

Synthesis and Property Investigation of Three Core-Shell Fluoroacrylate Copolymer Latexes

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Received 29 April 2008; accepted 14 October 2008

DOI 10.1002/app.29577

Published online 9 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Three core-shell fluoroacrylate copolymer latexes with different fluorinated side chain structure were synthesized in this article by semicontinuous seed emulsion polymerization, using butyl acrylate (BA) and methyl methacrylate (MMA) as acrylate monomer and trifluoroethyl methacrylate (TFEM, C₆H₇O₂F₃), hexafluorobutyl methacrylate (HFBM, C₈H₈O₂F₆), and dodecafluoroheptyl methacrylate (DFHM, C₁₁H₈O₂F₁₂) as fluorine-containing acrylate monomer. The core-shell fluoroacrylate copolymer latexes were named as BA/MMA/TFEM, BA/MMA/HFBM, and BA/MMA/DFHM, respectively. The latex particle morphology and the particle size were determined by transmission electron microscopy and differential scanning calorimetry. The final chemical structure of the latex was analyzed by NMR. The effect of the fluorinated side chain

on the core-shell copolymer latex and film properties, as well as on the superiority of core-shell copolymer latex to general fluoroacrylate copolymer latex was investigated by energy dispersive X-ray detector, thermogravimetric analysis, and the determination of contact angle. The analysis results indicated that the particle of fluoroacrylate copolymer latex presented uniform sphere core-shell structure. Compared with core-shell BA/MMA/TFEM and BA/MMA/HFBM, BA/MMA/DFHM exhibited not only better surface property as increasing temperature but also better thermal stability. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1615–1621, 2009

Key words: fluoroacrylate copolymer; core-shell structure; latex; fluorinated side chain structure

INTRODUCTION

Fluoroacrylate copolymers have ultralow surface tension and related hydrophobicity, very good anti-chemical and thermostability, low flammability and low refractive index, as well as excellent mechanical behavior.^{1–4} Therefore, fluoroacrylate copolymers have prominent superiority and encouraging application prospect as protective coating.^{5–7} In the case of their application as protective coating for unbleached ancient sandstone monument, fluoroacrylate copolymers have been focused on suitable preparation method and reasonable design of molecular chain structure based on properties tailored to different requirement.^{8–14} Among these polymers, fluoroacrylate copolymer latex provided necessary property for this purpose, especially the core-shell fluoroacrylate latex which was composed of fluorine-free acrylate core and fluorine-containing acrylate shell obtained by emulsion polymerization.

The core-shell latex had typical advantage in film formation compared with general emulsion.^{15–18} Because of the differences in hydrophobic properties and surface tension of core and shell, fluorine-containing acrylate shell preferentially migrated to the surface during the film formation for maintaining the excellent physical and chemical properties, and fluorine-free acrylate core migrated to inner layer for providing the good adhesion toward stone substrate. This made it possible to prepare target polymer for the purpose of improving the stone strength and protecting the stone monument from weathering by the design of fluorine-free acrylate polymer core and fluorine-containing acrylate polymer shell.^{19–21}

The properties of core-shell fluoroacrylate copolymer can be improved by increasing the amount of the fluorinated monomer.²² But the relatively high market prices of the fluorinated acrylate monomers made it impracticable. It has been reported that the surface properties of fluoroacrylate copolymers were related to the organization of fluorinated side chain, which was governed by the chain length, the chemical structure, and the flexibility of main chain.^{23–26} Therefore, studying the influence of fluorinated side chain structure on the properties of core-shell fluoroacrylate copolymer latex and comparing the properties of core-shell fluoroacrylate latex with general fluoroacrylate copolymer latex will be helpful to

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Contract grant sponsor: National Nature Science Foundation of China (NSFC); contract grant number: 20474050.

select suitable fluorinated acrylate monomer, design polymer microsphere, and reduce cost.

