P13FMA and PSA homopolymers were prepared by solution polymerization. P13FMA/PSA represents the mixture of the two homopolymers at different ratios. The random P13FMA-*co*-PSA copolymers were obtained by solution polymerization. The functional PSA-Br and block P13FMA-*b*-PSA copolymers were obtained by atom transfer radical polymerization (ATRP) method. The typical chemical structure is shown in Scheme 1.



Scheme 1 Chemical structure of copolymer representing P13FMA-*co*-PSA and P13FMA-*b*-PSA

Solution Polymerization

The solution polymerization was carried out in TFMB at 70 °C for 18 h, using AIBN as the initiator. Typically, 13FMA (12 g, 27.8 mmol) and SA (28 g, 86.3 mmol) monomer mixture (40 g) was added into TFMB solution (60 g, 410.6 mmol). Afterwards, AIBN (0.4 g, 2.4 mmol) was added into the mixture. Nitrogen was then used to degas the solution, and the reaction mixture was kept under stirring at 70 °C for 18 h. The amount of unreacted monomers was monitored by gas chromatography (GC) and the monomer conversion was more than 99%.

Atom Transfer Radical Polymerization (ATRP)

The functional homopolymer PSA-Br was first prepared by atom transfer radical polymerization (ATRP) and then used as a macroinitiator to prepare block copolymer P13FMA-*b*-PSA. Typically, SA (32.45 g, 100 mmol) and PMDETA (0.346 g, 2 mmol) were dissolved in TFMB (32.45 g, 222 mmol) under a nitrogen atmosphere. Subsequently, CuBr (0.144 g, 1 mmol) was added into the solution, and the mixture was stirred for 10 min at room temperature. Then, the mixture in the Schlenk flask was placed in a thermostated oil bath at 70 °C, and the initiator EtBr (0.181 g, 1 mmol) was added after 1 min to start the polymerization. P13FMA-*b*-PSA was prepared by the similar procedure to PSA-Br. Briefly, 13FMA (18.9 g, 44 mmol) and PMDETA (0.347 g, 2 mmol) were dissolved in TFMB (31.5 g, 216 mmol) under a nitrogen atmosphere. Subsequently, CuBr (0.144 g, 1 mmol) was added into the solution, and the mixture was stirred for 10 min at room temperature. Then, the mixture in the Schlenk flask was placed in a thermostated oil bath at 70 °C, and the initiator PSA-Br (12.6 g, 1 mmol) was added after 1 min to start the polymerization. During the polymerization, samples were taken periodically for GPC and GC analyses. The reaction was stopped by exposing the solution to air, and then the mixture was diluted with THF, filtered through an activated (neutral) alumina column to remove the copper catalyst. The remaining unreacted monomer was removed by precipitation in acetone. The polymers were dried under vacuum at room temperature to a constant mass.

Preparation of Polymer Films

The fluorinated polymer was dissolved in TFMB with a concentration of 1 wt%, and the solution was then filtered using a 0.22 μm nylon filter. A silicon wafer was coated with this solution by the spin-coating method (3000 r/min, 30 s). The film was dried at room temperature for 30 min, and then put into a vacuum oven (−0.95 MPa) at 120 °C for another 12 h. The film thickness was measured to be about 150 nm from a cross-sectional image acquired by scanning electron microscopy (SEM, JSM-7100F, JEOL).

Gas Chromatography (GC)

The amount of unreacted monomers was monitored by gas chromatography (GC, 6890N, Agilent Technologies) with a capillary packed column (30 m × 0.32 mm × 0.50 μm). The column oven was temperature programmed starting with an initial isothermal temperature at 120 °C. Then, the temperature increased with 10 K/min to reach 250 °C, and remained at this temperature for 11 min. The vaporizing chamber and detector temperatures were held at 300 °C. *n*-Dodecane was used as an internal standard. GC measurement was used to control the monomer conversion (more than 98%).

Gel Permeation Chromatography (GPC)

The polymer was dissolved in THF to obtain a solution with 6 wt% solid content, which was passed through a

filter of 0.45 μm to obtain the sample for analysis. The number-average molecular weights (M_n) and molecular weight distributions (PDI) of the copolymers were determined by gel permeation chromatography (GPC), using an Agilent 1260 GPC apparatus with two Styragel columns (TSKgel G4000H_{XL} and TSKgel G3000H_{XL}, TOSOH). THF was used as the eluent at a flow rate of 1.0 mL/min. The narrowly-distributed polystyrene was used as the calibration standards.

Wetting Properties

The static and dynamic contact angles were measured using a drop shape analyzer (DSA 30, KRÜSS GmbH). The static contact angles of water (H_2O) and methylene iodide (CH_2I_2) were measured, in which the volume of each droplet was 2 μL . The surface free energy was calculated from the static contact angles by Eqs. (1) and (2), which was proposed by Owens and Wendt^[38], who extended the Fowkes concept^[39].

$$\gamma_s^d + \gamma_s^p = \gamma_s \quad (1)$$

$$(1 + \cos \theta) \cdot \gamma_l = 2(\gamma_s^d \cdot \gamma_l^d)^{1/2} + 2(\gamma_s^p \cdot \gamma_l^p)^{1/2} \quad (2)$$

where γ_s is the surface free energy of the solid; γ_s^d and γ_s^p represent the solid dispersion force and polar components, respectively. Similarly, γ_l is the surface free energy of the liquid, γ_l^d and γ_l^p represent the liquid dispersion and polar components, respectively. The γ_l^d and γ_l^p values for water are 21.8 and 51.0 mN/m and those of methylene iodide are 50.8 and 0 mN/m, respectively.

