Preparation and Surface Properties of Core-Shell Polyacrylate Latex Containing Fluorine and Silicon in the Shell

Xinyan Xiao, Rui Xu

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

ABSTRACT: The core-shell polyacrylate latex particles containing fluorine and silicon in the shell were successfully synthesized by a seed emulsion polymerization, using methyl methacrylate (MMA) and butyl acrylate (BA) as main monomers, dodecafluoroheptyl methacrylate (DFMA), and γ-(methacryloxy) propyltrimethoxy silane (KH-570) as functional monomers. The influence of the amount of fluorine and silicon monomers on the emulsion polymerization process and the surface properties of the latex films were discussed, and the surface free energy of latex films were estimated using two different theoretical models. The emulsion and its films were characterized by particle size distribution (PSD) analysis, transmission electron microscopy (TEM), Fourier transform infrared spectrum (FTIR), nuclear magnetic resonance (^{1}H-NMR and ^{19}F-NMR) spectrometry, contact angle (CA) and X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), and thermogravimetry (TG) analysis. The results indicate that the average particle size of the latex particles is about 160 nm and the PSD is narrow, the synthesized latex particles exist with core-shell structure, and a gradient distribution of fluorine and silicon exist in the latex films. In addition, both the hydrophobicity and thermal stability of the latex films are greatly improved because of the enrichment of fluorine and silicon at the film-air interface, and the surface free energy is as low as 15.4 mN/m, which is comparable to that of polytetrafluoroethylene (PTFE). © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1576–1585, 2011

Key words: core-shell emulsion polymerization; fluorine and silicon; low surface free energy; gradient coatings; hydrophobicity

INTRODUCTION

The bionic superhydrophobic films, which refer to these on which the water contact angles (CA) are larger than 150° and the sliding angles are less than 10°, have aroused much interest recently due to their outstanding properties of low flow resistance and self-cleaning.[1] These coating films with superhydrophobic properties can be widely used in industrial applications and daily life, such as stain resistant/water resistant protective coatings and anti-snow/anti-icing windows and antenna. The polymer containing fluorine and silicon have been widely used as hydrophobic coatings due to its low surface free energy and admirable comprehensive properties, such as water and oil repellency, high mechanical and thermal stability, chemical inertness, biocompat-ibility, and low friction coefficient. How to improve the surface properties by advanced polymerization technique and surface modification method is the key to prepare advanced functional coatings. Qu et al.[2] prepared composite particles with core-shell structure resulting from the combination of silica seed and hydrophobic copolymer by emulsion polymerization, which is useful for preparing high performance hydrophobic coating. Dai et al.[3] reported a novel core-shell fluorinated acrylic and siliconated polyurethane (FSiPUA) hybrid emulsion which was synthesized by a seed emulsion polymerization. The results showed that the water and the oil repellency for FSiPUA had been improved significantly with a suitable content of fluorine and siloxane. Liang et al.[4] synthesized three core-shell fluoroacrylate copolymer latexes with different fluorinated side chain structure by semi-continuous seed emulsion polymerization, which exhibited not only better surface property as increasing temperature but also better thermal stability.

On the basis of previous research,[5,6] the core-shell emulsion polymerization and self-assembly gradient technique were combined to prepare a novel coatings with better water repellency and thermal stability, using methyl methacrylate (MMA) and butyl
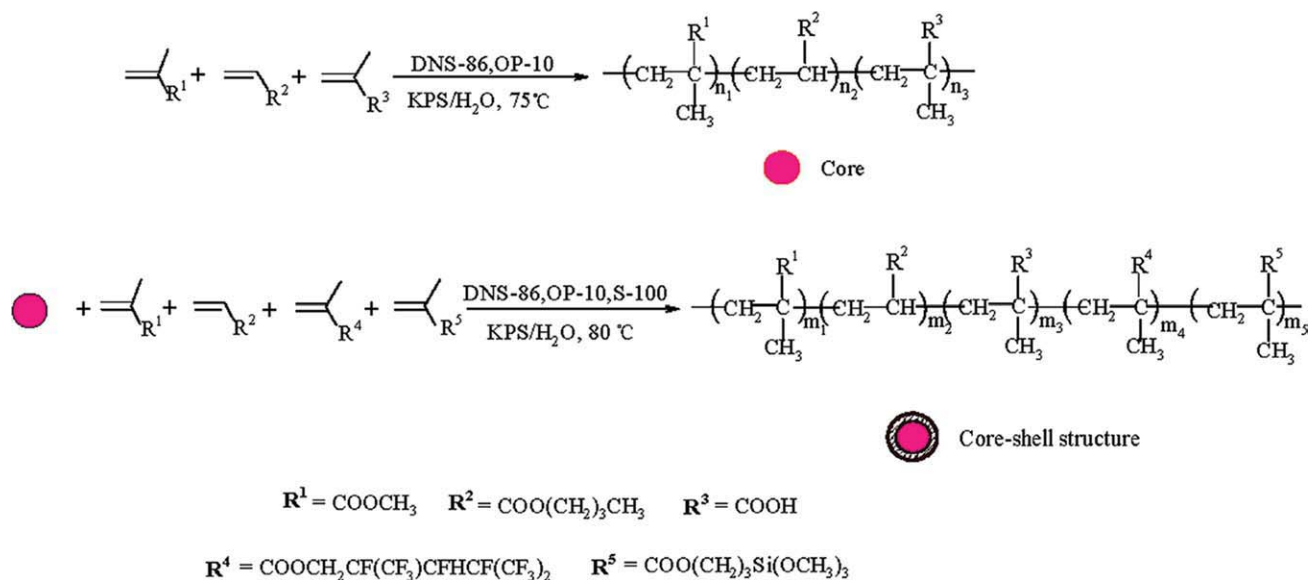
Scheme 1 The synthetic routes of polyacrylate emulsion containing fluorine and silicon. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

acrylate (BA) as main monomers, dodecafluoroheptyl methacrylate (DFMA) and γ-(methacryloxy) propyltrimethoxy silane (KH-570) as functional monomers. The influences of the amount of fluorine and silicon monomers on the emulsion polymerization process and the surface properties of latex films were discussed, and the surface free energy of latex films were estimated using two classical theoretical models. Further, the hydrophobicity and thermal stability of the latex films were investigated by CA and thermogravimetry analysis.

