

Miniemulsion Polymerization of Fluorinated Siloxane-Acrylate Latex and the Application as Waterborne Textile Finishing Agent

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ABSTRACT: Fluorinated siloxane-acrylate polymer latex was synthesized via miniemulsion polymerization, which was carried out by pseudo one-step method. In the synthesis protocol, the monomers of octamethylcyclotetrasiloxane (D_4), tetravinyltetramethylcyclotetrasiloxane (D_4^v), methyl methacrylate, butyl acrylate, *N*-methylol acrylamide, and dodecafluoroheptyl methacrylate (DFMA) were first mixed and homogenized into a miniemulsion, which was stabilized by dedecylbenzene sulfonic acid. The ring-opening polymerization of cyclosiloxane was then steadily performed under miniemulsion conditions and followed by the postaddition of radical initiators to initiate the polymerization of acrylate and DFMA monomers. The influences on the emulsion properties by acrylic monomer with different addition protocol were investigated in this work. In addition, the synthesized latexes were characterized by using dynamic laser scattering, transmission electron microscope, differential scanning calorimetry, and Fourier transform infrared spectroscopy. These results indicated that the introduction of D_4^v in the latex can successfully suppress the phase separation between the thermodynamically incompatible components for the formation of uniform hybrid latex particles. The further application of the as-synthesized latex was investigated as a new kind of waterborne textile finishing agent. Moreover, the influences of the content of D_4^v and DFMA on the finishing properties, especially for the softness, the water repellence, and the antimoisture properties, were systematically studied in this work. With a proper design on the content of the D_4^v and DFMA, stable textile finishing emulsion was prepared, which can endow the fabric both desirable softness and excellent water resistances. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40162.

KEYWORDS: applications; composites; morphology

Received 12 August 2013; accepted 3 November 2013

DOI: 10.1002/app.40162

INTRODUCTION

Recently, the synthesis of environmental-friendly textile finishing agents with multifunction has attracted particular enthusiasm in modern textile industries.¹ Among the various kinds of purchasable textile finishing agents in the market, the waterborne latexes of fluoropolymers are superior due to the excellent water-repellent finishing effects endowed by the special low surface energy of fluorochemicals.² However, the textile products would lose their good soft handle feeling after the treatment using such fluoropolymer as finishing agents. On the other hand, waterborne organosilicon emulsion is the most ideal choice as the softeners, based on the proper flexibility on their molecular chains.³ Besides, the synthesis of fluorosilicon copolymers can be carried out via the introduction of fluorinated side chains on the organosilicon main chains, which can endow the textile with both the desirable soft feelings and the resistance

performance to water and oil.⁴ And hence, they showed the great potential on the practical application as textile finishing agent.

The studies on the films of fluorinated organosilicon polymers with excellent surface properties have been widely concerned in the past decade. However, the published literature about the investigation on synthesis and properties of textile finishing polymer latex is still quite limited, and most of works about them were just published in the patent form. Based on these works, the fluorinated organosilicon polymer latexes can be prepared via the direct polymerization of fluoro-containing silicone monomers by using the special synthetic processes, and most of them are very complex.⁵ As an alternative, fluoro-containing silicone polymers can also be prepared by the copolymerization of fluorinated and silicone monomers.⁶ Although homogeneous esterification, addition, etherification, and/or ring-opening

reactions are all utilized for the synthesis of such kind of fluorinated organosilicon polymers, which are usually carried out in organic solvents,^{7–11} the heterophase polymerization in aqueous medium is also available and shows the special advantages on the environmental and healthy earnings for their production and application as textile finishing agents.¹² In addition, the synthesis of waterborne fluorinated organosilicon polymer latex by using the ordinary commercial fluorinated and silicone monomers is attractive due to that the tedious synthesis of special monomers can be avoided. However, the synthesis of waterborne fluorinated organosilicon polymer latex is still a challenge, which is attributed to that the ordinary fluorinated and silicon monomers are hydrophobic and incompatible between each other. Thus, it is not easy to incorporate them together via the conventional emulsion polymerization. Moreover, for the final latex, the content of gel and/or floating oil are generally at a high level, and the severe phase separation always occur in final latex particles, which in turn hinders the desired synergetic properties of their final product.