The dynamic contact angle was measured when a new boundary surface was formed constantly due to the fact that the drop was enlarged or reduced during the measurement.

When the drop front advances, the angle is called the advancing contact angle (θ_a), and it represents the ability of the liquid to wet the surface. On the contrary, the angle caused by drop front receding is called the receding angle (θ_r), which shows the ability of the liquid to dewet from the surface^[12]. The difference between the advancing and receding angles is referred to as the contact angle hysteresis ($\theta_a - \theta_r$), and it is usually the result of the surface reorganization and surface molecular motion^[2].

Scanning Electron Microscopy (SEM)

The surface morphology of the copolymer film was observed by a field emission scanning electron microscope (FE-SEM) apparatus (JEOL Co., Ltd., JSM-7100F). The coated wafer was cut to a piece of 5 mm $\times$ 5 mm $\times$ 1 mm and attached to an aluminum sample stage with electron conductive paste. Platinum (Pt) was carefully evaporated onto the sample surface. The surface structure was observed at several different magnifications to see the surface morphology and film thickness.

Water Repellency and Oil Repellency

The polymer was diluted with TFMB to a solid content concentration of 1 wt%. A 200 mm $\times$ 200 mm CVC fabric (cotton/polyester, 65/35) was dipped into this solution for about 1 min, and then taken out and dried at 170 $^\circ\text{C}$ for 120 s. The water repellency and oil repellency were assessed by the AATCC 22-2010 and AATCC 118-2007 methods, respectively (AATCC: American Association of Textile Chemists and Colorists).

X-ray Photoelectron Spectroscopy (XPS)

The surface chemical composition of the copolymer film was studied using an XPS instrument (ESCALAB 250Xi, Thermo Fisher). The XPS spectra were recorded with a 400 μm spot size and a monochromatic Al K α X-ray source (1486.6 eV). The X-ray gun was operated at a power of 250 W and the high voltage was kept at 140 kV with a take-off angle of 90 $^\circ$. All the spectra were calibrated by the C_{1s} peak of the C—C bond at 284.6 eV.

Differential Scanning Calorimetry (DSC)

The DSC data of polymer samples (4–10 mg) were obtained from a Q100 instrument (TA). The samples were preheated to 200 $^\circ\text{C}$ to eliminate the effects of thermal history. Subsequently, they were cooled down to -80 $^\circ\text{C}$ and then run from -80 $^\circ\text{C}$ to 180 $^\circ\text{C}$ at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of Fluorinated Copolymers

The monomer conversions and 13FMA contents in a random copolymer P13FMA-*co*-PSA prepared by solution polymerization are shown in Table S1 in the supporting information (SI). Gas chromatography (GC) analysis results showed that the monomers were almost completely converted, and the results of fluorine element analysis showed that the actual contents of 13FMA in the copolymers were consistent with the theoretical values. The number-average molecular weights (M_n) and molecular weight distributions (PDIs) of typical random copolymers are listed in Table S2 (in SI). For the copolymers prepared by solution polymerization, the M_n values were *ca.* 8.00×10^3 g/mol, and the PDIs were in the range of *ca.* 1.73–2.08.

The SA conversions, M_n values and PDIs of PSA-Br prepared by ATRP under different reaction times are shown in Table S3, Figs. S1 and S2 (in SI), which clearly showed that the monomer conversions and molecular weights increased with an increase in the reaction time and also these polymers had relatively low PDIs (1.1–1.3).

As shown in Fig. S3 (in SI), the block copolymer P13FMA-*b*-PSA formed micelles in the THF mobile phase with an elution time of approximately 11.5 min. The actual molecular weight of the polymer was different from the theoretical molecular weight and the polymer was insoluble in the mobile phase under the condition of high fluorine content. So, the GPC measurement was not suitable for characterizing the actual content of the fluorinated monomer in the copolymer.

Table S4 (in SI) summarizes the 13FMA contents of P13FMA-*b*-PSA prepared by ATRP under different reaction time. The fluorine element analysis results showed that the 13FMA monomer contents in the block copolymer increased with an increase in the reaction time and exhibited an approximately linear growth process (Fig. S4 in SI).

Effect of 13FMA Content on Surface Free Energy and Surface Reorganization

To evaluate the surface free energy and surface reorganization of the fluorine-containing random copolymers, the static contact angles of H₂O and CH₂I₂ droplets on the surface of P13FMA-*co*-PSA films were measured. As listed in Table 1, the static contact angles for H₂O and CH₂I₂ increased rapidly with an increase in the 13FMA content up to 30 wt% and thereafter increased more slowly. We further calculated the surface free energy of these copolymers using the Owens and Wendt method. When the 13FMA content increased from 0 wt% to 30 wt%, the surface free energy decreased from 24.9 mJ/m² to 12.2 mJ/m². However, when the 13FMA content increased from 30 wt% to 100 wt%, the surface free energy exhibited only a slight decrease from 12.2 mJ/m² to 9.8 mJ/m². The advancing contact angle (θ_a) exhibited a rapid increase, while the receding angle (θ_r) decreased rapidly when the 13FMA content in the P13FMA-*co*-PSA films increased from 0 wt% to 40 wt%. As a result,

Table 1 Static contact angle, surface free energy and dynamic contact angle of P13FMA-*co*-PSA films ^a as a function of 13FMA content