EXPERIMENTAL

Materials

DFMA, were obtained from XEOGIA Fluorine-Silicon Chemical Company, Harbin, China, DFMA was consisted of $CH_2C(CH_3)COOCH_2CF(CF_3)CHFCF(CF_3)_2$ and $CH_2C(CH_3)COOCH_2CF(CF_2CF_3)CH(CF_3)_2$, both of them are isomeric compounds. Sulphonate anionic fluorosurfactant (S-100: $R_fOC_6H_4SO_3Na$) were obtained from XEOGIA Fluorine-Silicon Chemical Company, Harbin, China. MMA, BA, and methacrylic acid (MAA), analytical pure, were obtained from Yuanli Chemical Company, Tianjin, China. The emulsifier ammonium allyloxtmethylate nonylphenol ethoxylates sulfate (DNS-86) was purchased from Guangzhou Shuangjian Trading Company, China. γ-(methacryloxy) propyltrimethoxy silane (KH-570: $CH_2C(CH_3)COO(CH_2)_3Si(OCH_3)_3$), used as crosslinking reagent, was purchased from Zhongguanmei Trading Company, Guangzhou, China. Toctylphenol polyoxyethylene ether (OP-10) as nonionic emulsifier, potassium persulfate (KPS) as initia-

tor and sodium bicarbonate ($NaHCO_3$) as buffering reagents, analytical pure, were used as received. The water used in this experiment was distilled followed by deionization.

Synthesis of fluorine and silicon-containing polyacrylate emulsion

The polyacrylate emulsion containing fluorine and silicon was synthesized as follows: (in Scheme 1).

First, the emulsifier mixture (containing 2.0 g DNS-86, 1.0 g OP-10, 0.2 g S-100, and deionized water 40.0 g) was prepared through magnetic stirring in a 100 mL beaker. Here, ammonium allyloxtmethylate nonylphenol ethoxylates sulfate (DNS-86), used as reactive anionic emulsifier, can react with monomers and become a part of the copolymers, which decreases the negative effects of general emulsifiers on the nature of the latex films. Toctylphenol polyoxyethylene ether (OP-10), used as nonionic emulsifier, can enhance emulsion polymerization stability. Sulphonate anionic fluorosurfactant (S-100), used as fluorosurfactant, can reduce surface tension and solubility in aqueous environments of fluorinated monomer.

Second, the core phase (containing MMA 15.0 g, BA 45.0 g, MAA 3.0 g, deionized water 40.0 g, and 1/3 of emulsifier mixture) and the shell phase (containing MMA 30.0 g, BA 10.0 g, DFMA 16.0 g, KH-570 5.0 g, deionized water 40.0 g, and 1/3 of emulsifier mixture) were introduced into a 500 mL four-necked flask with mechanical stirrer and pre-emulsified for about 1 h respectively.

Third, 1/3 of the emulsifier mixture, buffering solution ($NaHCO_3$), 1/2 of the core phase pre-

TABLE I
The Average Particle Size and Monomer Conversion of the Latex Samples

Sample	DFMA (% w/w[a])	KH-570 (% w/w[a])	Solid content (%)	Average particle size (nm)	Polydispersity index	Monomer conversion (%)
1	0	0	40.1	144	0.017	96.6
2	4	0	44.6	158	0.023	98.1
3	8	0	45.5	155	0.014	98.6
4	12	0	43.2	152	0.022	98.3
5	16	0	45.8	156	0.029	98.5
6	20	0	44.7	149	0.031	97.3
7	16	3	42.1	161	0.047	96.3
8	16	5	43.6	163	0.038	96.5
9	16	7	40.7	174	0.068	93.1

[a] % w/w indicates the mass ratio of DFMA or KH-570 to total monomer.

emulsion and 1/3 of KPS solution (KPS 0.80 g and deionized water 40.0 g) were fed into the four-necked flask equipped with reflux condenser, mechanical stirrer, dropping funnels, and inlet for nitrogen with a stirring rate of 210 rpm. The emulsion polymerization took place after the mixture was heated to 75°C in the water bath. Then 1/3 of KPS solution and the rest of the core phase pre-emulsion were dropped into the four-neck flask in 2 h, respectively. The emulsion polymerization was carried out at 80°C for 1 h after KPS and the core phase pre-emulsion was dropped completely. The shell pre-emulsion and the rest of KPS solution were dropped into the flask in 3 h, while the emulsion polymerization was taking place at 85°C for another 1 h.

At last, the synthesized emulsion was cold to 40°C, and then ammonia was dropped into the synthesized emulsion to control the pH value of emulsion in the range of 6–7.[7]

Table I lists the resulting solid content, average particle size, and monomer conversion of the latex samples.

Characterization

Two to three gram of emulsion was cast onto a glass plate and dried at 80°C until constant weight was obtained. The solid content and monomer conversion of the latex were calculated by the following equations, respectively:

$$\text{Solid content (wt\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\% \quad (1)$$

where W_0 is the weight of the petri dish, and W_1 and W_2 are the weights of emulsion before and after drying to the constant weight, respectively.

$$\text{Conversion (wt\%)} = \frac{\text{Solid content(wt\%)} \times (W_3 - W_4)}{W_5}$$
$$\times 100\% \quad (2)$$

where W_3 is the total weight of all the constitutes put in the flask before polymerization, W_4 is the weight of the constitutes that could not volatilize during the drying period, and W_5 is the total weight of the monomers.

The particle size and polydispersity of the latexes were measured by means of light scattering using ZS Nano S particle sizer (Malvern Instruments, UK). Samples were diluted with distilled water into an appropriate concentration as indicated by the instrument.

The morphology of the latex particles were observed on a transmission electron microscope (TEM, JEM-100CXII, Japan) using 2% aqueous phosphortungstic acid as a staining agent.

Fourier transform infrared (FTIR) spectra of KBr powder-pressed pellets were recorded on a Tensor 27 (Germany) fourier transform infrared spectrometer in the range from 4000 to 400 cm^{-1} in transmission.

