

Role of acrylic acid in the synthesis of core-shell fluorine-containing polyacrylate latex with spherical and plum blossom-like morphology

Kunquan Li, Xingrong Zeng, Hongqiang Li, Xuejun Lai

College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

Correspondence to: X. Zeng (E-mail: psxrzeng@gmail.com)

ABSTRACT: The core-shell fluorine-containing polyacrylate latex was successfully synthesized by two-stage semicontinuous emulsion copolymerization of methyl methacrylate (MMA), butylacrylate (BA), acrylic acid (AA), and dodecafluoroheptyl methacrylate (DFMA). The fluorine-containing polyacrylate latex was characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), dynamic light scattering (DLS), zeta potential, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC). The effects of AA content on monomer conversion, polymerization stability, particle size, crosslinking degree, carboxyl groups distributions (latex surface, aqueous phase or buried in latex), as well as mechanical properties and water absorption rate of latex film were investigated. The obtained fluorine-containing polyacrylate latex exhibited core-shell structure with a particle size of 120–150 nm. The introduction of AA was beneficial for the increase of monomer conversion and the polymerization stability, and had little effects on the mechanical property of latex film. However, the hydrophilicity of AA made the water resistance of latex film get bad. With the increase of AA content, the carboxyl groups preferred to distribute on aqueous phase, and the possibility of homogeneous nucleation increased and more oligomers particles were formed. Moreover, the oligomers would distribute to the latex and continued to grow up, making the latex morphology changed from spherical to plum blossom-like. The core-shell latex had two T_g corresponding to the rubber polyacrylate core and hard fluorine-containing polyacrylate shell, and the latex film possessed excellent thermal stability. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42527.

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INTRODUCTION

Recently, fluorine-containing acrylate polymers have been widely applied in the areas of coatings and adhesives because of their outstanding film properties such as hydrophobicity/oleophobicity, low coefficient of friction, high thermal and chemical stability, and good weather durability.^{1–4} The fluorine chains offer low surface energy and the acrylate groups provide excellent adhesion to various substrates. Among the fluorinated polymers, core-shell fluorine-containing polyacrylate latex, composed of a fluorine-free core and fluorine-containing shell, has gained much concerns.^{5,6} The special core-shell structure makes the fluorine rich in the shell, which benefits the migration of fluorine chains to the surface during the film-forming process, and endows the fluorine-containing polyacrylate latex with desired physical and chemical properties while less fluorine-containing monomers are needed.^{7–9} Moreover, the core-shell emulsion polymerization is able to adjust the composition and structure of latex by incorporating the functional monomers in the shell.^{10,11}

Although the core-shell fluorine-containing polyacrylate latex shows promising applications in practical life, it still suffers some problems. For instance, the distinct difference of polarity between the fluorine chain and water medium restricts the transformation of fluorine-containing monomers from droplet to latex through continuous aqueous phase, resulting in the low monomer conversion and poor stability of latex.^{12,13} In addition, the core-shell polyacrylate latex with fluorine rich in the shell will lead to the bad adhesion to substrates due to the low polarizability of fluorine atom.^{14,15} To solve these problems, Cheng *et al.*¹⁶ synthesized a fluorinated monomer containing one hydroxyl group to increase the hydrophilicity of monomer, and the fluorinated monomer would cover the polyacrylate core to form a core-shell latex. Yang *et al.*¹⁷ adopted a fluorinated surfactant to synthesize fluorine-containing polyacrylate latex, and found that the fluorinated surfactant was beneficial for the improvement of conversion and compatibility between the water phase and fluorinated monomers. However, the synthesis of fluorine-containing monomer or emulsifier is involved in

complicated and time-consuming processes, and the latex stability is always neglected in these studies.

Acrylic acid (AA) is a conventional functional acrylate monomer and has been widely used in polyacrylate emulsion copolymerization.^{18–20} It is well known that AA is amphiphilic due to the existence of alkyl and carboxylic groups, and it can provide water layer and electrostatic interaction for the latex stability. In addition, the amphiphilicity of AA will reduce the interfacial tension between the monomers and water phase, which is helpful for the transportation of hydrophobic monomers from droplet to latex.^{21,22} Moreover, the carboxyl groups in AA improve the adhesion of latex to substrate and provide functional groups for potential crosslinking.^{23,24} Therefore, AA is considered as a good candidate for the modification of fluorine-containing polyacrylate latex. Until now, numerous researches have been done to study the effects of AA on the polyacrylate latex.^{25,26} But less attentions are paid to the AA modified fluorine-containing polyacrylate latex, and how the AA affects the morphology and structure of fluorine-containing polyacrylate latex, as well as carboxyl groups distributions (latex surface, aqueous phase or buried in the latex) are seldom reported.