13FMA (wt%)	Static contact angle ^b (°)		Surface free energy ^c (mN/m)			Dynamic contact angle ^d (°)		
	Water	CH ₂ I ₂	γ_s^d	γ_s^p	γ_s	θ_a	θ_r	$\theta_a - \theta_r$
0	96 ± 1	70 ± 1	22.9	2.1	24.9	100 ± 2	59 ± 2	41
10	103 ± 2	76 ± 1	19.6	1.1	20.7	110 ± 3	55 ± 2	55
20	106 ± 2	86 ± 2	14.6	1.5	16.1	116 ± 3	49 ± 2	67
30	111 ± 3	94 ± 2	11.0	1.2	12.2	125 ± 4	44 ± 3	81
40	114 ± 3	95 ± 1	10.6	0.9	11.4	128 ± 4	28 ± 3	100
50	114 ± 2	97 ± 2	9.9	0.9	10.8	135 ± 4	36 ± 3	99
60	115 ± 3	97 ± 2	9.9	0.8	10.7	120 ± 3	29 ± 2	91
80	116 ± 3	98 ± 2	9.5	0.8	10.2	119 ± 2	32 ± 2	87
100	116 ± 2	99 ± 1	9.0	0.8	9.8	117 ± 2	35 ± 2	82

^a Annealed at 170 °C for 12 h; ^b Static contact angle against water (2 μ L) and methylene iodide (CH₂I₂, 2 μ L) and tested at 10 °C; ^c γ_s^d : dispersion force component; γ_s^p : polar component; γ_s : surface free energy; ^d Dynamic contact angle against water (15 μ L; θ_a : advancing contact angle; θ_r : receding contact angle), measured at 30 °C

the contact angle hysteresis ($\theta_a - \theta_r$) increased from 41° to 100° . These results indicated that the capacity for surface reorganization increased rapidly with an increase in the 13FMA content of P13FMA-*co*-PSA films.

As shown in Fig. 1, we investigated the surface free energy and surface reorganization of P13FMA-*co*-PSA copolymer films with varying 13FMA contents, and found that the polymer films exhibited relatively high surface free energy and low surface reorganization at low 13FMA contents. Conversely, the results for the surface free energy and surface reorganization were different at high 13FMA contents. It should be noted that the surface free energy tended to gradually decrease with an increase in 13FMA content. In contrast, the degrees of surface reorganization increased drastically under the same conditions. Thus, the random P13FMA-*co*-PSA copolymer cannot achieve a low surface free energy and low surface reorganization simultaneously due to their inverse correlation.

We further explored the surface free energy and surface reorganization of the P13FMA-*b*-PSA block copolymer films with different 13FMA contents. As shown in Fig. 2, when the 13FMA content was more than 5 wt%, the surface free energy fell below 10 mN/m, while the random copolymer P13FMA-*co*-PSA required a greater 13FMA content (more than 30 wt%) to obtain the same surface free energy. The dynamic contact angle results implied that the contact angle hysteresis of P13FMA-*b*-PSA changed little with an increase in the 13FMA content and the value remained constant at *ca.* 40° , which was in contrast to the trend for the random copolymer P13FMA-*co*-PSA. This result demonstrated that the 13FMA content of the block copolymers did not affect the stability of the copolymer film.

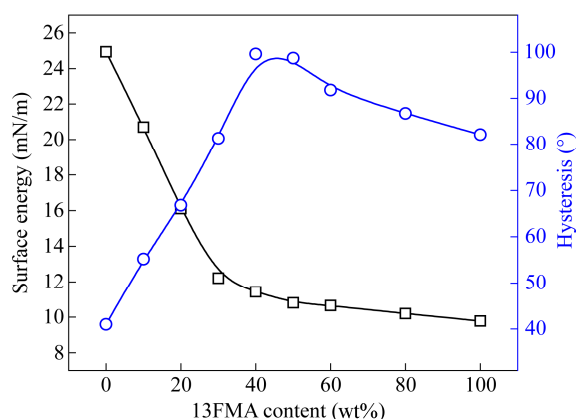


Fig. 1 Surface free energy ($\square$) and contact angle hysteresis ($\circ$) of P13FMA-*co*-PSA films as a function of 13FMA content

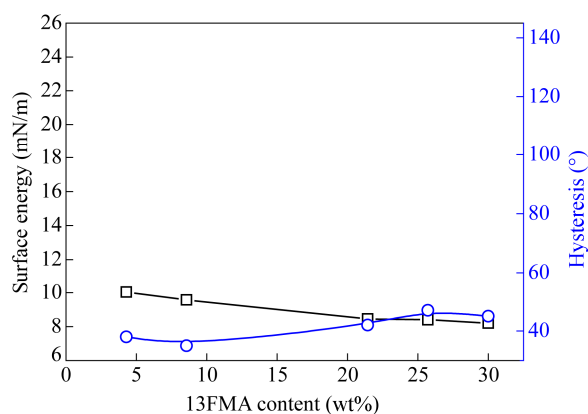


Fig. 2 Surface free energy ($\square$) and contact angle hysteresis ($\circ$) of P13FMA-*b*-PSA films as a function of 13FMA content

Effect of 13FMA Content on Water Repellency and Oil Repellency

The copolymer solutions were applied to the surfaces of CVC fabrics by a dip-coating process. The surface free energy and surface reorganization properties of the processed CVC fabrics were assessed by the AATCC 118 and AATCC 22 methods, respectively. Figure 3 shows the water repellency and oil repellency levels of CVC textiles finished with P13FMA-*co*-PSA, and indicated that the oil repellency of the processed fabrics significantly improved. The oil repellency level improved from 0 (infiltrated by kaydol oil, surface tension 31.2 mN/m) to 6 (not infiltrated by *n*-decane, surface tension 23.5 mN/m) with an increase in 13FMA content. This phenomenon indicated that the surface free energy of the fabric treated with P13FMA-*co*-PSA significantly decreased with an increase in the 13FMA content, which was in accordance with the static contact angle results. However, the water repellency value of the processed CVC fabrics fell from 100 points (no water infiltration or adhesion) to 80 points (infiltrated by water). This result indicated that surface reorganization of the copolymer increased and the surface structural stability deteriorated with an increase in 13FMA content in P13FMA-*co*-PSA. This reverse variation of water repellence and oil repellence was in accordance with the trend in Fig. 1.