^{1}H-NMR and ^{19}F-NMR spectra were recorded on a VNS-400 nuclear magnetic resonance apparatus (Varian Company), and the sample was dissolved in deuterated reagent CDCl$_3$.

CA experiments were carried out on a DATA-PHYSICS CA goniometer (OCA20, Germany) with the plate method at 25°C with deionized water and diiodomethane. Reported CA for the latex films were averages of five measures with 1–2° accuracy.

The X-ray photoelectron spectra (XPS) analysis was performed on an ESCALAB250 (UK) with Al Kα (X-ray) lamp-house. The dry latex film was prepared on the clean glass surface by removing all the water and moisture under vacuum condition at room temperature. The forceps was used to peel off the film from glass substrate in dust-free room, and the resulted film for XPS analysis was about 240 μm. The compositions of film-air and film-glass interfaces were determined by XPS, respectively.

The glass transitions temperatures (T_g) of copolymer were measured by NETZSCH 204 differential scanning calorimeter (NETZSCH Company,
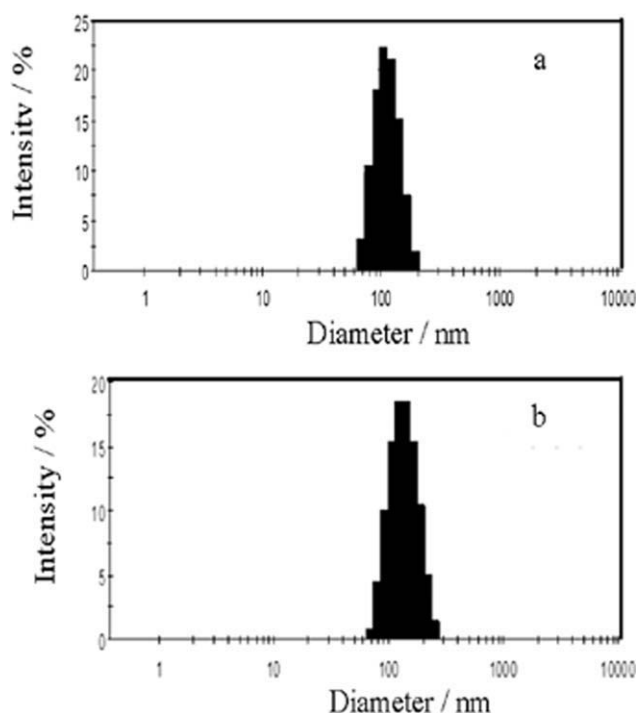
Figure 1 PSD of the core latex (a) and the final core-shell latex (b).

Germany) under nitrogen atmosphere at a heating rate of 20°C min^{-1} from -60 to 100°C.

Thermogravimetry (TG) analysis was performed with NETZSCH STA 449C under the nitrogen atmosphere at a heating rate of 10°C min^{-1} in the range of 35–550 °C.

Surface free energy calculation

It is well-known that Young[8] equation [eq. (3)] could be applied to describe the CA of pure liquids on a solid, and Neumann et al.[9] derived an equation-of-state for solid–liquid interfacial tension later [eq. (4)]. By combining Young equation with Neumann's equation, the surface free energy of a solid γ_S could be evaluated from a single measurement of CA of a liquid with a known surface tension γ_L.

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \tag{3}$$

$$\gamma_{SL} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L \gamma_S} e^{-\beta(\gamma_L - \gamma_S)^2} \tag{4}$$

where γ_L is the experimentally determined surface free energy of the liquid, Θ is the CA, γ_S is the surface free energy of the solid, γ_{SL} is the solid–liquid interfacial energy, and β is an empirical constant with an average value of 0.0001057 [(m^{2}mJ^{-1})^2].

It is accepted widely that the intermolecular energy between two materials results from the summation of a dispersion component and a polar component.[10] As the surface free energy is proportional

to the intermolecular energy, the surface free energy γ can be considered as a sum of a dispersion component γ^d and a polar component γ^p. The total surface free energy of the latex films and its components were calculated according to Fowkes' equation[11] [eq. (5)], by measurement of the water CA and the diiodomethane CA, in which the polar and dispersion components of surface tensions are known.

$$\gamma_L(1 + \cos \theta) = 2\left(\sqrt{\gamma_s^d \gamma_L^d} + \sqrt{\gamma_s^p \gamma_L^p}\right) \tag{5}$$

where γ_L is the surface tension of wetting liquid, and γ_L^d and γ_L^p are the dispersive and polar components, respectively. γ_s^d and γ_s^p are the dispersive and polar components for the latex film, respectively. The total surface energy γ_s is the sum of γ_s^d and γ_s^p.

RESULTS AND DISCUSSION

PSD and TEM micrograph of the latex particles

Figure 1 shows the particle size distribution (PSD) by intensity of the core latex and the core-shell latex of sample 5. The Z-average particle size of the final core-shell latex (156 nm) is bigger than that of the core latex (105 nm), and the polydispersity indexes for the prepared latex samples (in Table I) are less than 0.08. The designed latex with core-shell structure and similar PSD was formed, as the shell monomers were polymerized on the outer layer of core phase.

Figure 2 shows the TEM micrograph of the latex particles of sample 5. It can be seen from Figure 2 that all latex particles exist with clear core-shell structure due to the difference of electron penetrability to the core phase and the shell phase. The light and dark regions in the particles correspond to the polyacrylate core phase and the fluorinated
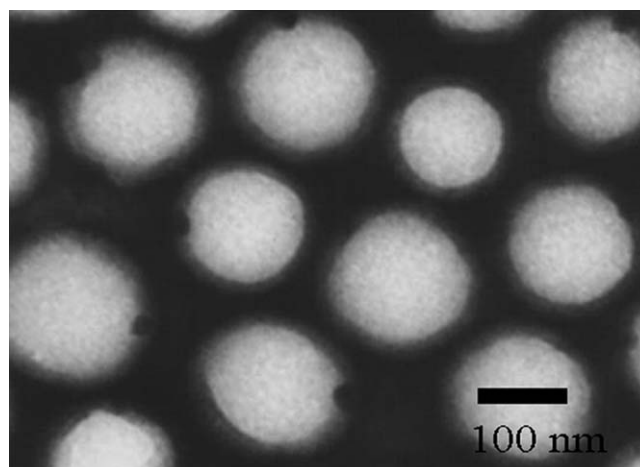