In this study, a core-shell fluorine-containing polyacrylate latex was synthesized by two-stage semicontinuous emulsion copolymerization of methyl methacrylate (MMA), butylacrylate (BA), acrylic acid (AA), and dodecafluoroheptyl methacrylate (DFMA) using a polymerizable emulsifier of allyloxy nonylphenol polyoxyethylene (10) ether ammonium sulfate (DNS-86) as emulsifier and potassium persulfate (KPS) as initiator. The DFMA and AA monomers were incorporated at the second stage as a hard shell to cover a rubber polyacrylate core which was mainly synthesized by MMA and BA. The fluorine-containing polyacrylate latex was characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), dynamic light scattering (DLS), and zeta potential. The effects of AA content on the monomer conversion, polymerization stability, particle size, zeta potential, crosslinking degree, morphology and structure of latex, carboxyl groups distributions (latex surface, aqueous phase or buried in the latex) as well as mechanical properties and water absorption rate of latex film were systematically investigated. The thermal property of latex film were studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, A. R.), butylacrylate (BA, A. R.), and acrylic acid (AA, A. R.) were received from Tianjin Fuchen Chemical Reagent Factory (China). Dodecafluoroheptyl methacrylate (DFMA, 96%) was acquired from Harbin Xeogia Fluorine-Silicon Chemical Company (China). The polymerizable anionic emulsifier of allyloxy nonylphenol polyoxyethylene (10) ether ammonium sulfate (DNS-86, 98%) was obtained from Guangzhou Shuangjian Trading (China). Potassium persulfate (KPS, A. R.) and ethanol (A. R.) were supplied by Guangdong Guanghua Chemical Factory (China). Ammonia solution (NH₃·H₂O, 25–28%) was provided by Chinasun Specialty Products Company (China). All of the reagents were used as received.

Table I. Recipes for the Synthesis of Fluorine-Containing Polyacrylate Latex

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Core					
MMA	15.0	15.0	15.0	15.0	15.0
BA	25.0	25.0	25.0	25.0	25.0
DNS-86	1.20	1.20	1.20	1.20	1.20
KPS	0.40	0.40	0.40	0.40	0.40
H ₂ O	73.0	73.0	73.0	73.0	73.0
Shell					
MMA	20.0	20.0	20.0	20.0	20.0
BA	10.0	10.0	10.0	10.0	10.0
DFMA	14.0	14.0	14.0	14.0	14.0
AA	0	1.4	2.8	4.2	5.6
DNS-86	1.32	1.36	1.40	1.44	1.48
KPS	0.20	0.20	0.21	0.22	0.23
H ₂ O	50.4	52.5	54.6	56.6	58.7

Synthesis of Fluorine-Containing Polyacrylate Latex

The recipes for the synthesis of fluorine-containing polyacrylate latex were given in Table I, and the AA content was variable as 0, 2%, 4%, 6%, and 8% based on the weight percent of AA to MMA and BA. The latex was synthesized by a two-stage core-shell semicontinuous emulsion polymerization. The detail processes were described as follows:

At the first stage, the mixed monomers (15 g MMA and 25 g BA) were pre-emulsified by emulsifier aqueous solution (1.20 g DNS-86 dissolved in 43 g H₂O) under vigorously stirring with a speed of about 3000 r/min by a high-speed dispersion homogenizer for 15 min to form the core pre-emulsion. After that, 25 g H₂O was injected into a 250 mL four-necked glass flask equipped with teflon mechanical stirrer, reflux condenser and dropping funnels, and the temperature of the reactor was raised to 80°C in a water bath. Then the core pre-emulsion was added dropwise with KPS aqueous solution (0.40 g KPS dissolved in 5 g H₂O) into the glass flask in 2 h under mechanical stirring, and then the polymerization continued for another 1 h.