Compared with the conventional emulsion polymerization process, the miniemulsion polymerization shows the great benefits for the polymerization of hydrophobic silicone and fluorinated monomers in aqueous medium. Different from the traditional emulsion system, there is no mass transport process during the miniemulsion polymerization process and the nucleation and propagation processes mainly occur in the monomer droplets, both of which result in the much easier incorporation of the hydrophobic monomers.¹³ It has been reported by Keddie et al.¹⁴ that both the chain extender reaction of polyurethane and the free radical polymerization (FRP) of polyacrylate can be carried out in one miniemulsion polymerization process, and the polyurethane-acrylic hybrid latexes were prepared and applied as pressure-sensitive adhesives.

Since the two kinds of polymerizations based on different mechanisms in one droplet is accessible via miniemulsion polymerization technique, in this work, we combined the ring-opening polymerization (ROP) of cyclosiloxanes and FRP of fluorinated acrylic monomers in one miniemulsion system, so as to prepare the fluorinated siloxane-acrylate polymer latex through the simplified reaction protocol. Dodecylbenzene sulfonic acid (DBSA) was employed as emulsifier in this study, which can also serve as the initiator (INISURF) for the ROP reaction of cyclosiloxane monomers. The ROP reaction was first carried out, and FRP reaction was subsequently initiated after the second addition of FRP initiator. Moreover, tetravinyltetramethylcyclotetrasiloxane (D_4^V) was also introduced into the miniemulsion system as a kind of coupling monomers, so as to improve the compatibility of the two polymer phases within the latex particle. It is a novel polymerization protocol that the silicone and fluorinated monomers were added into one batch with the two step addition of the initiators, which was designed as pseudo one-step method in this study. The postformed fluorinated polyacrylate via the FRP of methylacrylate and dodecafluoroheptyl methacrylate (DFMA) was effectively grafted onto the polysiloxane chains due to the existence of reactable sites on the molecular chains as synthesized via ROP reaction of octa-

methylcyclotetrasiloxane (D_4) and D_4^V . The produced fluorinated polyacrylate-g-polyvinylmethylsiloxane (FA-g-PVMS) latex was systematically characterized and further applied as the textile finishing agent. The influences of D_4^V and DFMA on the performance of the latex and the finished fabric were also investigated in detail.