In this study, three core-shell fluoroacrylate copolymer latices were synthesized by the semicontinuous seed emulsion polymerization in the presence of mixed emulsifier of sodium lauryl sulfate (SDS) and octylphenylpolyoxyvinyl ether (TX-10) in the ratio of SDS/TX-10 = 1 : 2. Butyl acrylate (BA) was served as the core, methyl methacrylate (MMA), butyl acrylate (BA), and fluorinated acrylate monomers namely as trifluoroethyl methacrylate (TFEM, containing 34 wt % fluorine), hexafluorobutyl methacrylate (HFBM, containing 46 wt % fluorine), and dodecafluoroheptyl methacrylate (DFHM, containing 57 wt % fluorine) were served as the shell, respectively. The theoretical F content of all the investigated copolymers was about 16 wt % for maintaining an acceptable solubility in fluorine-free solvent. To present better protective properties, the glass transition temperature (T_g) of all shell copolymers were designed at about 30°C, which was not much higher than room temperature.⁵

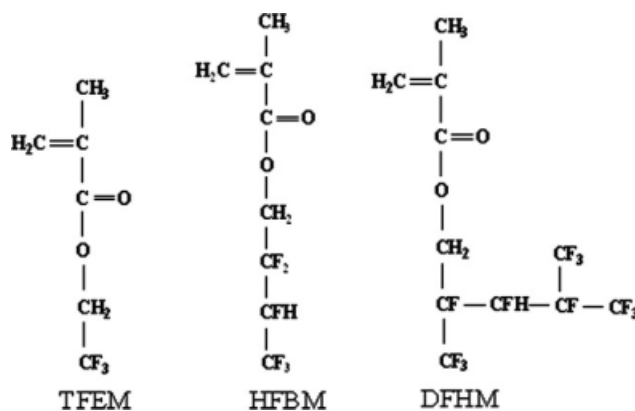
Nuclear magnetic resonance (NMR), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), static contact angle instrument, energy dispersive X-ray detector (EDX), and thermogravimetric analysis (TGA) were used to characterize the particle morphology and the particle size of latex, to investigate the effect of the fluorinated side chain structure on the core-shell copolymer latex and film properties and on the superiority of core-shell fluoroacrylate copolymer to general fluoroacrylate copolymer latex.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and butyl acrylate (BA) monomers, supplied by Aldrich, were washed first by 5 wt % aqueous solution of sodium hydroxide, and then by water, until pH value of the washings became neutral. The purified monomers were dried over anhydrous magnesium sulfate and stored at -5°C. Trifluoroethyl methacrylate (TFEM), hexafluorobutyl methacrylate (HFBM), and dodecafluoroheptyl methacrylate (DFHM) were used without purification and supplied by XUEJIA Fluorine-Silicon chemical Co. (Harbin, China). They are all transparent, odorless, and tasteless liquid, and the structural units are shown in Scheme 1.

Initiator ammonium persulfate (APS), chemical purity, was purified by recrystallization. Sodium lauryl sulfate (SDS) and octylphenylpolyoxyvinyl ether (TX-10), chemical purity, were mixed in the ratio of SDS/TX-10 = 1 : 2.



Scheme 1 Structural formulae of TFEM, HFBM, and DFHM.

Synthesis of core-shell fluoroacrylate copolymer latex

The core-shell fluoroacrylate copolymer latex was prepared by two-stage semicontinuous seed emulsion polymerization. All the polymerization steps were carried out under the protection of nitrogen atmosphere in a 250-mL four-neck flask equipped with reflux condenser, mechanical stirrer, separating funnel, and inlet for nitrogen gas.

First, BA was emulsified in a mixed emulsifier (SDS/TX-10) at 50°C for 0.5 h, a part of initiator (APS) was added when temperature was increased to 80°C. Keep this temperature for 0.5 h for the production of core polymer. Second, the mixture of BA/MMA/fluorinated monomer (TFEM, HFBM, and DFHM, respectively) for the shell and another part of APS were added drop-by-drop during 3–4 h. After the addition of all these materials, the temperature was increased additionally 5°C and lasted for 0.5 h. Finally, when the reaction was over, the temperature was lowered to 25°C and the reaction was terminated by the addition of NaHCO₃ (pH = 6–7).

