

## Fabrication and Hydrophobic Properties of Fluorinated Polyacrylate Latexes via Semi-Continuous Seeded Emulsion Polymerization

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### Abstract

Fluorinated polyacrylate latexes have been synthesized by semi-continuous seeded emulsion polymerization using methyl methacrylate (MMA), n-butyl acrylate (nBA) and styrene (St) as monomers, dodecafluoroheptyl methacrylate (DFMA) or 1H,1H,2H,2H-perfluorooctyl trimethoxysilane (FAS-13) as fluoromonomer. Fourier transform infrared spectroscopy (FT-IR) confirmed that fluorine-containing groups had been introduced into the chain of the polyacrylate. Scanning electron microscopy coupled with energy-dispersive X-ray detector (SEM-EDX) and static contact angles (CAs) shown that a gradient decent of fluorine existed along the depth profile of fluorinated polyacrylate latex films, but silicon and oxygen were enriched remarkably on the film-air interface of P (MMA/BA/St/FAS-13). The hydrophobic performance of P (MMA/BA/St/FAS-13) latex film surpassed those of other latex films.

**Keywords:** Fluorinated polyacrylate; Hydrophobicity; Semi-continuous seeded emulsion polymerization; Core-shell structure

### 1. Introduction

Fluoropolymers show great attractiveness due to their unique thermal, chemical, and mechanical stabilities and low surface energies [1]. These attributes make fluoropolymers candidates in fuel cell membranes [2], biotechnology [3], and other applications. However, fluorine-containing acrylate homopolymers can not meet the demand of the production for the poor film-forming property and weak bond capacity. In order to overcome the above defects, copolymerization of fluorine-containing acrylic monomer and other fluorine-free acrylic monomer have been adopted. The prepared fluorinated polyacrylate not only keeps good adhesion of the acrylic resin, but also has a unique hydrophobicity and oleophobicity of fluoropolymer.

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Until now, a variety of fluorine-containing acrylate copolymer materials have been synthesized by electrochemical, graft, radical, RAFT or ATRP copolymerization approaches [4-8]. As we all know, the wettability and adhesion of coatings are mainly determined by their chemical compositions and surface structures. And the current studies on fluorinated polymers having a low surface free energy even with low fluorine content are mainly concentrated in the construction of polymer structures [9] as well as the optimization of the preparation process [10]. However, in most of these studies, fluorine-containing acrylic monomers were introduced in emulsion polymerization, which would affect the hydrophobicity of latex film. Because of intertwining and embedding between the molecular chains in the film-forming process, it would hinder the migration of the fluorine-containing segments to the interface of latex film-air. To avoid this phenomenon, we attempt to replace fluorine-containing acrylic monomers with fluorosilanes.

Furthermore, in our previous research [11], core-shell silicon-acrylate compounding latex was fabricated by a semi-continuous seeded emulsion polymerization. The result showed that the silicon-polyacrylate latex had a obvious core-shell structure and the comprehensive property of silicon-polyacrylate was improved. In this paper, fluorinated polyacrylate emulsion has been prepared by copolymerization of fluorine-containing acrylate, fluorosilane with acrylate monomers in an aqueous medium by a semi-continuous seeded emulsion polymerization. The resulted core-shell fluorinated polyacrylate latex films were characterized by fourier transform-infrared (FT-IR) spectrometry and scanning electron microscope coupled with energy-dispersive X-ray detector (SEM-EDX). The hydrophobicity of fluorinated polyacrylate latex films was investigated by contact angle (CA) test.

## 2. Experimental

### 2.1. Materials

Methyl methacrylate (MMA), n-butyl acrylate (BA) and styrene (St), analytical pure, were obtained from Fuchen Chemical Company, Tianjin, China. Dodecafluoroheptyl methacrylate (DFMA) and 1H, 1H, 2H, 2H-perfluorooctyl trimethoxysilane (FAS-13) were from XEOGIA Fluorine-Silicon Chemical Co., Ltd. of China. Ammonium persulfate (APS) as initiator and sodium bicarbonate ( $\text{NaHCO}_3$ ) as buffering reagents, analytical pure, were used as received. The emulsifiers, perfluoro branched chain ether type surface active agent (S201), sodium dodecyl sulfate (SDS) and nonylphenol polyoxyethylene ether, 2-sulfonic acid, succinic acid monoester disodium salt (MS-1), were used as received from Zibo Haijie Chemical Company. The water used in this experiment was distilled followed by deionization.