EXPERIMENTAL

Materials

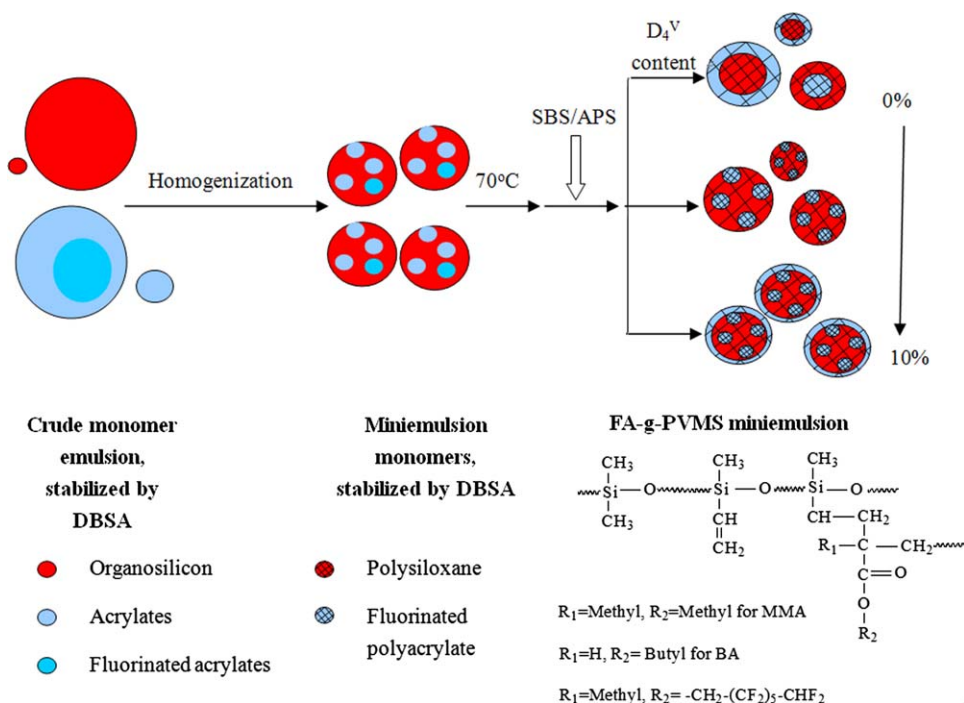
Octamethylcyclotetrasiloxane (D_4 , $\geq 99\%$) and tetravinyltetramethylcyclotetrasiloxane (D_4^V , $\geq 99\%$) were purchased from Sage Chemical Co. Ltd., People's Republic of China. DBSA ($\geq 99\%$) was purchased from Shanghai Resin Co., People's Republic of China. DFMA at industrial grade was purchased from Haerbin Xuejia Fluorosilicone Chemical Company, People's Republic of China. Methyl methacrylate (MMA), butyl acrylate (BA), and *N*-methylol acrylamide (NMA) were all at analysis grade and purchased from Beijing Dongfang Chemical Plant. Ammonium persulfate (APS) and sodium bisulfite (SBS) were purchased from the Beijing Chemical Plant with analytical grade. All of the reagents were used as received without any further purification. The deionized water used in this work was prepared in our laboratory.

Pseudo One-Step Miniemulsion Polymerization of FA-g-PVMS

The mixtures of D_4 and D_4^V were prepared with the different weight ratio for the following miniemulsion polymerizations. First, the mixture of D_4 and D_4^V (15 g), MMA (6 g), BA (6 g), and a proper amount of NMA and DFMA were added into a flask with the aqueous solution of DBSA (0.9 g in 70 g water). Subsequently, the mixture was pre-emulsified under a mechanical stir at 1000 r/min for 10 min. The crude emulsion was then transferred into a high-pressure homogenizer (AH110D, ATS Engineering Inc., Canada) for the further miniemulsification process. The mixture was homogenized at 90 MPa with a flow rate of 10 L/h for four times. Meanwhile, the homogenizing chamber was cooled using a cooling jacket containing 5°C of water. The obtained miniemulsion was then transferred into a four-neck flask equipped with a mechanical stirring, a thermometer, and the nitrogen inlet and outlet. The miniemulsion was purged for 20 min with nitrogen under the stirring at room temperature, and then the temperature was increase to 70°C in a thermostated water bath. After 3 h of reaction time, the aqueous solution of APS and SBS was dropped into the miniemulsion to initiate the FRP within 1 h. After another 2 h of reaction time, the emulsion was cooled down to room temperature. The final emulsion was neutralized to pH 7–8 using ammonia. The reaction protocol is briefly shown in Scheme 1.

Two-Step Polymerization of FA-g-PVMS

The two-step synthesis of FA-g-PVMS was also carried out in this work for the comparison. In addition, the formulation of the reaction was similar to that as described in "Pseudo One-Step Miniemulsion Polymerization of FA-g-PVMS". However, the process was clearly divided into two parts: the monomer miniemulsion of D_4 , D_4^V , and DBSA was first prepared by homogenization. The ROP process of D_4 and D_4^V was then carried out via a typical miniemulsion polymerization for the preparation of PVMS latex.¹⁵ The polymerization of acrylic



Scheme 1. Schematic illustration of the pseudo one-step polymerization of FA-g-PVMS miniemulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monomers (including DFMA) was secondly carried out via seeded semicontinuous polymerization using the PVMS latex as the seed with the acrylic monomers and the radical initiators supplied in secondary batch.