At the second stage, 20 g MMA, 10 g BA, 14 g DFMA, and a certain amount of AA were emulsified by emulsifier aqueous solution (1.32–1.48 g DNS-86 dissolved in 45.4–53.7 g H₂O). Then the shell pre-emulsion and the KPS aqueous solution (0.20–0.23 g KPS dissolved in 5 g H₂O) were fed into the core latex within 2 h. When the feeding was completed, the polymerization was allowed to react for another 1 h. Finally, the fluorine-containing polyacrylate latex was cooled to room temperature, and the pH was adjusted to 6–8 by NH₃·H₂O.

Characterization

Monomer conversion was measured by gravimetric analysis. About 1 g latex was dried at 100°C to constant weight, and monomer conversion was measured according to the following equation:

$$\text{Monomer conversion} = \frac{W_1 - W_2}{W_3} \times 100\% \quad (1)$$

where W_1 , W_2 , and W_3 represented the weight of latex after drying, involatile compositions and monomers in the latex, respectively.

The final emulsion was filtered and the coagulum was collected. Coagulum ratio was defined as the weight percent of the dried coagulum to the total monomers.

Crosslinking degree of latex was estimated by extraction with tetrahydrofuran (THF) under reflux for 8 h, and calculated according to the following equation:

$$\text{Crosslinking degree} = \frac{W_b}{W_a} \times 100\% \quad (2)$$

where W_a and W_b represented the weight of latex before and after extraction.

The carboxyl groups distributions (latex surface, aqueous phase, or buried in the latex) were determined by conductometric titration.^{26,27} First, the latex was diluted with water to a concentration of about 1.5%, and the pH was adjusted to about 11.5 by NaOH solution. Then the latex was titrated with HCl solution at a concentration of 0.022 mol/L, and the conductivity of system through the whole titration process was determined by a conductivity meter (SX723, Shanghai San-Xin Instrumentation, China). The carboxyl groups on the surface (C_s) of latex and aqueous phase (C_a) were calculated based on the conductometric titration curve, and the carboxyl groups buried in the latex (C_b) were obtained by a mass balance of carboxyl groups.

Fourier transform infrared spectroscopy (FTIR) spectra were collected in a range from 4000 to 400 cm^{-1} on a Bruker Tensor 27 spectrometer (Bruker Optics, Germany) with a spectral resolution of 4 cm^{-1} using KBr pellet method.

Particle size of latex was determined by a dynamic light scattering (DLS) detector (90 plus, Brookhaven Instruments Corporation, America). Sample was diluted with water until the concentration was about 0.1% before testing.

Zeta potential was measured and recorded on ZetaPlus (90 plus, Brookhaven Instruments Corporation, America).

Morphology of latex was observed by a transmission electron microscopy (TEM) instrument (Hitachi H-7650, Japan) under an acceleration voltage of 80 kV. Latex was diluted with water to make a concentration of 0.1%, and dyed by 2% phosphotungstic acid before observation.

Thermal stability study was performed on a thermal gravimetric analysis (TGA, TGA209F3, Germany) with a heating rate of 10°C/min from 35 to 600°C under nitrogen atmosphere.

Differential scanning calorimetry (DSC) was utilized to measure the glass transition temperature (T_g) of latex. The testing was carried out by a NETZCH DSC-200 instrument (Germany) at a scanning rate of 10°C/min from -50°C to 150°C under nitrogen atmosphere.

The latex was dried at 100°C to constant weight, and about 1 g polymer was collected in plastic wrap, and then immersed in water for 24 h. Water absorption rate were calculated according to the following equation,

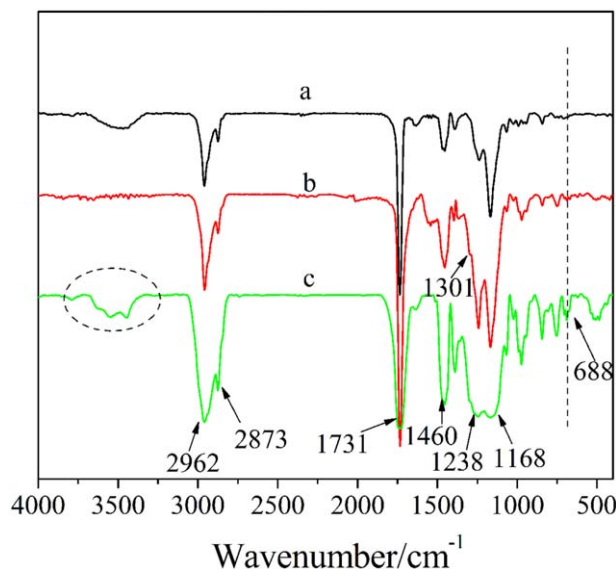


Figure 1. FTIR spectra of polyacrylate core (a), fluorine-containing polyacrylate latex (b), and AA modified fluorine-containing polyacrylate latex (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\text{Water absorption rate} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (3)$$