### 2.2. Synthesis of fluorinated polyacrylate latexes

The recipes for the synthesis of fluorinated polyacrylate latexes are described in Table 1. The core-shell emulsion was synthesized in three stages, namely seed polymerization, core phase formation and shell phase formation. The detailed steps are as follows:

*Seed polymerization:* According to Table 1, emulsifier mixture and buffer solution

(NaHCO<sub>3</sub>) were introduced into a three-neck flask equipped with a reflux condenser, a tap funnel and a mechanical stirrer with a stirring rate of 200rpm. The mixture of MMA and BA was added into the flask at 50°C for 30min. The initiator aqueous solution (0.1g of APS was solved in 5g of water) was added to the flask at 50°C followed by stirring of another 30min. The mixture solution was heated to 80°C and maintained for 1h in a water bath after the emulsion polymerization took place.

*Pre-emulsification of core and shell phases:* core phase (containing 1.5g of MMA , 4.8g of BA, and emulsifier solution (0.095g of MS-1/SDS and 3.0g of deionized water) ) and shell phase (containing 10.8g of MMA, 16.5g of BA, 2.1g of St, 4.2g of DFMA or FAS-13, emulsifier solution (0.03g of S201, 0.095g of MS-1/SDS and 11.0g of deionized water) ) were prepared similarly by a high-shear dispersion homogenizer and stirred at high speed for 5 minutes to form a pre-emulsion.

Table 1 Recipes for the synthesis of fluorinated polyacrylate latexes.

Sample code	C1	C2	C3
<b>Seed</b>			
MS-1/SDS (g) *	1.0	1.0	1.0
NaHCO <sub>3</sub> (g)	0.2	0.2	0.2
MMA (g)	1.5	1.5	1.5
BA (g)	4.8	4.8	4.8
APS (g)	0.1	0.1	0.1
DI water (g)	30	30	30
<b>Core phase</b>			
MS-1/SDS (g) *	0.095	0.095	0.095
MMA (g)	1.5	1.5	1.5
BA (g)	4.8	4.8	4.8
APS (g)	0.03	0.03	0.03
DI water (g)	6.7	6.7	6.7
<b>Shell phase</b>			
MS-1/SDS (g) *	0.45	0.45	0.45
S201 (g)	0.03	0.03	0.03
MMA (g)	10.8	10.8	10.8
BA (g)	16.5	16.5	16.5
St (g)	2.1	2.1	2.1
DFMA(g)		4.2	
FAS-13 (g)			4.2
APS (g)	0.16	0.16	0.16
DI water (g)	30	30	30

\* Note: MS-1: SDS (mass ratio) = 4:1.

*Core polymerization:* The core phase pre-emulsion and APS solution (0.03g of APS and 4.2g of deionized water) were introduced into the flask separately at an appropriate dropping rate at 80°C. The emulsion polymerization was carried out at 80°C for 1 h after APS and core

phase pre-emulsion were fed in completely.

*Shell polymerization:* The shell pre-emulsion and APS solution (0.16g of APS and 19g of deionized water) were dropped into the flask in 3.5 h. After that, the emulsion polymerization was carried out at 85 °C for another 1.5 h.

Finally, the pH value of the emulsion was adjusted to 6-7 with aqueous ammonia.

### 2.3. Measurements

Fourier transform infrared (FT-IR) spectra of KBr powder-pressed Pellets were recorded on a 5DX Fourier transform-infrared spectroscope.

Static contact angles (CA) of water on the fluorinated polyacrylate latex films were measured with an OCA20 contact angle goniometer (Dataphysics Company, Germany) by the sessile drop method with a microsyringe at room temperature. More than 8 data were averaged to get a more reliable value for each sample.

Scanning electron microscopy coupled with energy-dispersive X-ray detector (SEM-EDX) analysis was performed on a JEM 3010 Scanning electron microscope. The dried emulsion 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 the glass substrate in dust-free room. The surface topography and compositions along the depth profile of fluorinated polyacrylate films were both determined.