The water repellency and oil repellency of the CVC fabrics treated by P13FMA-*b*-PSA block copolymer

solutions are shown in Fig. 4. It is evident from Fig. 4 that the finished fabrics had a high oil repellency level (*ca.* 5) even at low fluorine content. In addition, the water repellency properties exhibited no decline, and remained constant at 100 points with an increase in 13FMA content. Thus, the fluorine-containing block copolymers achieved good water repellency and oil repellency simultaneously. The variation of the water and oil repellency for P13FMA-*b*-PSA was fully consistent with the results shown in Fig. 2.

Figure 5 intuitively shows the effect of 13FMA content on the water/oil repellent properties of CVC textiles finished with P13FMA-*co*-PSA and P13FMA-*b*-PSA copolymers.

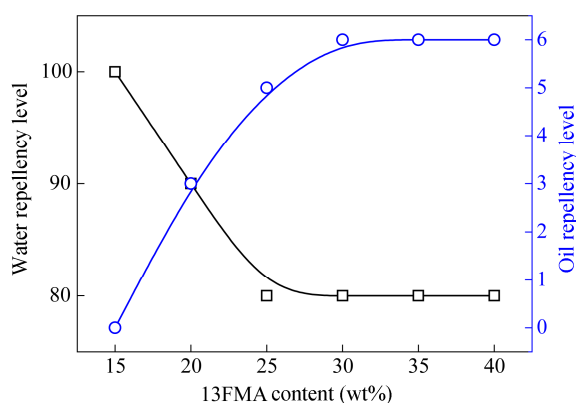


Fig. 3 Water repellency level (□) and oil repellency level (○) of CVC textiles treated with P13FMA-*co*-PSA as a function of 13FMA content at 30 °C

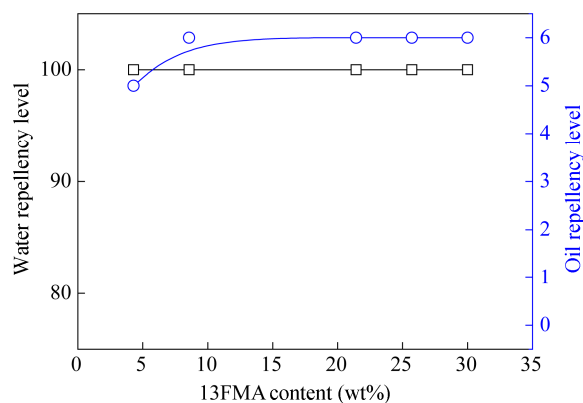


Fig. 4 Water repellency level (□) and oil repellency level (○) of CVC textiles treated with P13FMA-*b*-PSA as a function of 13FMA content at 30 °C

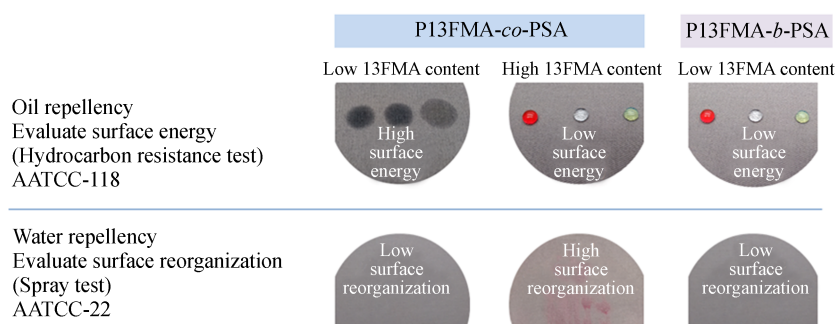


Fig. 5 Effect of 13FMA content on the water/oil repellent properties of CVC textiles finished with P13FMA-*co*-PSA and P13FMA-*b*-PSA copolymers (The online version is colorful.)

Chemical Composition of Fluorinated Copolymer Films

It is well known that the wetting behaviour of a polymeric film surface is dependent on its physical roughness and chemical structure^[40]. The surface roughness of the films obtained by spin-coating was investigated by SEM and AFM techniques. The results showed that all the films possessed smooth and flat surfaces, with R_a values (an arithmetical mean deviation of the profile) less than 0.5 nm, indicating that the effect of surface roughness was negligible^[41]. Therefore, as shown in Table 1, the differences in contact angles were mainly caused by the chemical structures on the surface of the polymeric films.

The chemical composition of the topmost surface region was quantitatively analysed by XPS, as shown in Fig. 6. The F_{1s}/C_{1s} ratios of the random and block copolymer films were much higher than those of the bulk polymers owing to the surface enrichment effect of the perfluoroalkyl segments. The F_{1s}/C_{1s} value for the P13FMA-*co*-PSA copolymer was 0.92 at a 13FMA content of 30 wt%, which was close to the value for P13FMA homopolymer (*ca.* 1.08). Thus, P13FMA-*co*-PSA and P13FMA homopolymer had the same surface free energy when the 13FMA content in P13FMA-*co*-PSA was more than 30 wt%, as shown in Fig. 1. The

F_{1s}/C_{1s} ratio for P13FMA-*b*-PSA was much higher than that for P13FMA-*co*-PSA at the same 13FMA content. This result indicated that the block copolymer was more conducive to the surface enrichment of fluoroalkyl groups, and had a lower surface free energy and better oil repellency. Similar results have been reported previously^[42–44].