where W_1 and W_2 represented the weight of latex before and after immersion.

The pencil hardness, flexibility, impact strength and adhesion of latex film were tested according to the GB/T 6739-2006, GB/T 1731-1993, GB/T 1732-1993, and GB/T 9286-1998 using tin-plate as substrate, respectively.

RESULTS AND DISCUSSION

FTIR

Figure 1 shows the FTIR spectra of polyacrylate core (a), fluorine-containing polyacrylate latex (b), and AA modified fluorine-containing polyacrylate latex (c). In Figure 1(a), the peaks at 2962 cm^{-1} and 2873 cm^{-1} are ascribed to the stretching vibrations of $-\text{CH}_2$ ($-\text{CH}_3$), and the bands located at 1460 cm^{-1} are caused by the distortion vibration of $-\text{CH}_2$. The absorption near 1731 cm^{-1} , 1238 cm^{-1} and 1168 cm^{-1} are attributed to the stretching vibration of $\text{C}=\text{O}$, and asymmetrical and symmetrical stretching vibration of $\text{C}-\text{O}$, respectively.²⁸ Compared with Figure 1(a), two new peaks at 1301 cm^{-1} and 688 cm^{-1} are observed in Figure 1(b,c), which are caused by the $\text{C}-\text{F}$ stretching vibration and $-\text{CF}_2$ wagging vibration from DFMA,^{29,30} indicating that the fluorine-containing polyacrylate latex has been synthesized. Whereas in Figure 1(c), the spectra show new peaks near 3500 cm^{-1} and strong absorption at 1168–1238 cm^{-1} in comparison with Figure 1(b), owing to the existence of $-\text{OH}$ and $\text{C}-\text{O}$ from carboxyl groups in AA.

Monomer Conversion and Coagulum Ratio

Monomer conversion and coagulum ratio of fluorine-containing polyacrylate latex with different AA content are shown in Figure 2. With the increase of AA content from 0% to 8%, the monomer conversion gradually increases from 93.2% to 98.8%, whereas the

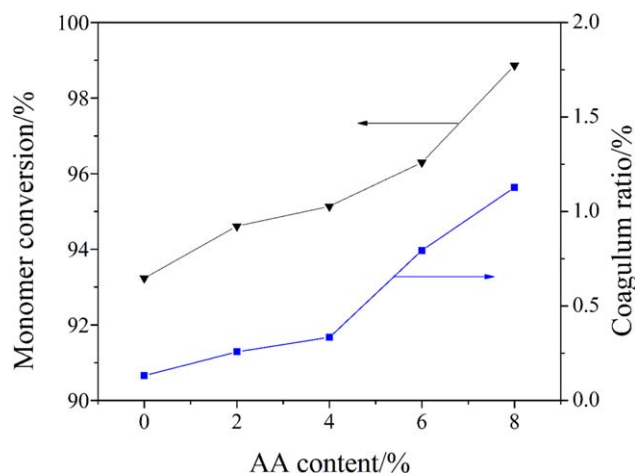


Figure 2. Effects of AA content on monomer conversion and coagulum ratio of fluorine-containing polyacrylate latex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coagulum ratio enlarges from 0.1% to 1.1%. It is well known that the fluorine-containing monomer is hydrophobic due to the existence of C–F group, and the DFMA is restricted to transfer from monomer droplets to the latexes through the aqueous phase, leading to a low monomer conversion.¹⁷ AA is an amphiphilic monomer, and can act as a bridge for the transportation of DFMA to latex, which is beneficial for the increase of monomer conversion. However, at high AA content, the homogeneous nucleation of AA in aqueous phase took place due to the good water-solubility of AA, and large numbers of particles adhered to each other and some large latexes were agglomerated and deposited. Moreover, the carboxyl groups in AA may lead to cross-linking reaction between the latex. Therefore, with the increase of AA content, the coagulum ratio increased.²³