Emulsion Characterization

The monomer conversion was determined via gravimetric method. The samples were dried at 140°C for 4 h. In addition, the conversion was calculated by the following eq. (1):

$$\text{conv \%} = \frac{m_t - m_s}{m_0 - m_s} \times 100\% \quad (1)$$

where m_t , m_s , and m_0 are the mass of the residual substance, the emulsifier contained in the sample, and the solid substance at 100% conversion, respectively. For the two-step polymerization process, the conversions of cyclosiloxane and acrylic monomer were determined using the samples after the first step and the second step reaction process, respectively. Meanwhile, for the pseudo one-step method, only the total monomer conversion can be obtained. The particle size and distribution of the synthesized latexes were characterized by a commercial dynamic laser scattering (DLS, Zetasizer NanoZS, Malvern). The samples were dried in a vacuum oven at room temperature for 24 h before the other characterizations. Transmission electron microscope (TEM) was carried out by HITACHI H-800 electron microscope at an acceleration voltage of 200 kV. Differential scanning calorimetry (DSC) measurements of the as-prepared samples were performed with a NETZSCH DSC 204 F1 system at heating and cooling rate of 10 K/min under a nitrogen purge. The value of the midpoint of the transition in the second heating process was taken as the glass transition temperature T_g .

The transmission Fourier transform infrared (FTIR) spectra were recorded using Bruker Tensor 37 spectrometer. A total of 32 scans were accumulated for signal averaging of each IR spectral measurement to ensure a high signal-to-noise ratio with a 4 cm^{-1} resolution.

Application in the Textile Finishing Agents

The as-synthesized latex (4 g) was diluted by deionized water (100 mL) for the application as textile finishing agent. In addition, the cotton fabrics were treated by padding method with the diluted emulsion. Subsequently, these fabrics were dried at 90°C for 4 min and at 170°C for another 2 min. These cotton fabrics after the treatment as above were further employed for the performance evaluation of the as-prepared waterborne textile finishing agent.

Textile Softness

The textile softness was characterized by hand. Five random people have been asked to evaluate the hand feelings on the finished fabric. The softness of the fabric treated by pure silicone finishing emulsion was defined as grade 5, while the softness of the untreated fabric was defined as grade 1.

Water-Repellent Grade

The water-repellent grade was evaluated by the method of 3M-II-1988. In this method, a series of mixed solvent with various ratios between isopropanol and water was used as the standard test solvent, which was sorted by their isopropanol composition and listed in Table I, and the test was started from the standard solvent by a smallest largest rule. About 0.05 mL of the test solvent was dropped on the fabric at three different areas with the separate distance more than 2 in. The highest water-repellent grade of the solvent, which can sustain global or elliptical for

Table I. Standard Solution for Water-Repellent Test

Water-repellent grade	Solvent composition		Water-repellent grade	Solvent composition	
	Isopropanol (%)	Water (%)		Isopropanol (%)	Water (%)
1	2	98	7	50	50
2	5	95	8	60	40
3	10	90	9	70	30
4	20	80	10	80	20
5	30	70	11	90	10
6	40	60	12	100	0

10 s after being dropped onto the surface of the fabric, was defined as the water-repellent grade of the fabric.

Antimoisture Grade

The antimoisture was evaluated according to the Chinese standard of GB/T4745-1997. The fabric was fixed with the bevel at 45° to the nozzle, which was connected to a water funnel. About 250 mL of water was sprayed from the nozzle on to the center of the fabric. The fabric was then taken off and tapped on a hard surface with the fabric upside down. The antimoisture grade was defined by comparison the tested surface with the standard graphs shown in Figure 1.

Water Contact Angle (WCA)

Contact angles of water (WCA) on the latex film or the fabric were measured using OCA 20 video-based contact angle measuring device (Dataphysics, Germany) at room temperature. The results reported here are the mean values of at least 10 replicates.