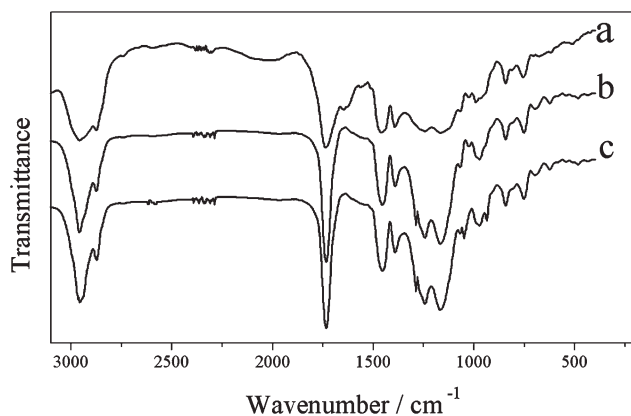**Figure 2** TEM micrograph of latex particles of sample 5.

Figure 3 FTIR spectra of the latex films: (a) sample 1; (b) sample 5; (c) sample 8.

polyacrylate shell phase, respectively. The particles are uniform spheres with the average diameter of about 160 nm, which is consistent with the results measured by PSD analysis (shown in Fig. 1).

FTIR analysis

Figure 3 indicates FTIR spectra of the fluorine-free polyacrylate latex (a), the fluorinated polyacrylate latex (b), and the fluorinated and silicated polyacrylate latex (c). It could be seen that curve b and c which contain DFMA are sharper and more intensified than curve a at 1735 cm^{-1}, which is resulted from the stretching vibration absorption of C=O bond. The characteristic stretching peaks at 1453 cm^{-1} and 1392 cm^{-1} are attributed to —OCH$_3$ groups in MMA, and 975 cm^{-1}, 844 cm^{-1}, and 751 cm^{-1} are attributed to —OCH$_3$ groups in BA. Comparing curve b and curve c with curve a, the new peaks at 688 cm^{-1} and 623 cm^{-1} are attributed to the stretching vibration and wagging vibrations of C—F bonds, and 1288 cm^{-1} is attributed to —CF$_3$ groups.[3] The absorption peaks at 1245 cm^{-1} and 1166 cm^{-1} become sharper and more intensified, which is resulted from the stretching vibration absorption of the C—F bond at 1100–1240 cm^{-1}, overlapping with the stretching vibration absorption of ester groups at 1250 cm^{-1}. Furthermore, the absorption peak at 1050 cm^{-1} and 937 cm^{-1} in curve c are assigned to the characteristic absorption of Si—O—Si bonds and Si—C bonds, and the appearance of Si—O—Si bonds gives the evidence of hydrolysis and condensation reactions (crosslinking) of Si(OR)$_3$ groups and suggests the formation of crosslinked silica network structure. So it reveals that DFMA and KH-570 has mostly copolymerized with acrylic monomers.

^{1}H-NMR and ^{19}F-NMR analysis

Figure 4 shows the ^{1}H-NMR spectrum of latex film of sample 8. It could be found that chemical shift of

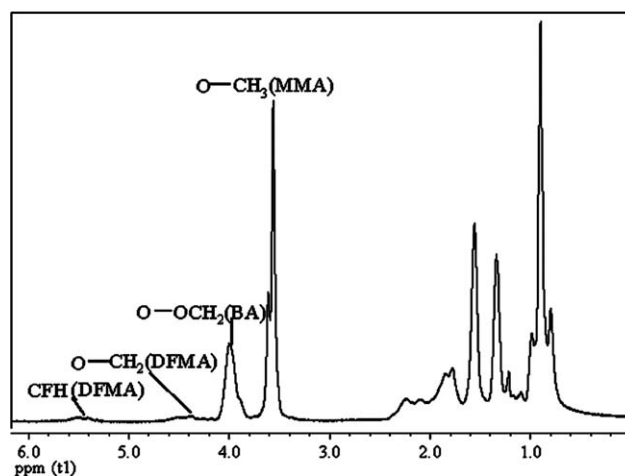**Figure 4** ^{1}H-NMR spectrum of the latex film.

—O—CH$_3$ in MMA is 3.5 ppm, and —O—CH$_2$ in BA is 4.0 ppm. The peaks at the chemical shift, δ of 4.5 and 5.5 ppm are attributed to —O—CH$_2$ and —CFH in DFMA, respectively. The two weak peaks occur in ^{1}H-NMR due to the low content of DFMA.[12]

The ^{19}F-NMR spectrum of latex film of sample 8 in Figure 5 provides further information. We assign the peaks at –71.8, –74.3, and –75.5 ppm to —CF$_3$ groups, the peaks between –183 and –188 ppm to —CF$_2$ group, and the peaks between –207 and –210 ppm to —CF group.[13,14] Therefore the ^{1}H-NMR and ^{19}F-NMR spectra of the latex film reveal that MMA, BA, and DFMA has effectively participated in emulsion copolymerization and formed the polyacrylate latex containing fluorine in the shell.

Surface properties

Hydrophobicity and oleophobicity of the latex films

Surface properties of polymers are usually governed by the structure and chemical composition of the outermost surface layer.[15] Preliminary investigations of the novel polymers' surface properties were conducted by determination of the CA, and CA on the fluorinated polymer film is commonly used as a criterion for the hydrophobicity and oleophobicity of the solid surface. Thus water and diiodomethane
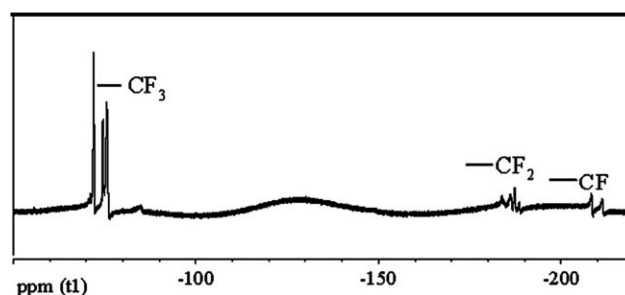