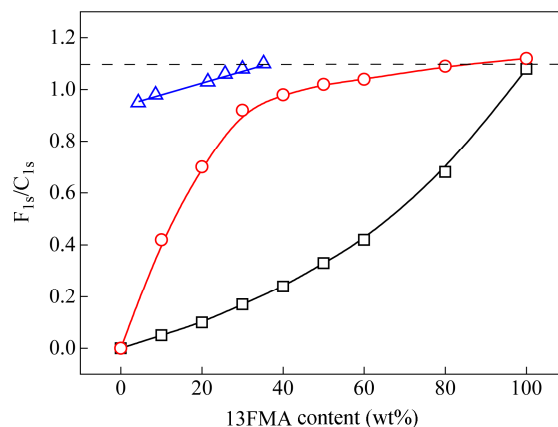


Fig. 6 F_{1s}/C_{1s} ratio determined by XPS at the surface as a function of 13FMA content in copolymer films: (○) P13FMA-*co*-PSA, (△) P13FMA-*b*-PSA, (□) bulk copolymer P13FMA-*co*-PSA (*i.e.* not a thin film)

In the above-mentioned study, the fluorine contents of the copolymer films were much higher than those in the corresponding bulk polymers owing to the surface enrichment effect of the perfluoroalkyl segments. The block copolymer contained more continuous 13FMA segments statistically and was better than a random copolymer in fluoroalkyl micro-phase separation and surface enrichment. Therefore, it exhibited a higher utilization of fluorine atoms and lower surface free energy at the same fluorine concentration.

Temperature Dependence of Surface Reorganization

The temperature dependence of the receding contact angle (θ_r) for P13FMA-*co*-PSA, P13FMA, P13FMA-*b*-PSA and PSA films is shown in Fig. 7. When the test temperature was below 17 °C, the θ_r values for all polymers were higher than 75°. However, the θ_r values began to decrease drastically at 17, 27 and 45 °C for the P13FMA-*co*-PSA, P13FMA and P13FMA-*b*-PSA films, respectively, with an increase in temperature. These temperatures approximately agreed well with the glass transition temperature (T_g) or melting temperature (T_m) determined by DSC measurements, as shown in Table 2. Thus, it is considered that the T_g or T_m values of the polymers play a decisive role in the change of θ_r value. The fluorine-containing groups will migrate into the polymer interior and the non-fluorine groups move to the interface to reduce the interfacial free energy when the fluorine-containing

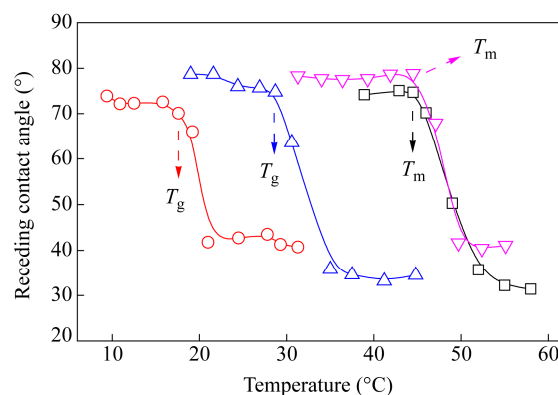


Fig. 7 Effect of temperature on the receding contact angle (θ_r) for different copolymer films: (○) P13FMA-*co*-PSA, (△) P13FMA, (▽) P13FMA-*b*-PSA and (□) PSA

Table 2 Glass transition temperature (T_g) and melting temperature (T_m) of polymers, determined by DSC measurement

Sample	T_g (°C)	T_m (°C)
P13FMA- <i>co</i> -PSA ^a	19	41
P13FMA- <i>b</i> -PSA ^b	28	47
P13FMA	34	—
PSA	—	48

^a 13FMA content was 31.7 wt%; ^b 13FMA content was 30.3 wt%

copolymer is in contact with the liquid. When the test temperature was above the T_g or T_m of the polymer, the polymer segment mobility on the surface got increased, leading to a rapid decrease in the θ_t value.

Notably, some researches have indicated that the crystallization of the SA side chain improved surface structural stability^[26, 31, 32]. In this paper, comparing the mutational point temperature for θ_t of P13FMA-*co*-PSA and P13FMA-*b*-PSA, we found that the crystallization of the SA side chain had a different effect on the surface reorganization in the two copolymer structures. The mutational point for P13FMA-*co*-PSA corresponded to its T_g value, while it corresponded to T_m for P13FMA-*b*-PSA.

DSC measurements were carried out to study the crystallization behaviour of SA in the polymer and further investigate the effect of crystallization of SA side chains on the surface structural stability of the random and block copolymers. By plotting the melting enthalpy (ΔH_m) of the random and block copolymers normalized with the melting enthalpy of the PSA homopolymer ($\Delta H_m(\text{PSA})$) in Fig. 8, it is clearly shown that the fluorinated monomer perturbed the crystallinity of the SA by decreasing the melting enthalpy more than the 13FMA mass fraction in P13FMA-*co*-PSA. However, the crystallinity of SA for P13FMA-*b*-PSA correlated well with the estimated SA content. Compared with P13FMA-*co*-PSA, P13FMA-*b*-PSA had a higher crystallinity for the same 13FMA content.