Particle Size and Crosslinking Degree

In Figure 3, it shows that the particle size of latex was 143 nm without adding AA, and the crosslinking degree is about 43.3%, which may be caused by the chain transfer reaction during the polymerization. With the increase of AA content to 4%, the

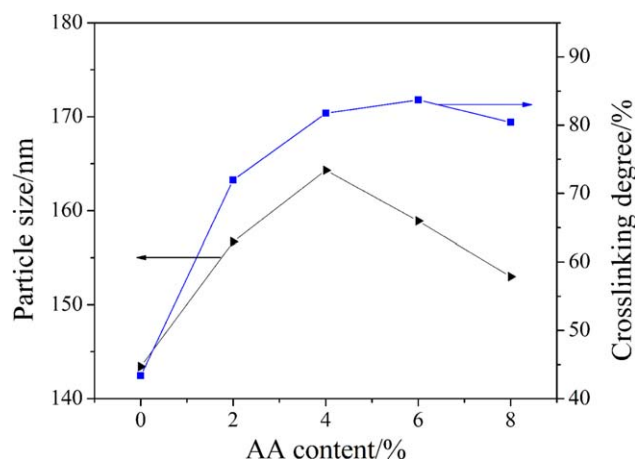


Figure 3. Effects of AA content on the particle size and crosslinking degree of fluorine-containing polyacrylate latex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

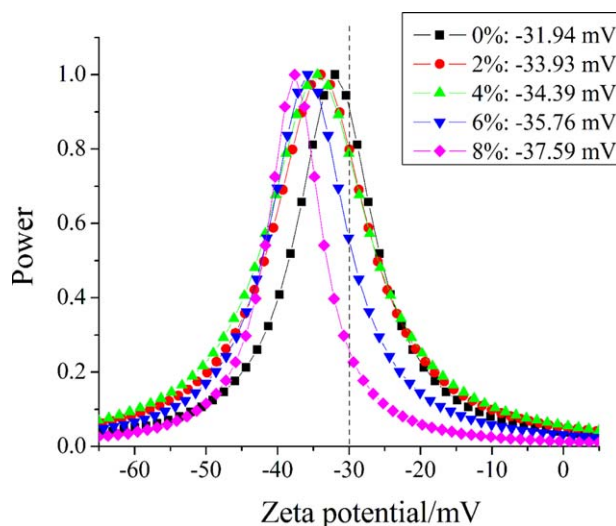


Figure 4. Effects of AA content on the zeta potential of fluorine-containing polyacrylate latex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

condensation of carboxyl groups in AA occurs and the cross-linking degree increases to nearly 80.0%, leading to a larger particle size of 164 nm. As AA is mainly located on the surface of the latex after polymerization, its hydrophilic carboxyl groups have hydration effects and can provide electrostatic repulsion, which is good for the stability of latex. Therefore, with the increase of AA content, the hydration effects reinforce and water layer enlarges, resulting in the large particle size. For the further increase of AA content from 4% to 8%, the crosslinking degree almost keeps constant at 80.0% whereas the particle size gradually decreases to 153 nm. This is because that at high AA content, partial AA monomers will participate in homogeneous nucleation to form oligomers in aqueous phase, and the oligomers contribute to the increase of particle number and the decrease of particle size. Meanwhile, the copolymerization of AA in the polymer chain and crosslinking reaction of carboxyl groups are restricted.²⁶

Zeta Potential

Zeta potential is a good indicator to evaluate the latex stability, and the latex is considered as stable when its zeta potential is more positive than 30 mV or more negative than -30 mV, depending on the property of surface charge.³¹ From Figure 4, the zeta potentials of the synthesized latexes are lower than -30 mV, indicating that the latexes possess good stability in aqueous phase. In addition, the zeta potential of latex decreases from -31.94 mV to -37.59 mV with the AA content ranging from 0% to 8%. It is attributed to the fact that the copolymerization of AA in the shell phase will make the carboxyl groups distribute on the latex surface, and the carboxyl groups provide more negative charges for the electrostatic interaction, which promotes the stability of latex.