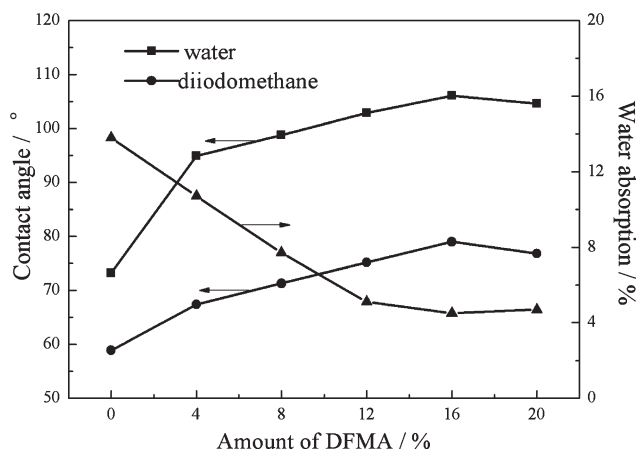**Figure 5** ^{19}F-NMR spectrum of the latex film.

Figure 6 Influence of the amount of DFMA on hydrophobicity of the latex films.

were selected as measured liquids in our experiment, and the CA of water and diiodomethane are shown in Figure 6. It could be found that both the water CA and the diiodomethane CA are enhanced significantly even with a small amount of DFMA increasing. This phenomena could be explained as that the hydrophobic and oleophobic fluorinated groups preferentially migrated to the outmost surface of the latex films during the film formation due to their lower surface free energy.[16,17] When the amount of DFMA in copolymer increases, the lowest energy of the film surface is obtained due to many perfluoroalkyl groups being covered on the coating surface. When the fluorine amount in the polyacrylate latex film is 16.0%, the maximal CA of water (106.1°) and diiodomethane (79.0°) are obtained, which are accordant with Cui et al.,[18] due to the enrichment of fluorinated groups in the film surface (shown in Table II). The CA measurement reveals that both the hydrophobicity and the oleophobicity of the latex films are enhanced by the fluorine content on the surface.

The water absorption of the latex film in Figure 6 suggests that the water-resistance of the latex film is effectively enhanced by introducing fluorinated monomer into the copolymer. Hydrophobic fluorinated groups could prevent water molecules penetrating through the film surface and into the film inner, thus the water resistance of the films was enhanced. The better the water resistance, the less the water absorption of the fluorinated polymer films is. Thus, the water absorption decreases with an increasing of DFMA amount. The results of CA and water absorption reveal that both the hydrophobicity and the oleophobicity of the latex films are enhanced by the fluorine content on the surface of the latex films.

By combining fluorinated resin and silicated resin, polyacrylate copolymer with better hydrophobicity could be obtained. The fluorinated groups may migrate to the inside of latex films and hence lead to the decrease of the film properties when the environment surrounding of the latex films changes, for instance, by being immersed into the water.[19] The silicated monomer with multifunctional groups can be used as a crosslinker to fix fluoroalkyl groups on the surface of the latex films.[20] The hydrolysis and condensation reactions of alkoxysilane groups are expected to lead to postcrosslinking after film formation.[14] However, alkoxysilanes are inherently susceptible to premature hydrolysis and condensation reactions in the aqueous phase during polymerization and storage process, which should be avoided, because the extensive hydrolysis and condensation reactions between particles would lead to the formation of coagulum during the emulsion polymerization.[21] In our study, KH-570 was selected with a longer chain and larger steric hindrance to construct a cross-linked silica network and obtained a lower hydrolysis reaction rate. The influence of the amount of KH-570 on the coagulation rate of the polymerization process and hydrophobicity of the latex

TABLE II
Surface Free Energy of the Latex Films

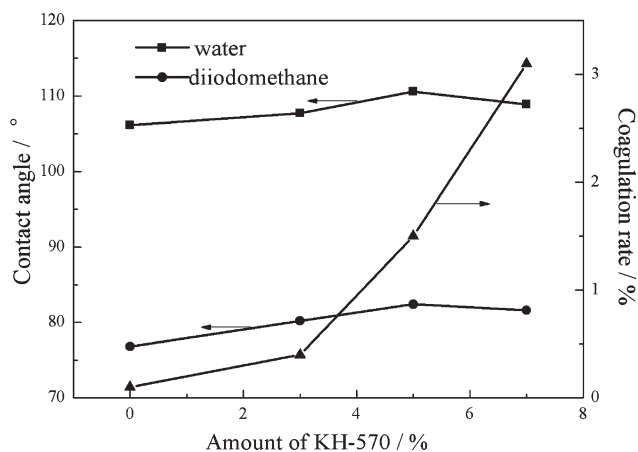| Sample	Water contact angle/ °	Diiodomethane contact angle/ °	Surface free energy calculated from one liquid (mN m^{-1})	Surface free energy calculated from two liquids (mN m^{-1})		
				γ_s^d	γ_s^P	γ_s
1	73.2	58.9	38.5	24.3	11.2	35.5
2	94.9	67.4	24.9	22.5	2.4	24.9
3	98.8	71.3	22.4	20.7	1.8	22.5
4	102.9	75.2	19.9	18.9	1.2	20.1
5	106.1	79.0	17.9	17.2	0.9	18.1
6	104.6	76.8	18.7	18.2	1.0	19.2
7	107.7	80.2	17.1	16.7	0.8	17.5
8	110.6	82.4	15.4	15.8	0.5	16.3
9	108.9	81.6	16.2	16.0	0.7	16.7

Figure 7 Influence of the amount of KH-570 on hydrophobicity of the latex films.

films were discussed, and the results are shown in Figure 7.

From Figure 7, it can be seen that the CA of water and diiodomethane are enhanced, due to the cross-linking reaction of KH-570, which could reconstruct the coatings surface by immobilizing the surface molecules and inhibit liquid phase penetration. Therefore, as the amount of KH-570 increases, more and more fluorinated chains are fixed on the surface, which is consistent with the conclusion of Xiong et al.[22] and Cui et al.[18] At a higher silicon content (>5.0%), the contact angles decrease, as the reaction system coagulates badly due to the hydrolysis and condensation of $Si(OCH_3)_3$ groups, which hinders more hydrophobic perfluoroalkyl groups orienting to film-air interface.[18] Especially, both the hydrophobicity and oleophobicity are enhanced by the addition of less fluorine and silicon in shell as desired.