To investigate the effect of fluorinated side chain structure on the superiority of core-shell fluoroacrylate copolymer latex to general fluoroacrylate copolymer latex, three fluoroacrylate copolymer latices using TFEM, HFBM, and DFHM, respectively, were prepared by batch emulsion polymerization correspondingly.

The polymerization condition and detailed recipes of the prepared samples were listed in Table I. Sample 1 represented core-shell fluorine-free polyacrylate latex. Samples 2, 4, and 6 represented core-shell fluoroacrylate copolymer latices namely as BA/MMA/TFEM, BA/MMA/HFBM, and BA/MMA/DFHM, respectively. Samples 3, 5, and 7 represented general fluoroacrylate copolymer latices.

Characterization of latices and films

A JEM-3010 TEM, performed in an ultrahigh vacuum chamber equipped with a hemispherical

TABLE I
The Polymerization Condition and Detailed Recipes of Prepared Samples

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Seed (batch) (0.5 h, 80°C)							
BA (g)	10	10	15	10	15	10	15
MMA (g)	0	0	2.7	0	5.5	0	10
SDS/TX-10 (g)	1.800	1.800	1.800	1.800	1.800	1.800	1.800
APS (g)	0.050	0.050	0.050	0.050	0.050	0.050	0.19
Water (g)	50	50	60	60	50	50	60
Fluorinated monomer (g)	0	0	16.8 (TFEM)	0	12.5 (HFBM)	0	10.00 (DFHM)
Shell (drop-by-drop) (3–4 h, 80°C)							
BA (g)	5	5	0	5	0	5	0
MMA (g)	10	2.7	0	5.5	0	10	0
Fluorinated monomer (g)	0	16.8 (TFEM)	0	12.5 (HFBM)	0	10 (DFHM)	0
APS (g)	0.0750	0.1470	0	0.1047	0	0.1250	0
Water (g)	6	10	0	10	0	10	0

electron energy analyzer, was used to observe the particle morphology and particle size. The particle morphology of core-shell latex was obtained after staining latex particle by phosphotungstic acid (PTA, $\text{H}_3\text{PO}_{40} \text{W}_{12} \times \text{H}_2\text{O}$) solution (pH = 6.4).

The thin films were prepared using the insoluble fraction after the latex samples were purified by precipitation in excess methanol. The insoluble fraction was washed in deionized water and dried under vacuum at 100°C for 1 h, then was cast in chloroform solutions (the weight concentration was ca.5%) and dried 3 days at room temperature on a cleaned glass panel without being contaminated.

Liquid $^1\text{H-NMR}$ spectra were recorded with a Bruker AVANCF300MHZ using CDCl_3 as solvent. A NETZCH DSC-200 was employed to measure the glass transition temperature (T_g) of sample. The scanning rate was 10°C/min in nitrogen atmosphere from -100 to 100°C. The thermal decomposition steps were investigated by NETZSCH STA-409PC TGA. The heat rate was kept 20°C/min in nitrogen atmosphere. The TGA and derivative thermogravimetry (DTG) curves were recorded from 55 to 750°C. An energy-dispersive X-ray detector (EDX) was employed to determine the elementary composition on the film surface. The determination of elementary composition was carried out at an acceleration voltage of 20 kV, lifetime >50 s, pulse counting rate \approx 2000 cps, and working distance 34 mm.

Contact angles were measured by the sessile drop method at room temperature using a JY-82 contact angle goniometer. Typically, three drops of the liquid were placed on the films surface and three readings of contact angles were taken for each drop. The average of nine readings was used as the final contact angle of each sample. Wetting liquid used for contact measurements was water and injection volume was 5 μL .