Carboxyl Groups Distribution

Figure 5 shows the conductometric titration curve of latex with HCl solution (a) and the carboxyl groups distribution with different AA content (b). In Figure 5(a), the conductometric

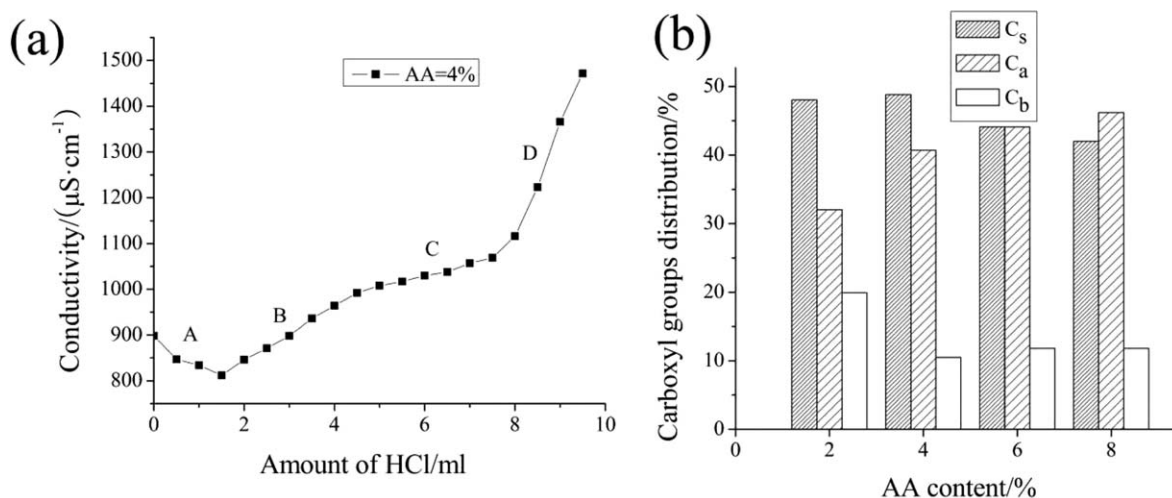


Figure 5. Conductometric titration curve of latex with HCl solution (a) and the carboxyl groups distribution with different AA content (b).

titration curve of latex with HCl solution is similar to other reports.²⁷ The decrease of conductivity in part A and the increase in part D are ascribed to the neutralization of NaOH and the existence of excess HCl, respectively. While the increase of conductivity in part B and part C are attributed to the neutralization of carboxyl groups on the latex surface and aqueous phase, respectively. The results of carboxyl groups distributions are presented in Figure 5(b). It shows that the carboxyl groups tend to bond on the latex surface with a high percentage over 40%, and the C_b possesses the lowest percentage compared with C_s and C_a due to the hydrophilicity of AA. When the AA content increases from 2% to 8%, the percentage of C_s enlarges

from 32.0% to 46.2%. It can be inferred that at high AA content, the probability of polymerization of AA in aqueous phase increases and the carboxyl groups tend to keep in aqueous phase. However, the increase of AA content has little effects on the percentage of C_s but the high hydrophilicity of AA prevents it from transferring into the latex, making the C_b decrease to a low percentage of 10%.

TEM

Figure 6 shows the TEM images of fluorine-containing polyacrylate latex with 0% (a–a₁), 4% (b–b₁), and 8% (c–c₁) of AA content. From Figure 6 (a,a₁), the fluorine-containing polyacrylate