RESULTS AND DISCUSSION

Influence of Polymerization Protocol

Two methods have been attempted to incorporate the fluorinated polyacrylate into polysiloxane latex, and the reactions were performed through the different polymerization protocols. The comparison of the two different polymerization protocols is listed in Table II. In the pseudo one-step method, all the monomers including the mixture of D₄ and D₄^v, methylacrylate, and DFMA were simultaneously added into one batch and homogenized by a high pressure homogenizer, which gave out the stable monomer miniemulsion with high efficiency.¹⁵ With the elevation of reactor temperature, the ROP reaction of D₄/D₄^v was initiated by DBSA and proceeded steadily based on the interfa-

cial propagation mechanism, which has been reported in our previous work.¹⁶ Meanwhile, the DFMA component was also served the co-stabilizer due to its extreme hydrophobicity and there was no obvious effect on the ROP reaction by the DFMA component. With the supplemental addition of FRP initiators in the pseudo one-step system, the reactive double bonds were initiated and polymerized so as to obtain the hybrid polymer latexes. In the two-step synthesis process, however, the addition of two kinds of monomers for ROP and FRP was clearly separated, in which the ROP reaction was carried out in the first step and the FRP reaction was initiated in the second step. The cyclosiloxane were miniemulsified and first polymerized in miniemulsion using DBSA as the INISURE.¹⁷ The miniemulsion of polysiloxane was further used as the seed for the second batch of acrylic monomers and the corresponding initiator solution in water was slowly dropped into the reaction system. And hence, the emulsion polymerization was carried out in a typical seeded semicontinuous manner. Compared with two-step method, the pseudo one-step method is obviously simple, in which the secondary addition of monomers and the relevant problem of system control can be avoid.

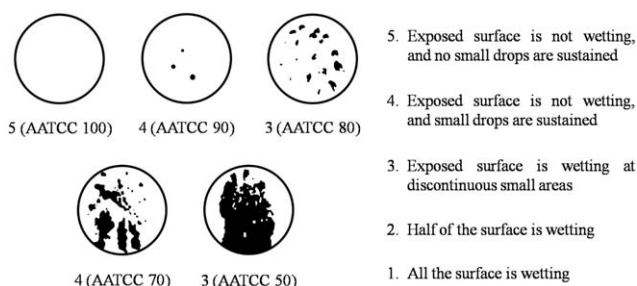
Further advantages of the pseudo one-step method on the polymerization were also proposed in this work as shown in Table II. It can be seen in Table II that the conversion of cyclosiloxane monomers was obviously increased from 87% (the two-step method) to above 95% (the pseudo one-step method). And the

Table II. Comparison on the Polymerization Protocols

	Two-step method	Pseudo one-step method
Reaction time (h)	7	5
Emulsifier content (%)	4–6	2–3
Cyclosiloxane monomer conversion (%)	87 ^a	>95 ^b
Acrylic monomer Conversion (wt %)	90 ^a	>95 ^b
Gel content	High	None
Diameter (nm)	190	170

^aThe individual monomer conversion after first step and second step polymerization was calculated.

^bThe total monomer conversion was calculated.