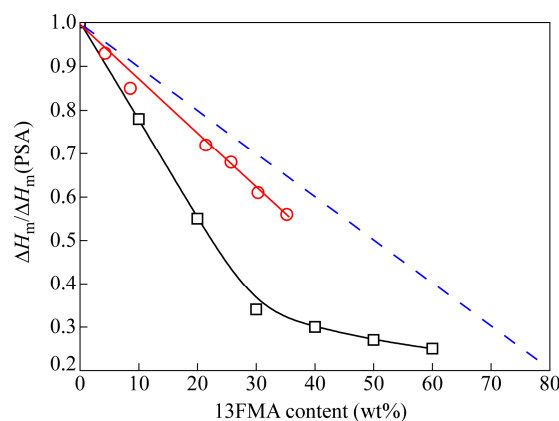
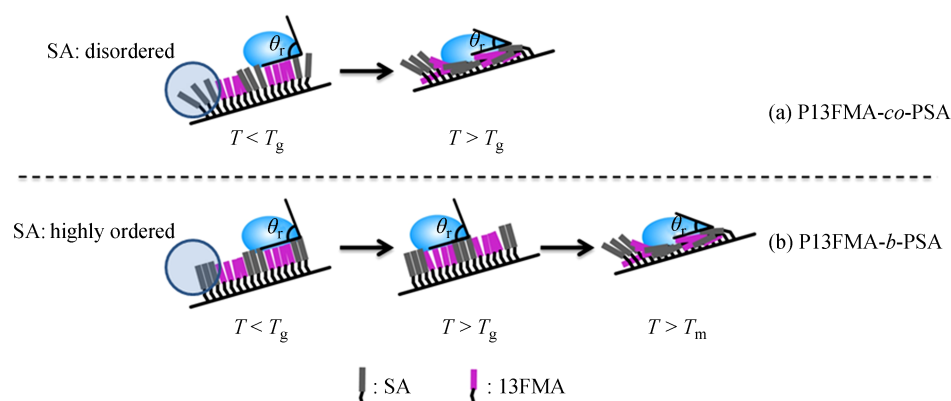


Fig. 8 Effect of 13FMA content on the crystallinity of SA for different copolymers ($\square$) P13FMA-*co*-PSA, ($\circ$) P13FMA-*b*-PSA. Straight dashed line shows the linear decrease in melting enthalpy with the increase of 13FMA content.

Based on the results in Table 1, Fig. 7 and Fig. 8, we identified the influence of temperature on the surface reorganization of P13FMA-*co*-PSA. Although the dynamic contact angle test temperature (30 °C) was above its T_g value, the SA segment remained relatively high crystallinity (*ca.* 55%) when the 13FMA content was less than 20 wt%. This results in inhibition of the surface reorganization of the fluorinated segments and the contact angle hysteresis being maintained at about 67°. When the 13FMA content was more than 20 wt%, the degree of crystallinity of the SA was significantly reduced and failed to effectively suppress the surface reorganization of the fluorinated segments, leading to a sudden increase in the contact angle hysteresis to *ca.* 100°. In contrast, the SA retained a relatively high degree of crystallinity with an increase in 13FMA content for P13FMA-*b*-PSA, which effectively inhibited the surface reorganization of fluorinated segments.

The impact of SA crystallinity on the surface structural stability is illustrated in Scheme 2. The SA segments were in a disordered phase because of their low degree of crystallinity in the random P13FMA-*co*-PSA copolymer. As the test temperature was higher than the T_g of the copolymer, the fluoroalkyl side chain and SA side chain could move freely, resulting in enhanced surface reorganization and decreased water resistance. In the block copolymer, the SA segments still retained a high degree of crystallinity, even when the test temperature was above its T_g . Thus, the movement of the fluoroalkyl side chains was hindered by crystallized SA, and the surface reorganization was not so significant. When the temperature rose to above T_m , the crystallization of the SA side chains was disrupted, resulting in the enhanced surface reorientation and significantly decreased waterproof performance. The water repellency decreased from 90 points to 60 points when the temperature was above the T_m , which further indicates that the crystalline structure of SA plays a positive role in the surface structural stability (Fig. 9).



Scheme 2 Schematic representation of the temperature dependence of surface reorganization for (a) P13FMA-*co*-PSA and (b) P13FMA-*b*-PSA (The online version is colorful.)

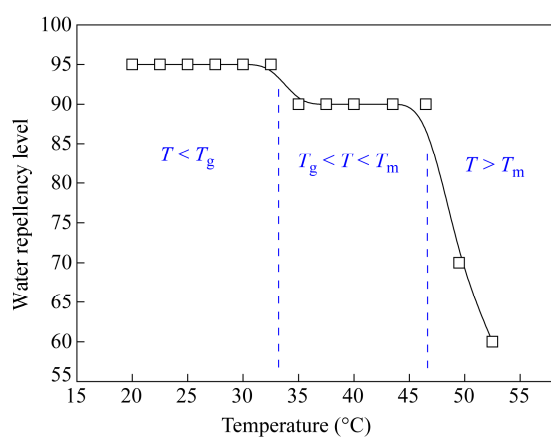


Fig. 9 Water repellency levels of CVC textiles treated with P13FMA-*b*-PSA as a function of temperature

Morphologies of the Polymer Films

A relatively continuous arrangement of 13FMA and SA units helps to achieve a stable low surface free energy at relatively low fluorine contents. Based on this theory, a blend of homopolymer P13FMA and homopolymer PSA (P13FMA/PSA) should achieve a more stable low surface free energy. The morphologies of various polymer films were observed by SEM measurement. Figure 10 shows SEM images of different polymer films finished with P13FMA-*co*-PSA, P13FMA-*b*-PSA, P13FMA, P13FMA/PSA and PSA. Remarkably, the surfaces of the block and random copolymer films were smooth and uniform (Figs. 10a and 10b), whereas on the film of the mixed homopolymer system, many circular hydrocarbon polymer ‘islands’ were enclosed in the fluorocarbon

polymer ‘sea’ and formed a ‘sea-island structure’ at the micrometre scale (Fig. 10d). This phenomenon can be attributed to the surface free energy difference of P13FMA and PSA and the formation of macro-phase separation^[29]. Fluoroalkyl groups are unable to completely cover the whole film surface with the existence of the sea-island structure in the blend system, hence it was difficult to obtain a homogeneous low surface free energy on the mixed polymer film.