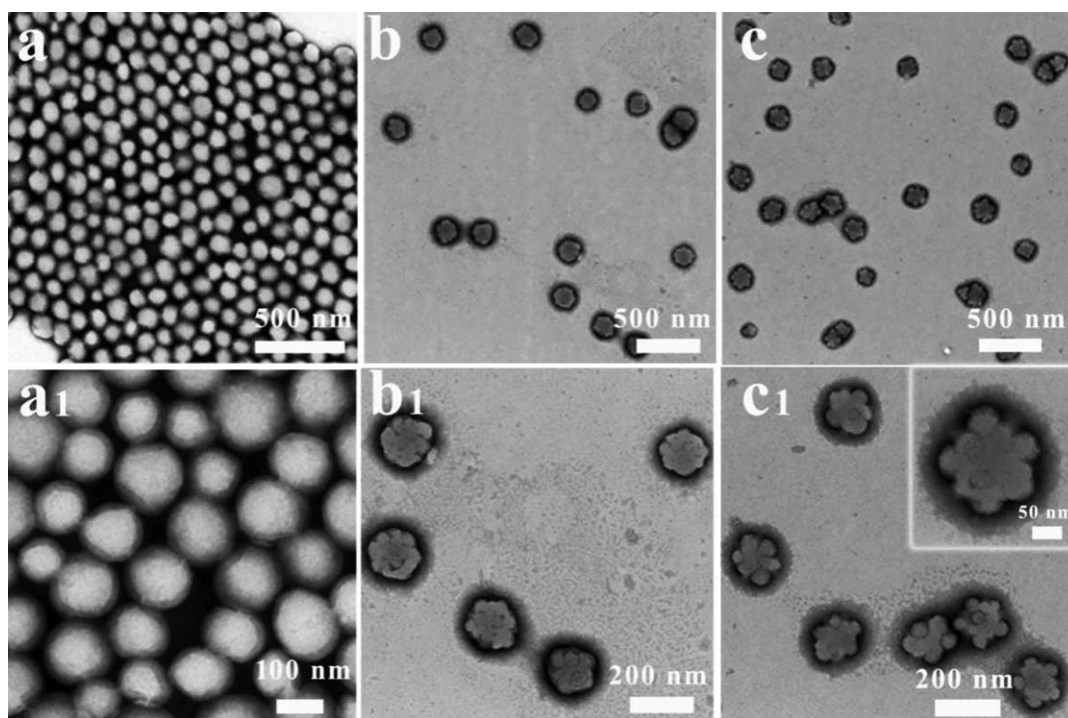


Figure 6. TEM images of fluorine-containing polyacrylate latex with 0% (a–a₁), 4% (b–b₁), and 8% (c–c₁) AA.

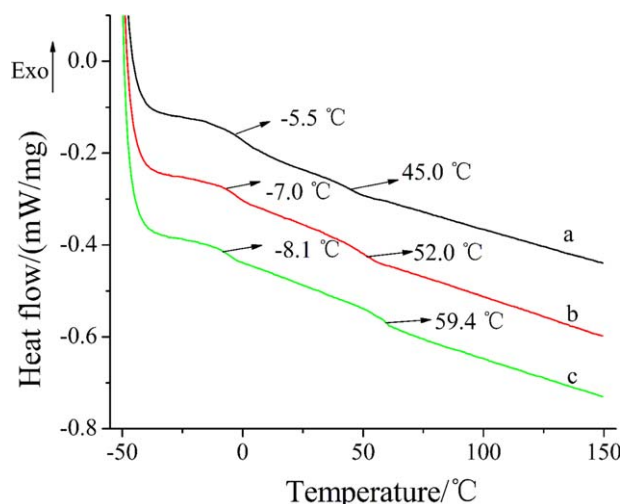


Figure 7. DSC curves of fluorine-containing polyacrylate latex film with 0% (a), 4% (b), and 8% (c) AA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

latex exhibits clear core-shell structure, where the light and dark regions represent the polyacrylate core phase and the fluorine-containing polyacrylate shell phase. Meanwhile, the spherical latex uniformly disperses in water with a particle size of about 120–150 nm, which is consistent with the analysis from DLS. After 4% of AA content was incorporated, in Figure 6(b,b₁), the latex still keeps good dispersion while the latex seems nonspherical and its surface is concavo-convex. When the AA content increases to 8%, this phenomenon becomes more obvious and a plum blossom-like latex can be observed, which has been shown in Figure 6(c,c₁). The reasons can be explained as follows. At the second stage of the two-stage semicontinuous emulsion polymerization, with the increase of AA content, the monomers became hydrophilic and the reaction sites changed from latex to the aqueous phase. Meanwhile, there were lots of latexes and a few of monomers, and the latexes would polymerize with the monomers as soon as they diffused into the latex, which was effective for the formation of core-shell latex. Hence, the polymerization places at second stage is mainly located between latex surface and aqueous phase. With the increase of hydrophilicity of monomers, the reaction sites are easy to move to aqueous phase, and the homogeneous nucleation takes place to form the oligomers. These oligomers will continue to grow up and diffuse into other particles, and then embed onto the surface of particles. Therefore, with the increase of AA content, the core-shell spherical latex