**Figure 1.** Standard of antimoisture test.

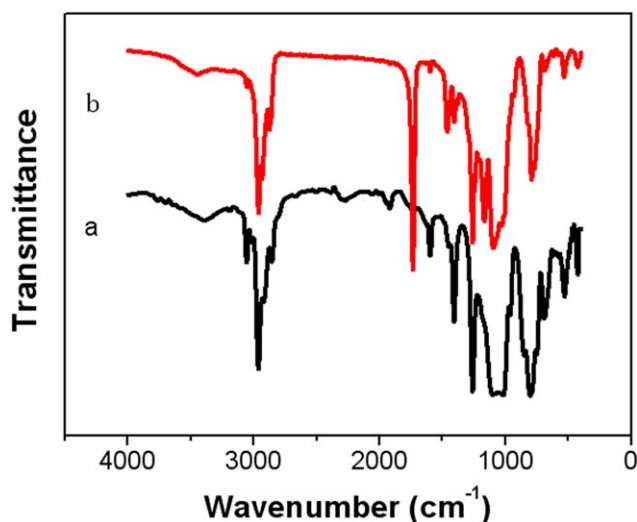


Figure 2. FTIR spectra of PVMS and FA-g-PVMS: (a) PVMS, (b) FA-g-PVMS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction time was also shortened in the pseudo one-step method. The optimized conversion for the cyclosiloxane monomers in the pseudo one-step method was expected to be caused by the hydrophobic property of DFMA monomer, which was served as an effective hydrophobe during the miniemulsion copolymerization process of D_4 and D_4^v as catalyzed by DBSA. The degradation of the droplets/particles was suppressed by the hydrophobe, which was against the emigration of the monomers or oligomers out of the reaction sites and in favor of the conversion improvement. In addition, the conversion of acrylic monomers was also improved in the pseudo one-step method, which can be explained by the avoidance of postaddition of hydrophobic fluorinated monomers. The diffusion of such kind of monomers from aqueous phase to the emulsion seed for further particle increment is hard restricted due to their low solubility in water. It is noteworthy that the gel content of the pseudo one-step method was correspondingly decreased, indicating the enhanced polymerization stability, even at the lower emulsifier content. The as-synthesized latexes via pseudo one-step method showed the notably improved monomer conversion and polymerization stability. Thus, in the following works, we employed as-synthesized latexes via pseudo one-step method for the further systematic investigation unless the otherwise indicating.

FTIR Characterization

FTIR spectrum of the as-synthesized FA-g-PVMS latex via pseudo one-step method in this study is shown in Figure 2(b) (red line). In addition, the FTIR spectrum of PVMS latex, which was synthesized by the miniemulsion polymerization of D_4 and D_4^v , is also shown in Figure 2(a) (black line) for the comparison.

In the FTIR spectrum of PVMS in Figure 2(a), the band around 1598 cm^{-1} can be clearly seen, which is due to the C=C stretching vibration of the vinyl groups of D_4^v . However, through the comparison of the IR spectra in Figure 2(a,b), it

can be found that the C=C stretching band was obviously decreased for the FA-g-PVMS latex, indicating the effective graft reaction between the C=C groups of FA units and D_4^v monomers. Meanwhile, for both PVMS and FA-g-PVMS, the band around 1262 cm^{-1} due to the C-Si stretching vibration can be observed as shown in Figure 2(a,b). In addition, the C-F stretching vibration band around 1161 cm^{-1} is clearly seen in the FTIR spectrum of FA-g-PVMS as shown in Figure 2(b). Therefore, it can be concluded that the graft reaction of the fluorinated acrylic segment on to the PVMS chains was successfully carried out, in which the vinyl groups on the polysiloxane introduced by D_4^v acted as the binding sites. In addition, it is also consistent with the results of the variational FTIR spectra in C=C stretching vibration band region.

Influence of D_4^v Content on the Properties of Latex

The vinyl groups were introduced on to the main chain of the polysiloxane via the copolymerization of D_4 and D_4^v , which provided the reactive sites for the further graft copolymerization of fluorinated acrylic as the side chain. In addition, it is confirmed that the structures, as well as the properties of the final FA-g-PVMS latexes are sensitive to the D_4^v content during the synthesis process. For the morphological investigation on the latex particles, the TEM images of the FA-g-PVMS latexes with the different amount of D_4^v as 0, 5, and 10 wt % are shown in Figure 3(a-c), respectively.