RESULTS AND DISCUSSIONS

Analysis of chemical component and structure of latex particles

The $^1\text{H-NMR}$ spectra represented in Figure 1 referred to copolymers of Sample 1(a), Sample 2(b), Sample 4(c), and Sample 6(d). Peaks at 3.63 ppm and 4.02 ppm, assigned to the O-CH_3 of MMA and O-CH_2 of BA, appeared in Figure 1(a–d). Compared with Figure 1(a) of nonfluorinated copolymer, the peak at the 4.38 ppm, assigned to O-CH_2 of TFEM, appeared in Figure 1(b); the peaks at the 4.37 ppm and 5.02 ppm, assigned to O-CH_2 and CFH of HFBM, appeared in Figure 1(c); and the peaks at the 4.55 ppm and 5.57 ppm, assigned to O-CH_2 and CFH of DFHM, appeared in Figure 1(d). $^1\text{H-NMR}$ spectra confirmed the formation of core-shell fluorinated copolymers BA/MMA/TFEM, BA/MMA/HFBM, and BA/MMA/DFHM.

According to the designed recipe of Sample 2, a latex particle with core-shell structure was expected because of the different hydrophilicities between PBA core and poly(BA/MMA/TFEM) shell. A significant contrast between core (light regions) and shell (dark regions) of the latex particles can be observed clearly in TEM micrograph of Sample 2 (Fig. 2) because of the difference of electron penetrability to the core and shell, which evidently proved the formation of the core-shell structure. TEM micrograph revealed effectively the core-shell structure of designed composite latex particle obtained by semi-continuous seed emulsion polymerization method. The diameter of spherical core-shell particles was about 80–100 nm and the thickness of shell was about 15 nm.

The DSC curves of films formed by BA/MMA/TFEM (Sample 2), BA/MMA/HFBM (Sample 4), and BA/MMA/DFHM (Sample 6) were showed in