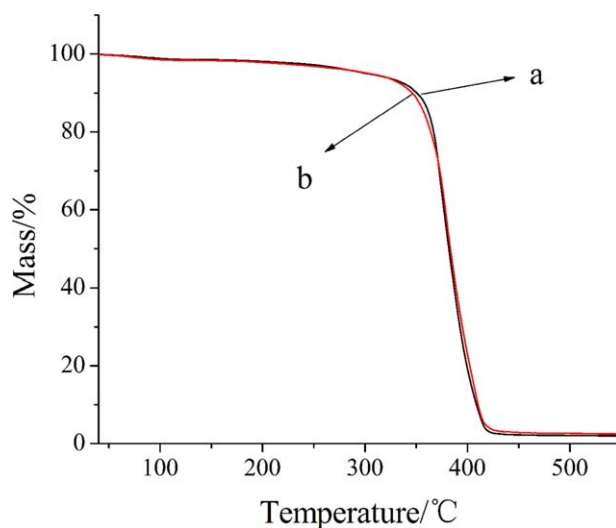


Figure 8. TG curves of fluorine-containing polyacrylate latex film with 0% (a) and 4% (b) AA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

becomes nonspherical and concavo-convex, and finally turns to plum blossom-like morphology.²⁷

DSC

The glass transition temperature (T_g) of latex is studied by DSC analysis. As shown in Figure 7, all of the tested latexes have two T_g , indicating that the latexes possess core-shell structure, which accords with the results from the TEM. Moreover, the latexes show rubber core with T_g from -5.5°C to -8.1°C and hard shell with T_g higher than 45.0°C . In addition, in Figure 7, the T_g of the shell phase gradually increases from 45.0°C to 59.4°C with the AA content ranging from 0% to 8%, which may be caused by the high T_g of PAA and the crosslinking reaction of latex in the presence of AA.

TG

From the TG curves shown in Figure 8, the initial, maximum weight loss rate and complete decomposition temperatures of fluorine-containing polyacrylate latex occur at about 360°C , 380°C , and 420°C , respectively. Meanwhile, the curves in Figure 8(a,b) show a similar trend, indicating that the incorporation of AA has little effects on the thermal stability of latex. The TG study shows that the core-shell fluorine-containing polyacrylate latex possesses good thermal stability because the fluorine chains with high bond energy are rich in the shell to protect the polymer segments from decomposing at high temperature.

Table II. Effects of AA Content on the Mechanical Properties and Water Absorption Rate of Fluorine-Containing Polyacrylate Latex Film

AA content/%	Pencil hardness	Flexibility/mm	Impact strength//kg.cm	Adhesion	Water absorption rate/%
0	HB	2	55	0	13.6
2	HB	2	55	0	25.8
4	HB	2	55	0	39.6
6	HB	2	55	0	40.2
8	HB	2	55	0	38.8

Mechanical Properties and Water Absorption Rate

As seen from Table II, the pencil hardness, flexibility, impact strength, and adhesion of all the fluorine-containing polyacrylate latex films are HB, 2, 55, and 0, respectively, indicating that the introduction of AA has little effects on the mechanical properties. However, as AA is hydrophilic, with the AA content increase from 0% to 8%, the water resistance of the latex film gets bad and the water absorption rate gradually enlarges from 13.6% to 39.8%.

CONCLUSIONS

The core-shell fluorine-containing polyacrylate latex was successfully synthesized by two-stage semicontinuous emulsion copolymerization of MMA, BA, AA, and DFMA. The obtained latex possessed good stability with a coagulum ratio below 1.1% and a zeta potential of negative than -30 mV. The introduction of AA was beneficial for the increase of monomer conversion and the polymerization stability, and had little effects on the mechanical property of latex film. However, the hydrophilicity of AA made the water resistance of latex film get bad. The AA content had a significant influence on the latex morphology. With the increase of AA content, the reaction sites are easy to move to aqueous phase and the homogeneous nucleation took place to form the oligomers which will continue to grow up and diffuse into other particles, leading to a non-spherical and plum blossom-like morphology. In addition, the prepared core-shell latex had two T_g corresponding to the rubber polyacrylate core and hard fluorine-containing polyacrylate shell, and possessed good thermal stability.

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