For the FA-g-PVMS latex particles without the addition of D_4^v monomer as shown in Figure 3(a), the phase separation with different morphologies can be obtained, even in one sample. Even though all of these particles behaved as the core-shell structure, the difference between them was still clearly found in Figure 3(a): about one-third of them were consisted of light core matrix and dark coronal (inverse core-shell structure) and about another two-thirds of them were consisted of dark core matrix and light coronal (normal core-shell structure). Besides, the distribution of particle size was wide. Considering the composition of such latex, we can determine that the dark phase should be attributed to the polysiloxane phase and the light phase should be attributed to the polyacrylate phase with the fluorinated acrylate copolymer units. It is well accepted that the phase separation within the latex particles is synchronously controlled by both dynamic and thermodynamic equilibriums. Based on the thermodynamic equilibrium, the hydrophobic segment with fluorinated polyacrylate monomer would diffuse into the inside of latex particles, which was driven by the hydrophobic forces. And hence, the latex particles with inverse core-shell structure were obtained. However, in the pseudo one-step polymerization process, the large-scale phase separation between fluorinated polyacrylate and pure polyacrylate phases should also occur, so that such phase separation with inverse core-shell structure would only occur when the fluorinated polyacrylate segment in shell layer polymers was rich. In contrast, when the composition of shell layer polymers was rich at pure polyacrylate segment, the latex particles with normal core-shell structures were generated. Therefore, the distribution of fluorinated polyacrylate in the shell layer polymer would affect the morphology of final latex particles. Meanwhile, the dynamic equilibrium also determined the structure of final latex particles. The