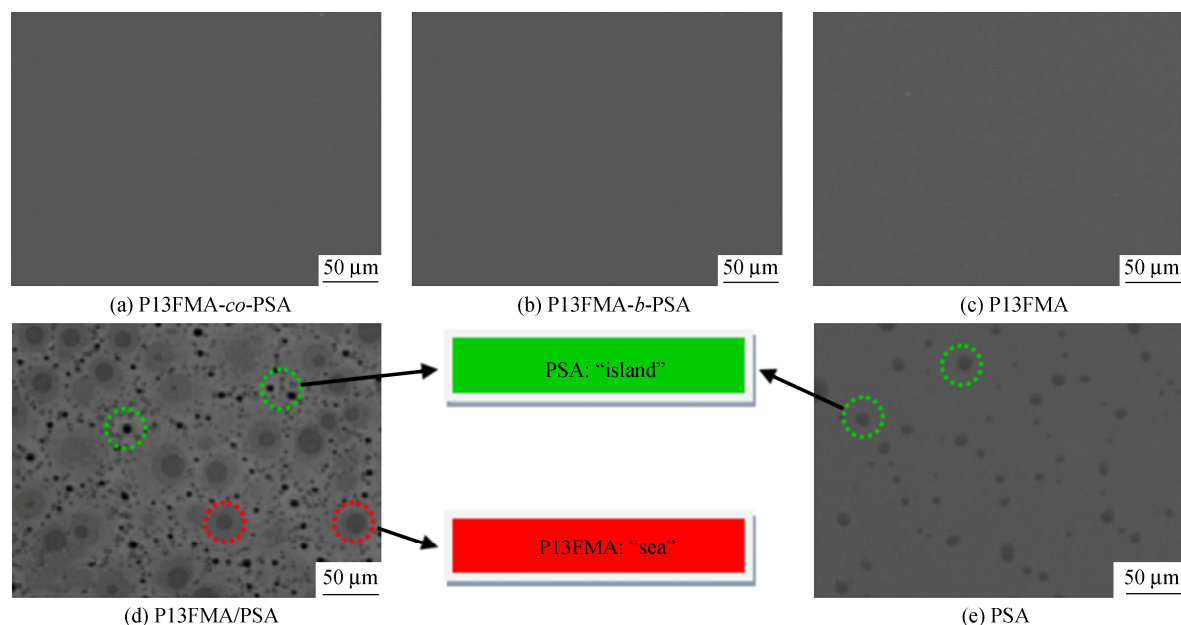


Fig. 10 Surface features of polymer films observed by SEM (The 13FMA contents in (a), (b) and (d) are 50 wt%). (The online version is colorful.)

CONCLUSIONS

The effects of sequence structure and 13FMA content on the surface free energy and surface reorganization of fluorinated methacrylate polymers based on 13FMA and SA were systematically studied. For the random copolymer P13FMA-co-PSA, the surface free energy and surface reorganization exhibit an inverse variation with increasing 13FMA content, and thus this kind of polymer cannot achieve low surface free energy and low surface reorganization simultaneously. There is a more continuous arrangement of 13FMA and SA segments in the block copolymer P13FMA-b-PSA; the consecutive 13FMA segments can obtain a lower surface free energy at the same 13FMA content and the consecutive SA chains can enhance the crystallinity of the SA segments and hinder the surface reorganization of the perfluoroalkyl groups. Thus, P13FMA-b-PSA can achieve low surface free energy and low surface reorganization simultaneously.

REFERENCES

- 1 Nishino, T., Meguro, M., Nakamae, K., Matsushita, M. and Ueda, Y., *Langmuir*, 1999, 15: 4321
- 2 Honda, K., Morita, M., Sakata, O., Sasaki, S. and Takahara, A., *Macromolecules*, 2010, 43: 454
- 3 Sung, L.P., Gu, X.H., Ho, D.L., Landis, F.A. and Nguyen, D., *Chinese J. Polym. Sci.*, 2009, 27(1): 59
- 4 Liu, M.F., Chen, Y.L., Zhang, C. and Bo, Z.S., *Chinese J. Polym. Sci.*, 2012, 30(2): 308
- 5 Martinelli, E., del Moro, I., Galli, G., Barbaglia, M., Bibbiani, C., Mennillo, E., Oliva, M., Pretti, C., Antonioli, D. and Laus, M., *ACS Appl. Mater. Interfaces*, 2015, 7: 8293
- 6 Smith, D.W., Iacono, S.T. and Iyer, S.S., "Handbook of fluoropolymer science and technology", John Wiley & Sons, New Jersey, 2014