## 3. Results and discussion

### 3.1. Composition and structure of the latex

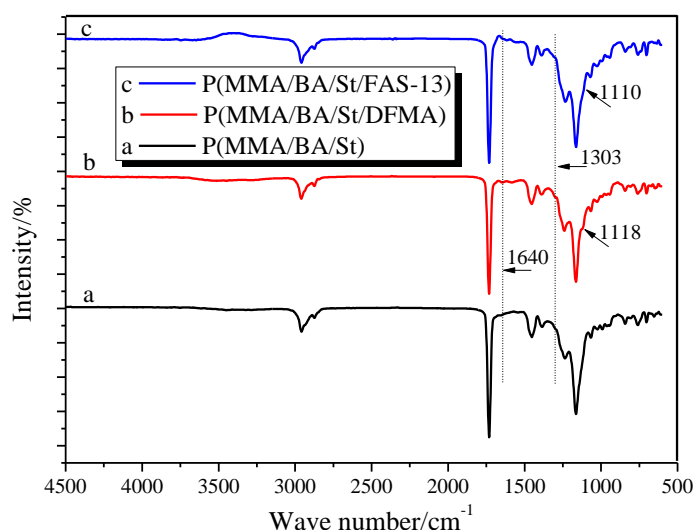


Figure 1 FT-IR spectra of latexes.

Fluorinated polyacrylate latexes (P (MMA/BA/St/DFMA) and P (MMA/BA/St/ FAS-13))

and non-fluorinated polyacrylate latex (P (MMA/BA/St)) have been prepared by semi-continuous seeded emulsion polymerization. In order to know whether the organic fluorine has been involved in the reaction as well as the chemical composition and structure of copolymers, FT-IR characterization was carried out. The FT-IR spectra of P (MMA/BA/St) (recipe 1, curve a), P (MMA/BA/St/DFMA) (recipe 2, curve b) and P (MMA/BA/St/FAS-13) (recipe 3, curve c) are shown in Figure 1. All FT-IR spectra exhibit that the characteristic absorption of the C=C bond at  $1640\text{ cm}^{-1}$  is extremely weak, indicating that the vast majority of monomers have taken part in the copolymerization [10, 12]. Compared with the spectrum (a), spectrum (b) and (c) show a new peak of C-F stretching vibration peak at  $1303\text{ cm}^{-1}$ , which indicates that DFMA or FAS-13 had participated in the reaction. At the same time, stretching vibration bond of Si-O in spectrum (c) at  $1070\sim 1110\text{ cm}^{-1}$  appears, confirming that FAS-13 can be copolymerized into the latex particles.

### 3.2. Hydrophobicity of the fluorinated polyacrylate films

Water contact angle is commonly used as a criterion for the evaluation of hydrophobicity of solid surface [13]. The higher the wetting resistance of film surface, the higher the contact angle is [14]. Contact angles with deionized water are shown in Figure 2. It can be observed that the surface contact angle of P (MMA/BA/St/FAS-13) latex film is higher than that of P (MMA/BA/St/DFMA) and P (MMA/BA/St), indicating that the hydrophobicity of (MMA/BA/St/FAS-13) latex film is the best among them.

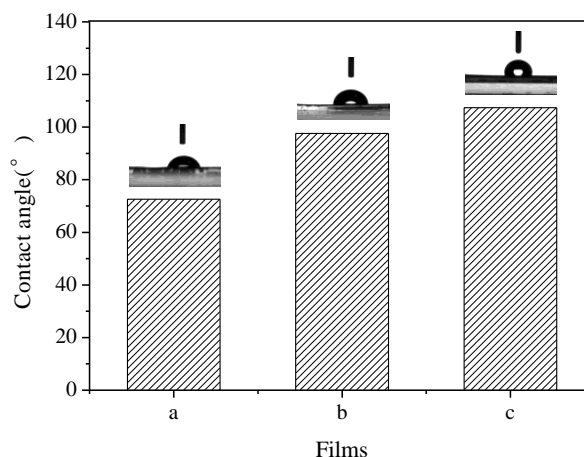


Figure 2 Results of contact angle of (a) P (MMA/BA/St), (b) P (MMA/BA/St/DFMA) and (c) P (MMA/BA/St/FAS-13) with water.