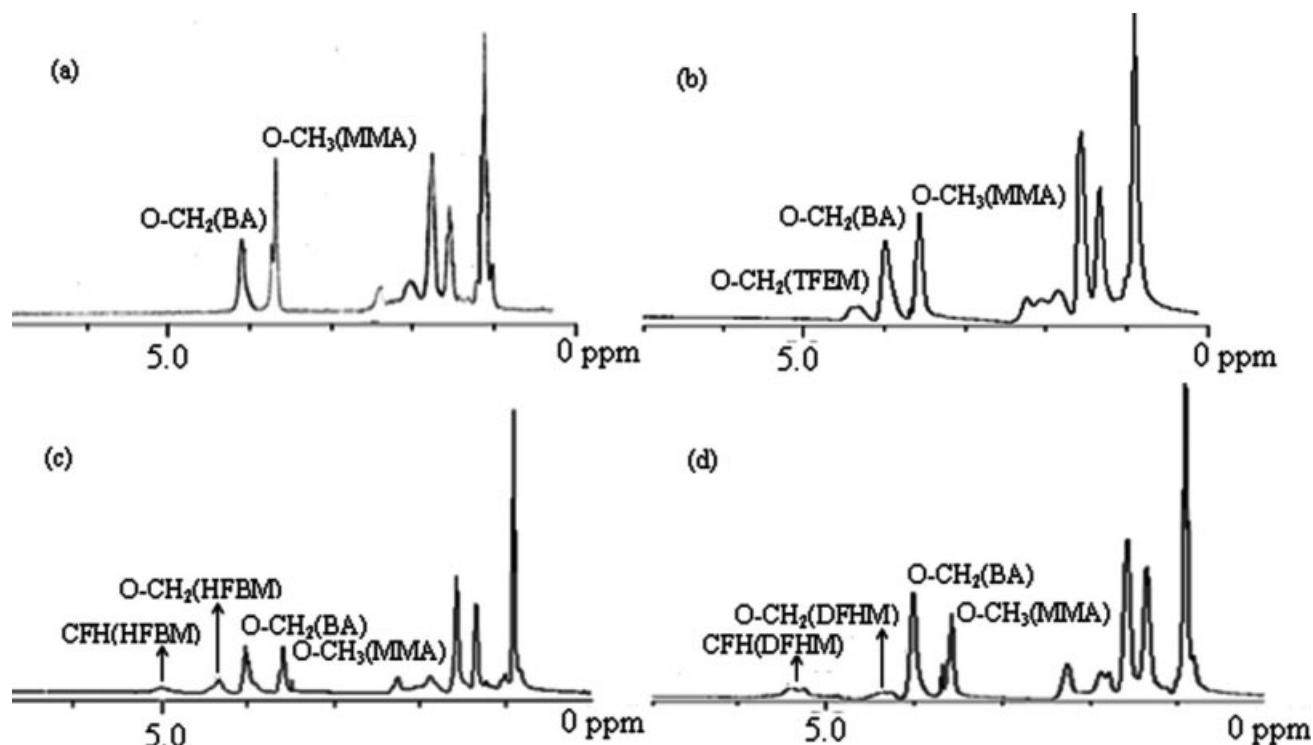


Figure 1 $^1\text{H-NMR}$ spectra of: (a) Sample 1, (b) Sample 2, (c) Sample 4, and (d) Sample 6.

Figure 3. The synthesized latices with core-shell structure were further proved by two glass transition temperatures, indicating core phase (T_1) and shell phase (T_2), respectively. Two glass transition regions can be regarded as the existence of immiscibility between core and shell components.

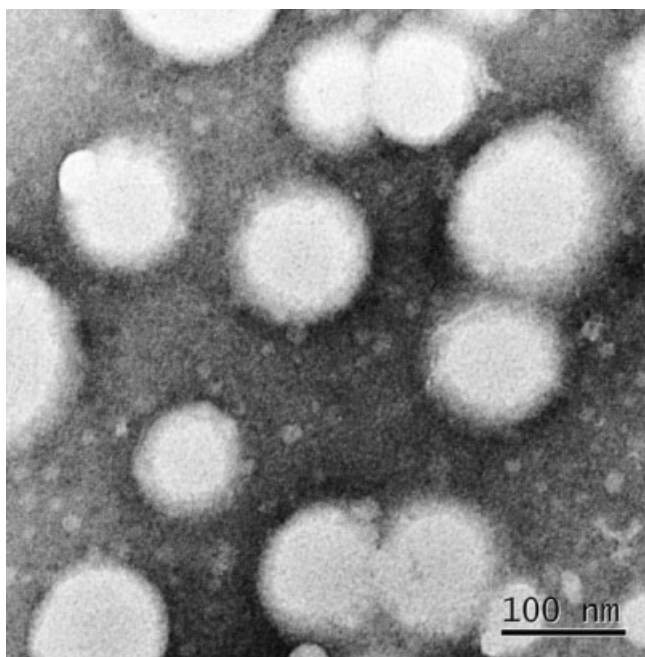


Figure 2 TEM image of Sample 2, showing uniform spherical core (light regions)/shell (dark regions) structure.

According to the designed recipes, two glass transition temperature values of all samples should be measured at -55°C (T_{g1}) for core and 30°C (T_{g2}) for shell. However, fluorinated side chain structure had a significant effect on the experimental values of two glass transition temperature values (T_1 and T_2). Compared with BA/MMA/HFBM [Fig. 3(b)] and BA/MMA/DFHM [Fig. 3(c)], T_1 and T_2 of BA/MMA/TFEM [Fig. 3(a)] were much closer and glass

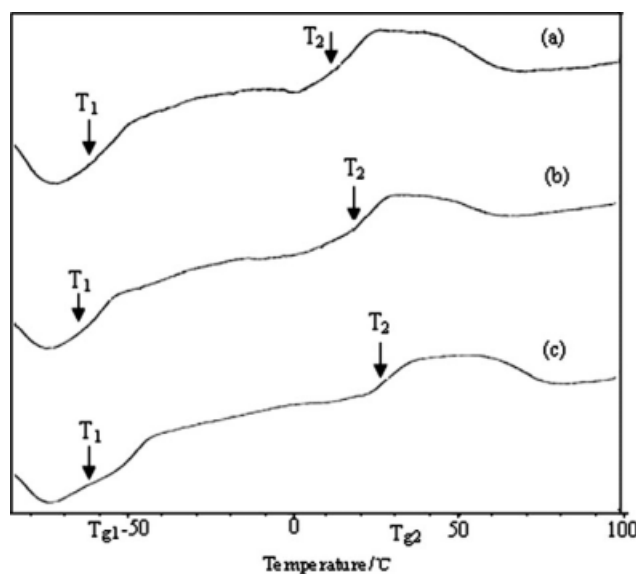


Figure 3 DSC curves of: (a) Sample 2, (b) Sample 4, and (c) Sample 6.