Surface free energy

It is generally agreed that the measurement of the CA of pure liquids, with known surface tension, on a given solid surface is the most practical way to obtain surface free energy.[23] The surface free energy of the latex films can be calculated according to one liquid method and two liquids method, respectively.[10] The surface free energy of the latex film samples are calculated according to eqs. (3)–(5), and the results are shown in Table II.

From Table II, it could be seen that the surface free energy of copolymer films decrease monotonically with an increasing of the amounts of DFMA and KH-570, and a small amount of fluorinated and silicated monomers induce a significant reduction of surface free energy. As the amount of DFMA increases, more perfluoroalkyl groups preferentially migrate to the surface of the latex films to lower the surface free energy. Meanwhile more fluorinated

groups are fixed on the surface of the latex films due to the cross-linking reaction with KH-570 amount increasing. It could also be found that there is only less difference of surface free energy between two methods, which shows that both methods could be used to give a description of surface free energy of the latex films. However, only the total surface free energy can be calculated using one liquid method, and both dispersion component γ^d and polar component γ^p could be calculated using two liquids method, which are necessary for a significant assessment of surface chemistry. The lowest surface free energy obtained in this study is 15.4 mN/m, which is comparable to that of PTFE.

XPS analysis

The XPS analysis was carried out to determine the chemical composition of the latex film of sample 8, and the results are shown in Figure 8 and Table III. Figure 8(a,b) are the survey for the film-air interface and the film-glass interface, respectively. The survey spectra reveals the characteristic signal of carbon (C_{1s} at 284.8 eV), oxygen (O_{1s} at 53.1 eV), fluorine (F_{1s} at 688.9 eV) and silicon (Si_{2p} at 168.4 eV) as expected. The chemical composition of the latex film can be obtained by spectrum of various elements. In the C_{1s} spectrum for the film-air interface [Fig. 8(c)], the main peaks are attributed to the —CF_3, C=O(C—F), C—O—C=O, C—C and C—Si groups, respectively. In the F_{1s} spectrum for the film-air interface and film-glass interface [Fig. 8(d)], the signal intensity of the fluorine in the film-air interface is stronger than that in the film-glass interface, which indicates that the fluorinated groups with lower surface free energy preferentially migrate to the outmost surface of film during the film formation. Furthermore, the cross-linking reaction of KH-570 facilitates the fixation of more fluorinated chains on the film-glass interface of the latex films.

The element composition of both the film-air interface and the film-glass interface is shown in Table III. We can see from Table III that the fluorine and silicon atom composition in the film-air interface are higher (29.53%, 3.89%) than that in the film-glass interface (20.78%, 2.6%). Meanwhile the atom composition of carbon and oxygen in the film-air interface are lower (46.23%, 20.35%) than that in the film-glass interface (54.07%, 22.56%). In one word, XPS analysis of the latex film displays that perfluoroalkyl and silicified groups have a gradient distribution in the structure of the latex film from the film-air interface to the film-glass interface.

To estimate the composition of chemical groups on the film surface, the following reasonable assumptions are put forward: First, only molecular chain containing DFMA and KH-570 with lower
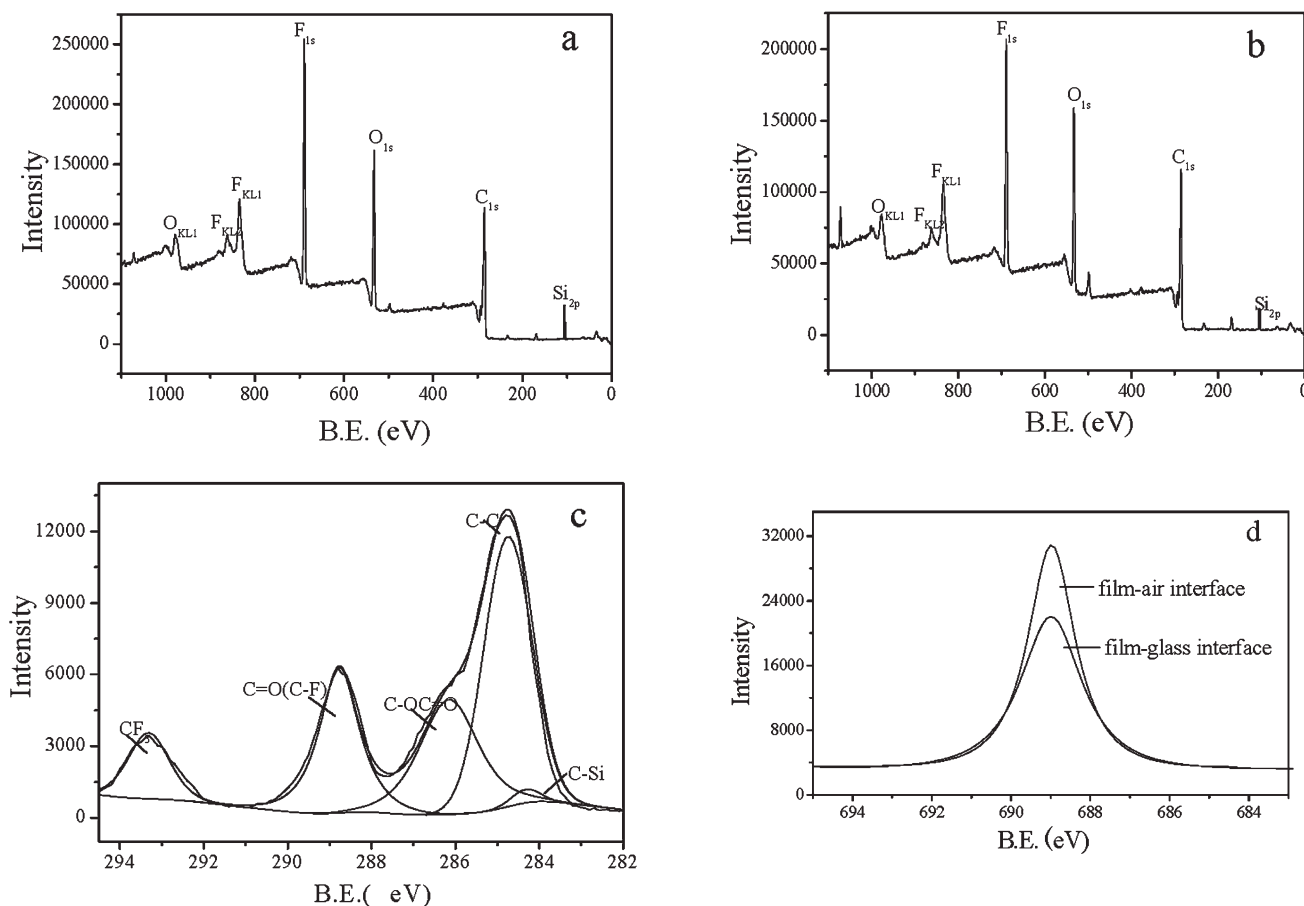
Figure 8 XPS spectra of the film of sample 8: (a) survey for the film-air interface; (b) survey for the film-glass interface; (c) interface deconvolution of C_{1s} signals for the film-air interface; (d) F_{1s} signals for the film-air interface and film-glass interface.