Actually, the surface wetting property depends on the surface topography and chemical compositions of films.

Figure 3 shows that the surfaces of these three copolymer films are rough, but the degrees of roughness are different. In comparison with Figure 3a, Figure 3b has a lot of smaller and denser streaks. This is mainly due to the capability of self-migration to the surface of fluorine-containing segments. However, the migration of fluorine-containing segments to

the surface in film-forming process is restrained by polymer chains when DFMA is involved in the emulsion polymerization. So there are a lot of streaks on the surface of P (MMA/BA/St/DFMA) film. Compared Figure 3a and Figure 3c, the degree of roughness of P (MMA/BA/St/FAS-13) decreased. Because FAS-13 does not contain double bond which can take part in emulsion polymerization, the fluorine-containing segments in the molecule of FAS-13 are prone to migrate to the interface of film-air. At the same time, the degree of phase separation of P (MMA/BA/St/FAS-13) film reduced. However, these rough structures can not be observed with the naked eyes, indicating that a micro-phase separation occurred in film-forming process.

In an effort to reveal the relationship between the hydrophobicity and the chemical compositions as well as the distribution of fluorine element in latex films, EDX analysis was operated.

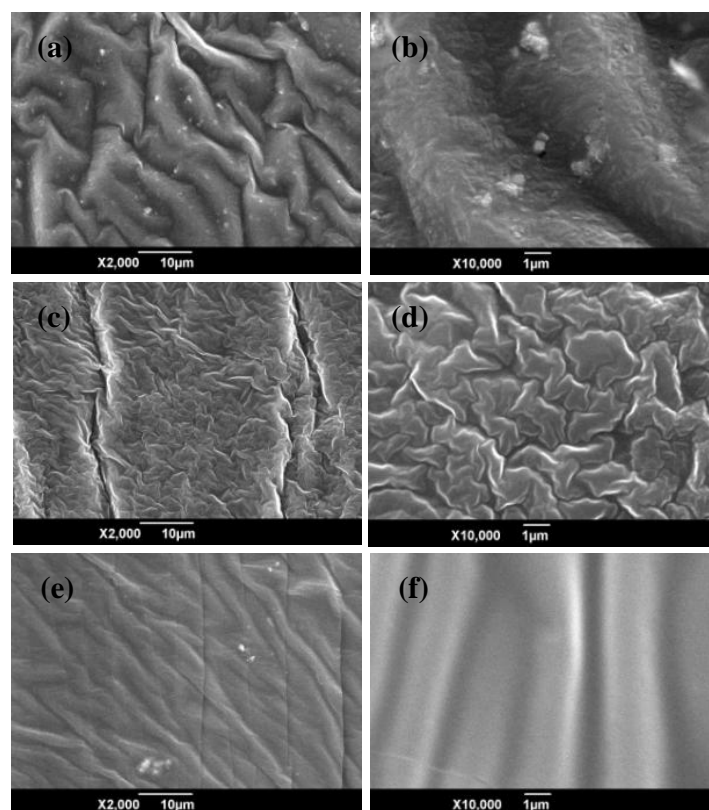


Figure 3 SEM images of (a) P (MMA/BA/St), (c) P (MMA/BA/St/DFMA), (e) P (MMA/BA/St/FAS-13), (b) magnified observation of (a), (d) magnified observation of (c) and (f) magnified observation of (e).

SEM-EDX analysis was carried out from the interface of the latex film-air to the interface of the latex film-glass and the right side is the interface of the latex film-air, the results are shown in Figure 4 and Table 2. As can be seen from Figure 4 and Table 2, in these two cases, a gradient descent of fluorine content existed along the depth profile of films.



Furthermore, the enrichment of fluorine content on the interface of P (MMA/BA/St/DFMA) latex film-air is lower than that of P (MMA/BA/St/FAS-13) latex film. It has been known that fluorinated materials are capable of self-migration to the surface [15]. As a fluorine-containing vinyl monomer, DFMA can participate in the emulsion polymerization. In the film-forming process, intertwining and embedding between the molecular chains occurred, which hindered the migration of the fluorine-containing segments. While for P (MMA/BA/St/FAS-13) latex film, the fluorine-containing segments are relatively free and they can easily migrate to the interface of latex film-air since FAS-13 has not participated in emulsion polymerization.