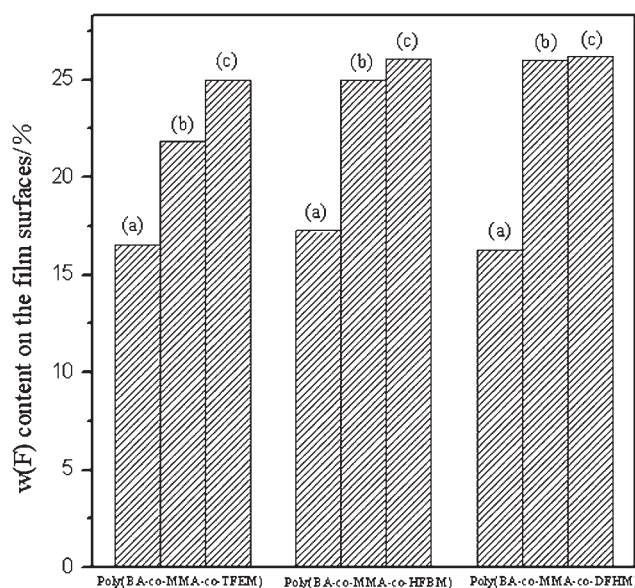


Figure 4 Fluorine content on the film surfaces of the three fluoroacrylate copolymers: (a) theoretical value, (b) general fluoroacrylate copolymers, and (c) core-shell fluoroacrylate copolymers.

transition peak was a little boarder, which implied a relatively good compatibility of core and shell components.

EDX analysis

The effect of fluorinated side chain structure on the fluorine content of films surface was investigated by EDX and the results were shown in Figure 4. The fluorine contents at the outermost layer of three copolymer films were higher than the theoretical value in the bulk [Fig. 4(a,c)], which showed a remarkable enrichment of fluorine on the film surface. This is because fluorine atoms have extremely low surface free energy and self-aggregated property, which cause the fluorinated segments to be preferentially oriented to the polymer surface during the film formation so as to decrease the surface energy of films. However, although fluorine content in BA/MMA/TFEM, BA/MMA/HFBM, and BA/MMA/DFHM was almost equal theoretically, the fluorine content on the BA/MMA/DFHM film surface was a little higher than that in BA/MMA/TFEM and BA/

MMA/HFBM. This suggested that fluorinated groups in long side chain were much easier to migrate to the surface during film formation [Fig. 4(c)].

On the other hand, compared with general fluoroacrylate copolymer, self-migration of fluorinated groups was favored and reinforced in three core-shell structure fluoroacrylate copolymer films [Fig. 4(b,c)]. In contrast with BA/MMA/TFEM and BA/MMA/HFBM, the surface fluorine content of BA/MMA/DFHM film almost resembled general fluoroacrylate copolymer [Fig. 4(b,c)]. This may be explained by the difference of reaction activity between fluorinated acrylate monomer and acrylate monomer. Various polymeric chain structures were produced when incorporating the fluorinated acrylate monomers into acrylate copolymer chains. DFHM exhibited lower copolymerization reaction activity when copolymerizing with acrylate monomers. Therefore, block or graft copolymer chain and homopolymer chain of DFHM were formed whether in core-shell fluoroacrylate copolymer or in general fluoroacrylate copolymer, which benefited the surface migration of fluorinated groups. Although TFEM or HFBM exhibited similar reaction activity to acrylate monomers, random copolymer chain was produced mainly in general fluoroacrylate copolymer, which was not favorable to surface migration of fluorinated groups.