surface free energy migrate to the surface of latex films during the film formation, which means that the surface of latex films are covered entirely with groups deriving from DFMA and KH-570; Second, the spreading area of various groups are same, wherever they are in the main chain or side chain. And the calculated composition of chemical groups on the film surface are shown in Table IV.[24,25]

Based on the results obtained above, the theory CA of the latex films could be estimated further according to Kulinich's approach.[24] For the simplest cases of flat and chemically heterogeneous surfaces composed of n phases, the wettability could be evaluated from eq. (6):

$$(1 + \cos \theta)^2 = \sum_{i=1}^{n} f_i (1 + \cos \theta_i)^2 \qquad (6)$$

where Θ is the equilibrium CA of a chemically heterogeneous and ideally flat surface; Θ_i CA for a pure homogeneous constituent phase with its area fraction f_i. The water CA of different chemical groups on smooth and flat surface are listed in Table IV.

Substituting the theory CA in Table IV to eq. (4), the equilibrium CA Θ for film-air interface could be obtained, i.e., $\Theta = 103.2°$, which is less than the experimental value (110.6°). In fact, the surface of the latex films are impossibly covered entirely with groups deriving from DFMA and KH-570, and there are alkyl groups deriving from other monomers (MMA and BA). Therefore, there are other factors that influence the CA of the latex films. On one hand, the CA is not only related to chemical composition, but also to the roughness on the surface. The water CAs in Table IV were obtained on certain pure surfaces, but the prepared latex films are not ideally flat, because the addition of DFMA into the copolymers might result in the formation of much

TABLE III
Atom Composition in the Both Side Interfaces of Sample 8

Item	$C_{1s}/\%$	$O_{1s}/\%$	$F_{1s}/\%$	$Si_{2p}/\%$
Film-air interface	46.23	20.35	29.53	3.89
Film-glass interface	54.07	22.56	20.78	2.60
Average in bulk	52.91	22.43	15.64	1.21

TABLE IV
Water Contact Angles on Certain Pure Surfaces[24,25]

Radical groups	Composition proportion/%	Contact angle (theoretical)/°
—CF$_3$	22.86	120
—CF	22.86	105
—CH$_3$	15.55	111
—CH$_2$	23.17	94
—COO	9.62	72
—SiO	5.95	102

rougher latex films.[26] In the case of hydrophobic surface, the apparent water CA is enhanced by surface roughness, and the so-called "Lotus effect" is a well-known example of the combined effect of hydrophobicity and surface roughness. Thus, the surface roughness plays a important role in surface properties, a slight increase of surface roughness leads to larger CA increase. On the other hand, the formation of crosslinked silicon network structure of KH-570 leads the latex film more compacted, so the water molecule can not penetrate to the film.

Furthermore, annealing treatment of the latex film had been proved to be a promising method for modifying the arrangement of fluorine-containing groups at the polymer-air interface,[27] and the appropriate annealing temperature was 90°C.

Thermal analysis

Differential scanning calorimetry (DSC) analysis

Figure 9 shows the DSC curve of the latex film of sample 8. Two glass transition temperatures (T_g), i.e., −20.4°C and 43.6°C, could be observed, which represent T_g of the core phase and the shell phase, respectively. This is because semi-continuous emulsion polymerization process was adopted when the polyacrylate latex containing fluorine and silicon
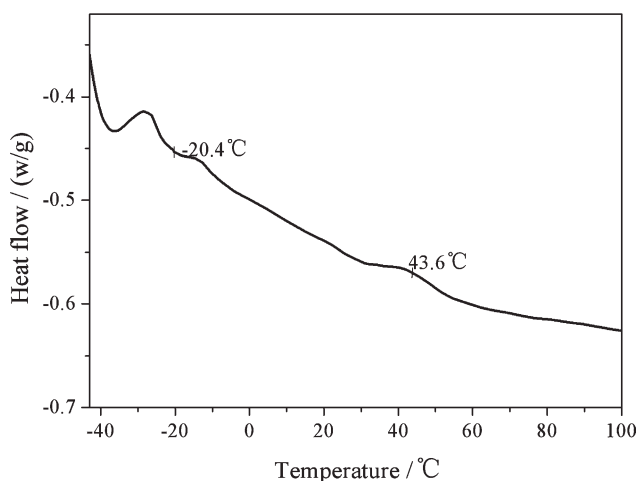
Figure 9   DSC curve of the latex film.

was synthesized, and the difference of monomer ratio in the core phase and the shell phase results their difference in the phase composition. The T_g values of the core phase and the shell phase are consistent with the theory T_g values estimated by Fox equation (–24.5 and 37.6°C). It is assumed that the monomer composition in copolymers is the same as that in theoretic formulation, and all monomers mostly participated in copolymerization. The DSC result shows that the core-shell structure is formed, which is corresponding to the core-shell structure of the latex particles shown in the PSD and TEM analysis (Figs. 1 and 2).