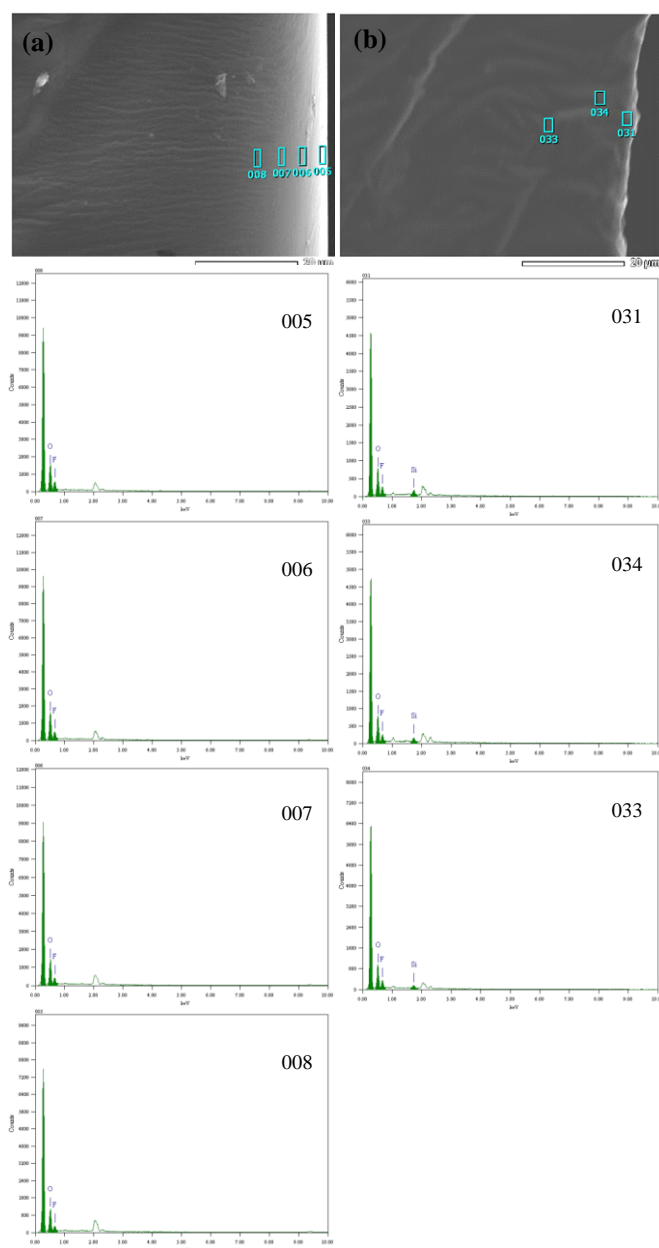


Figure 4 SEM-EDX analysis of the cross section of latex films of (a) P (MMA/BA/St/DFMA) and (b) P (MMA/BA/St/FAS-13).

Table 2 Results of SEM-EDX analysis of the cross section of latex film

Latex film	P (MMA/BA/St/DFMA)				P (MMA/BA/St/FAS-13)		
	005	006	007	008	031	034	033
C/%	65.76	66.22	67.04	68.85	57.17	59.79	60.11
O/%	26.83	27.39	27.31	26.15	30.59	28.58	29.68
F/%	7.42	6.39	5.66	5.00	11.20	10.89	9.32
Si/%	--	--	--	--	1.04	0.74	0.89

Note: "--" stands for "none".

In addition, Figure 4 and Table 2 also show that the contents of silicon element and oxygen element in P (MMA/BA/St/FAS-13) latex film have significantly improved, which may be due to the hydrolysis and condensation reactions of FAS-13 occurring in emulsion polymerization. To prove this deduction and realize the distributions and contents of elements on the surface of P (MMA/BA/St/FAS-13) latex film, SEM-EDX analysis was carried out and the results are shown in Figure 5 and Table 3. In Figure 5, 011, 014 and 015 are the surface SEM-EDX analysis of white granular substances on the surface of latex film, 012 and 013 are the grooves and heaves on the surface of latex film, respectively.