Therefore, compared with core-shell fluoroacrylate copolymer using fluorinated acrylate monomer with long fluorinated side chain in the shell, short fluorinated side chain in the shell may have more advantages over general fluoroacrylate copolymer latex in improving surface self-migration of fluorinated groups.

The effect of temperature on the surface properties of films

Fluorine content and the water contact angles were measured on the films surfaces after annealing the films at 25, 50, and 70°C for 24 h, respectively, and the results were listed in Table II. The contact angle has commonly been used as a criterion for the evaluation of surface hydrophobic properties, which was related to the surface fluorine content. The contact angles on the surfaces of all the films were all above

TABLE II
The Influence of Temperature on the Fluorinated Content and Water Contact Angles on the Film Surfaces

Sample	25°C		50°C		70°C	
	w(F) on the film surface/%	Water contact angle (°)	w(F) on the film surface/%	Water contact angle (°)	w(F) on the film surface/%	Water contact angle (°)
Sample 2	24.99	91.34	25.02	91.76	25.12	90.00
Sample 4	26.07	98.34	26.23	94.76	26.37	93.20
Sample 6	26.20	98.66	26.20	106.66	26.21	107.50

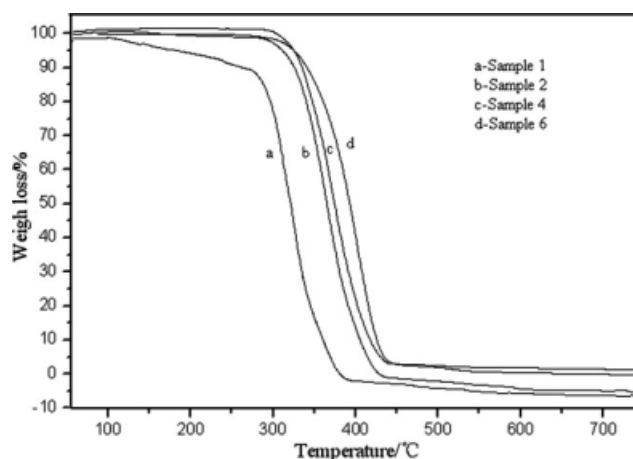


Figure 5 TGA thermograms of core-shell fluorine-free and fluorine-containing polyacrylate.

90° when the surface fluorine content was about 26 wt % (Table II). The surface fluorine content was nearly constant with the increase of annealing temperature for all the copolymers. It was noteworthy that with the increase of annealing temperature, the water contact angles on the films formed by BA/MMA/TFEM (Sample 2) or BA/MMA/HFBM (Sample 4) decreased slightly, but increased obviously on core-shell fluoroacrylate copolymer films by BA/MMA/DFHM (Sample 6). These results implied the relationship between temperature and self-organization of fluorinated side chain on the film surfaces formed by the core-shell fluoroacrylate copolymers.

It was reported that more the regularity of the arrangement of fluorinated groups increased, the more its surface properties were enhanced. For BA/MMA/DFHM, the regularity of the arrangement of fluorinated side chain was increased with the increasing of temperature, it enhanced the surface property. But for BA/MMA/TFEM and BA/MMA/HFBM, it was the opposite with the increasing of temperature.

Thermal stability of films

The TGA curves of three core-shell structure fluoroacrylate copolymers and acrylate copolymer were presented in Figure 5. The initial decomposition temperature values of core-shell fluoroacrylate copolymers were higher than acrylate copolymer, especially for BA/MMA/DFHM (Sample 6). It revealed that the introduction of fluorine atoms into polymer chains really led to a great increase in thermal stability because the carbon-fluorine single bond was the most stable one among all possible carbon-element bonds. In particular, DFHM can effectively contribute to improve thermal stability of acrylate copolymer through yielding core-shell structure copolymer with long fluorinated side chains.