- 7 Yagüe, J.L. and Gleason, K.K., *Macromolecules*, 2013, 46: 6548
- 8 Yamashita, T., Yamamoto, I. and Morita, M., *J. Photopolym. Sci. Technol.*, 2012, 25: 207
- 9 Dikić, T., Ming, W., van Benthem, R.A.T.M., Esteves, A.C.C. and de With, G., *Adv. Mater.*, 2012, 24: 3701
- 10 Morita, M., Kinoshita, Y., Adachi, Y., Yamashita, T. and Yamamoto, I., *J. Photopolym. Sci. Technol.*, 2011, 24: 401
- 11 Huang, P.Y., Chao, Y.C. and Liao, Y.T., *J. Appl. Polym. Sci.*, 2007, 104: 2451
- 12 Anton, D., *Adv. Mater.*, 1998, 10: 1197
- 13 Shimizu, T., "Fluorinated acrylic ester polymers", in "Modern fluoropolymers: High performance polymers for diverse applications", Ed. by Scheirs, J., John Wiley & Sons, New York, 1997, p. 516
- 14 Zhang, Q.H., Wang, Q.Y., Jiang, J.X., Zhan, X.L. and Chen, F.Q., *Langmuir*, 2015, 31: 4752
- 15 Ozbay, S. and Erbil, H.Y., *Colloids Surf., A*, 2014, 52: 9
- 16 Valtola, L., Hietala, S., Tenhu, H., Denifl, P. and Wilen, C.E., *Polym. Adv. Technol.*, 2009, 20: 225
- 17 Saïdi, S., Guittard, F., Guimon, C. and Gëribaldi, S., *Eur. Polym. J.*, 2006, 42: 702
- 18 Huang, P.Y., Chao, Y.C. and Liao, Y.T., *J. Appl. Polym. Sci.*, 2006, 100: 4711
- 19 Saïdi, S., Guittard, F., Guimon, C. and Gëribaldi, S., *Macromol. Chem. Phys.*, 2005, 206: 1098
- 20 Ha, J.W., Park, I.J. and Lee, S.B., *Macromolecules*, 2005, 38: 736
- 21 Huang, P.Y., Chao, Y.C. and Liao, Y.T., *J. Appl. Polym. Sci.*, 2004, 94: 1466
- 22 Thomas, R.R., Anton, D.R., Graham, W.F., Darmon, M.J., Sauer, B.B., Stika, K.M. and Swartzfager, D.G., *Macromolecules*, 1997, 30: 2883
- 23 Gu, Z.X., Zhang, M.Z., He, J.L. and Ni, P.H., *Colloids Surf. A: Physicochem. Eng. Aspects*, 2016, 502: 159
- 24 Prasad, S., Hanne, L. and Dhinojwala, A., *Macromolecules*, 2005, 38: 2541
- 25 Zhang, Q.H., Wang, Q.Y., Zhan, X.L. and Chen, F.Q., *Ind. Eng. Chem. Res.*, 2014, 53: 8026
- 26 Fujimori, A., Hoshizawa, H., Kobayashi, S., Kanai, K., Ouchi, Y. and Seki, K., *J. Polym. Sci., Part B: Polym. Phys.*, 2008, 46: 534
- 27 Huang, J.Q., Meng, W.D. and Qing, F.L., *J. Fluorine Chem.*, 2007, 128: 1469
- 28 Hartmann, P., Collet, A. and Viguièr, M., *Macromolecules*, 2006, 39: 6975
- 29 Fujimori, A., Masuya, R., Masuko, T., Ito, E., Hara, M., Kanai, K., Ouchi, Y., Seki, K. and Nakahara, H., *Polym. Adv. Technol.*, 2006, 17: 653
- 30 Ha, J.W., Park, I.J., Kim, D.K., Kim, J.H. and Lee, S.B., *Surf. Sci.*, 2003, 532-535: 328
- 31 de Crevoisier, G., Fabre, P., Leibler, L., Tencé-Girault, S. and Corpart, J.M., *Macromolecules*, 2002, 35: 3880
- 32 Morita, M., Ogisu, H. and Kubo, M., *J. Appl. Polym. Sci.*, 1999, 73: 1741
- 33 Alig, I., Jarek, M. and Hellmann, G.P., *Macromolecules*, 1998, 31: 2245
- 34 Pérez, F., Nadal, M., Navarro-Ortega, A., Fàbrega, F., Domingo, J.L., Barceló, D. and Farré, M., *Environ. Int.*, 2013, 59: 354
- 35 Frömel, T. and Knepper, T.P., "Biodegradation of fluorinated alkyl substances", in "Reviews of environmental contamination and toxicology", Ed. by de Voogt, P., Springer, New York, 2010, p. 161
- 36 Chengelis, C.P., Kirkpatrick, J.B., Myers, N.R., Shinohara, M., Stetson, P.L. and Sved, D.W., *Reprod. Toxicol.*, 2009, 27: 400
- 37 Wen, X.F., Ye, C., Cai, Z.Q., Xu, S.P., Pi, P.H., Cheng, J., Zhang, L.J. and Qian, Y., *Appl. Surf. Sci.*, 2015, 339: 109
- 38 Owens, D.K. and Wendt, R.C., *J. Appl. Polym. Sci.*, 1969, 13: 1741
- 39 Fowkes, F.M., *Ind. Eng. Chem.*, 1964, 56: 40
- 40 Bellanger, H., Darmanin, T., de Givenchy, T.E. and Guittard, F., *Chem. Rev.*, 2014, 114: 2694
- 41 Busscher, H.J., van Pelt, A.W.J., de Boer, P., de Jong, H.P. and Arends, J., *Colloids Surf.*, 1984, 9: 319
- 42 Urushihara, Y. and Nishino, T., *Langmuir*, 2005, 21: 2614
- 43 Nishino, T., Urushihara, Y., Meguro, M. and Nakamae, K., *J. Colloid Interf. Sci.*, 2004, 279: 364
- 44 Hikita, M., Tanaka, K., Nakamura, T., Kajiyama, T. and Takahara, A., *Langmuir*, 2004, 20: 5304