TG analysis

The TG curves of three latex films of sample 1, sample 5, and sample 8 are shown in Figure 10. It could be seen that the initial decomposing temperatures for the latex films of sample 5 and sample 8 are 375°C and 387°C, respectively, and the complete decomposing temperature are 482°C and 499°C, respectively. Whereas the decomposition of sample 1 began at 298°C and ended at 416°C, indicating the thermal stability of the latex films are significantly enhanced due to the addition of DFMA and KH-570. This phenomenon could be explained as that through seed emulsion polymerization, fluorinated and silicated acrylate monomer could be fixed in the shell of the latex particles and the perfluoroalkyl groups containing C—F bonds has very high bond energy. Thus the thermal stability copolymer is improved.

CONCLUSIONS

A series of acrylic copolymer latexes with core-shell structure containing fluorine and silicon in the shell have been synthesized by semi-continuous emulsion polymerization at the presence of a compound emulsifier. The average particle size of the synthesized
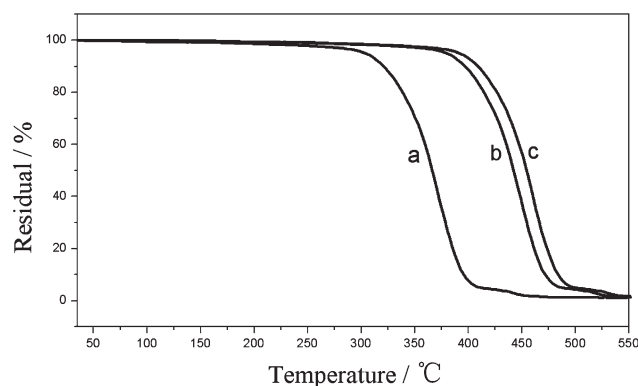
Figure 10   TG curves of the latex films: (a) sample 1; (b) sample 5; (c) sample 8.

latex is about 160 nm. DFMA and KH-570 have effectively participated in emulsion copolymerization with acrylic monomers. The CAs of deionized water and diiodomethane on the latex films increase with an increasing of the amount of DFMA and KH-570. The maximal equilibrium CA (110.6°) and the lowest surface free energy (15.4 mN/m) for film-air interface are reached when the amount of DFMA and KH-570 is 16% and 5%, respectively. The hydrophobicity and thermal stability of latex films are greatly improved with the addition of less KH-570. The fluorine- and silicon-containing groups have a gradient distribution in the prepared latex films from the film-air interface to the film-glass interface.

References

1. Miwa, M.; Nakajima, A.; Fujishima, A.; Hashimoto, K.; Watanabe, T. Langmuir. 2000, 16, 5754.
2. Qu, A. L.; Wen, X. F.; Pi, P. H.; Cheng, J.; Yang, Z. R. J Colloid Interface Sci 2008, 317, 62.
3. Dai, J. B.; Zhang, X. Y.; Chao, J.; Bai, C. Y. J Coat Technol Res 2007, 4, 283.
4. Liang, J. Y.; He, L.; Zheng, Y. S. J Appl Polym Sci 2009, 112, 1615.
5. Xiao, X. Y.; Liu, J. F. Chin J Chem Eng 2008, 16, 626.
6. Xiao, X. Y.; Wang, Y. Colloids Surf A: Physicochem Eng Aspects 2009, 348, 151.
7. Cheng, X. L.; Chen, Z. X.; Shi, T. S.; Wang, H. Y. Colloids Surf A: Physicochem Eng Aspects 2007, 292, 119.
8. Young, T. Philos Trans R Soc London 1805, 95, 65.
9. Neumann, A. W.; Good, R. J.; Hope, C. J.; Sejpal, M. J Colloid Interface Sci 1974, 49, 291.
10. Milojka, G.; Gerhard, S.; Wolfgang, G., Alexander, R.; Stefanie, T. Colloids Surf A: Physicochem Eng Aspects 2001, 181, 279.
11. Fowkes, F. M. Ind Eng Chem 1964, 56, 40.
12. Jiang, M.; Zhao, X. L.; Ding, X. B., Zheng, Z. H.; Peng, Y. X. Eur Polym J 2005, 41, 1798.
13. Li, K.; Wu, P. P.; Han, Z. W. Polymer 2002, 43, 4079.
14. Witucki, G. L. J Coat Technol 1993, 65, 57.
15. Shafrin, E. G.; Zisman, W. A. J Phys Chem 1960, 64, 519.
16. Thomas, R. R.; Glaspey, D. F.; Dubois, D. C., Kirchner, J. R.; Anton, D. R.; Lloyd, K. G.; Stika, K. M. Langmuir 2000, 16, 6898.
17. Winter, R.; Nixon, P. G.; Terjeson, R. J., Mohtasham, J.; Holcomb, N. R.; Grainger, D. W.; Graham, D.; Castner, D. G.; Gard, G. L. J Fluorine Chem 2002, 115, 107.
18. Cui, X. J.; Zhong, S. L.; Wang, H. Y. Polymer 2007, 48, 7241.
19. Schmidt, D. L.; Brady, R. F.; Lam, K., Schmidt, D. C.; Chaudhury, M. K. Langmuir 2004, 20, 2830.
20. Marcu, I.; Daniels, E. S.; Dimonie, V. L., Hagiopol, C.; Roberts, J. E.; El-Aasser, M. S. Macromolecules 2003, 36, 328.
21. Luo, Y. W.; Xu, H. J.; Zhu, B. Polymer 2006, 47, 4959.
22. Xiong, P. T.; Lu, D. P.; Chen, P. Z. Eur Polym J 2007, 43, 2117.
23. Bahramian, A.; Danesh, A. J Colloid Interface Sci 2004, 279, 206.
24. Kulinich, S. A.; Farzaneh, M. Surf Sci 2004, 573, 379.
25. Decker, E. L.; Garoff, S. Langmuir 1997, 13, 6321.
26. Ha, J. W.; Park, I. J.; Lee, S. B. Macromolecules 2005, 38, 736.
27. Park, I. J.; Lee, S. B.; Choi, C.; Kim, K. J Colloid Interface Sci 1996, 181, 284.