Table III showed that core-shell fluoroacrylate copolymers were more effective in improving the thermal stability of acrylate copolymer. However, the improving grade was tied much more to the nature of fluorinated comonomer in the shell. For BA/MMA/TFEM and BA/MMA/HFBM, the initial decomposition temperature was increased by 16 and 19°C, respectively. It can be explained by the fact that core-shell fluoroacrylate copolymer with higher fluorine content on the film surface can shield and protect the nonfluorinated segment beneath them more effectively (Fig. 4). But for BA/MMA/DFHM, the initial decomposition temperature of core-shell fluoroacrylate copolymer increased 25°C compared with general fluoroacrylate copolymer even though the fluorine content was almost equal (Fig. 4). This phenomenon may be attributed to lower reaction activity of DFHM, which led to a little fluorine-free polyacrylate with lower thermal stability by batch emulsion polymerization.

Derivative thermogravimetry (DTG) curves of fluorinated acrylate copolymers using DFHM were investigated and shown in Figure 6. Compared with the DTG of BA/MMA/DFHM, two maximum weight loss rate temperatures (T_{\max}) appeared in

TABLE III
Thermal Degradation Characteristics of all Copolymers

Sample	IDT ^a	$T_{50\%}$ ^b	$T_{70\%}$ ^b	$T_{100\%}$ ^b	T_{\max} ^c
Sample 1 (core-shell)	315	333	347	350	326
Sample 2 (core-shell)	349	369	385	387	371
Sample 3 (general latex)	333	368	385	397	360
Sample 4 (core-shell)	353	393	408	428	397
Sample 5 (general latex)	334	379	396	413	374
Sample 6 (core-shell)	356	397	412	429	404
Sample 7 (general latex)	331	382	400	430	357,380

^a Initial decomposition temperature (°C).

^b Temperatures corresponding, respectively, to a weight loss of 50%, 70%, and 100% compared to the initial weight.

^c Temperatures noted in DTG curve and corresponding to the temperature where the decomposition rate was maximum (DTG minimum).

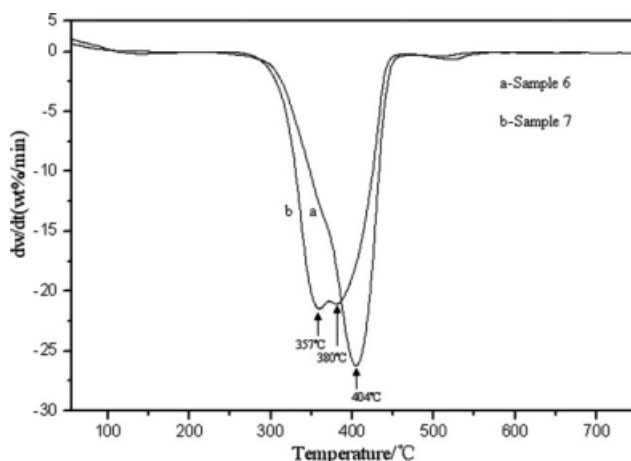


Figure 6 DTG thermograms of the fluorinated acrylate copolymers using DFHM.

DTG of general fluoroacrylate copolymer. The first maximum weight loss rate at 357°C may represent the decomposition of fluorine-free polyacrylate, which resulted in the premature degradation of general fluoroacrylate copolymer comparing that with core-shell structure.

CONCLUSIONS

Three core-shell fluoroacrylate copolymer latices were obtained by semicontinuous seed emulsion polymerization, in which BA served as the core and BA/MMA/(TFEM, HFBM, DFHM, respectively) served as the shell. The latex particles presented uniform spherical core-shell structure.

Compared with BA/MMA/TFEM and BA/MMA/HFBM, the long fluorinated side chain in BA/MMA/DFHM favored the fluorine migration toward the film surface. Moreover, contact angles measurements revealed that the surface property of BA/MMA/DFHM was enhanced with the increasing of temperature, which resulted from the tendency of regular arrangement of long fluorinated side chain. Thermal stability analysis indicated that the surface fluorine content of BA/MMA/DFHM latex resembled that of general fluoroacrylate copolymer,

but presented better thermal stability, which may imply the production of fluorine-free polyacrylate by batch emulsion polymerization.

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