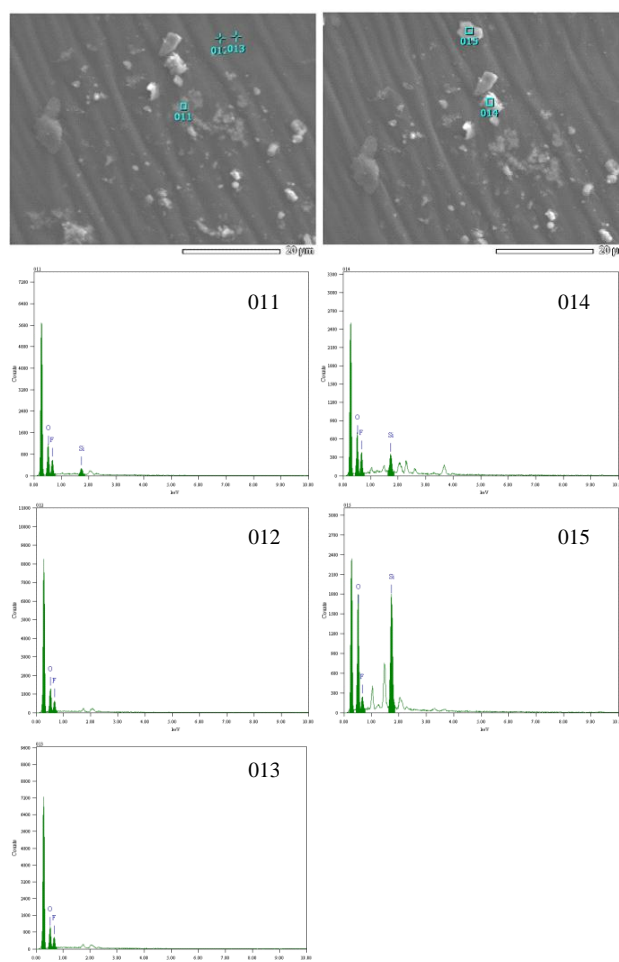




Figure 5 SEM-EDX analysis of the surface of P (MMA/BA/St/FAS-13)

Table 3 Results of SEM-EDX analysis of the surface of P (MMA/BA/St/FAS-13)

Element content/%	011	012	013	014	015
C	61.25	64.79	65.92	56.77	65.53
O	26.33	25.17	23.95	27.16	23.54
F	11.10	9.91	10.14	12.73	9.29
Si	1.739	--	--	3.33	1.64

Note: "--" stands for "none".

Figure 5 and Table 3 reveal that the main components of the white granular substances are C, O, F and Si elements, which can be inferred as polycondensates of FAS-13. So, to some extent, FAS-13 also could improve the roughness of the P (MMA/BA/St/FAS-13) latex film. The results also prove that the P (MMA/BA/St/FAS-13) latex film has a better hydrophobicity.

Combined the results of SEM-EDX and CA, it implies that the hydrophobicity of latex films is not only related to the fluorine contents, but also determined by the roughness of films.

#### 4 Conclusions

Fluorinated polyacrylate emulsions with core-shell structure were successfully synthesized via semi-continuous seeded emulsion polymerization technique. FT-IR spectra analysis and EDX confirmed that organic fluorine could be introduced into the emulsion particles. EDX and CA reveal that the hydrophobicity of P (MMA/BA/St/FAS-13) latex film surpassed those of P (MMA/BA/St/DFMA) and P (MMA/BA/St). A gradient decent of fluorine exists along the depth profile of fluorinated polyacrylate films, but silicon and oxygen are enriched remarkably on the film-air interface of P (MMA/BA/St/FAS-13). Furthermore, hydrolysis and condensation of FAS-13 occurred in emulsion polymerization.

#### Acknowledge

This research was supported by National Natural Science Foundation of China (51073091, 21006061), International Science & Technology Cooperation Program of China (2011DFA43490), Fok Ying-Tong Education Foundation (131108), Research Fund for the Doctoral Program of Higher Education of China (20116125110002) and Scientific Research Group of Shaanxi University of Science and Technology (TD12-03).

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