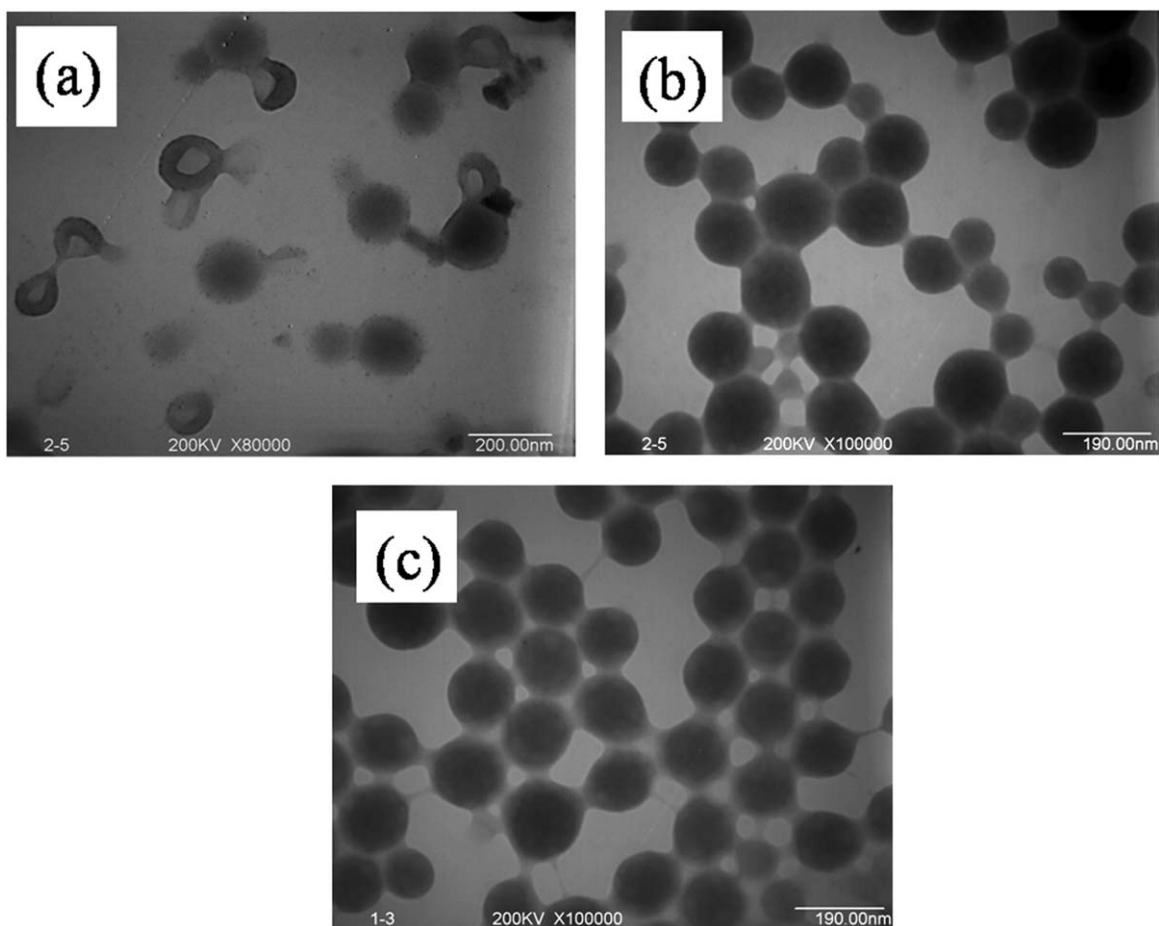


Figure 3. TEM micrographs of the FA-g-PVMS latex particles with different D_4^V : (a) 0, (b) 5 wt %, (c) 10 wt %.

coexistence of cyclosiloxane, acrylate, and fluorinated acrylate monomers and their corresponding polymers led to the more complex molecular chain diffusion in the different phases. The interface condition was influenced by the fluctuation of temperature and stirring conditions, which in turn resulted in

the un-uniform core-shell structure of FA-g-PVMS latex particles without D_4^V .

As the D_4^V content was increased to 5 wt % in the miniemulsion system, the homogenous latex particles were obtained as indicated by the TEM image in Figure 3(b). It is noteworthy that the phase separation between the polysiloxane phase and the polyacrylic phase with fluorinated polyacrylate copolymer units was successfully suppressed by the introduction of D_4^V . In addition, the phase separation was just localized in a limited extent, which is due to formation of hybrid structures relying

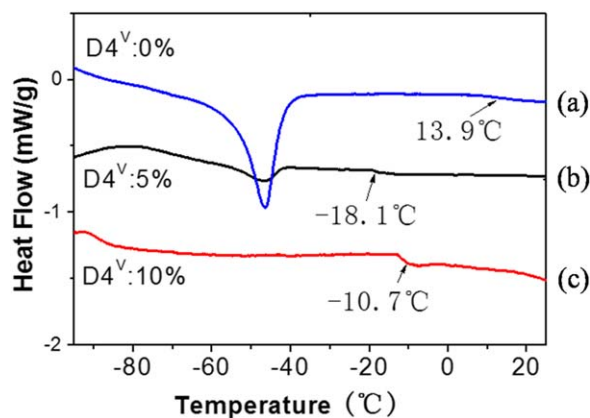


Figure 4. DSC thermograms of the FA-g-PVMS latex particles with different D_4^V contents: (a) 0 (blue line), (b) 5 wt % (black line), (c) 10 wt % (red line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Properties of the FA-g-PVMS Latex with Different D_4^V Content

D_4^V content (wt %)	0	5	10
Particle size (nm) ^a	173	172	170
PDI ^a	0.07	0.08	0.04
State of the polymer	Very stick	Stick	Not stick, soft
Fabric softness	Grade 4	Grade 3	Grade 1

^aThe diameter of latex particles was measured using DLS.

Table IV. Properties of FA-g-PVMS Latex with Different DFMA Content

DFMA content (%)	0	10	20	40
Textile softness	3	3	3	3
Contact angle (latex film) (°)	103	115	115	115
Contact angle (finished fabric) (°)	120	135 (rollable)	145 (rollable)	145 (rollable)
Water-repellent (3M-II-1988)	Grade 2	Grade 3	Grade 4	Grade 6
Antimoisture (GB/T4745-1997)	Grade 1	Grade 2	Grade 3	Grade 4

on the introduction of D_4^V . The distribution of particle size was also wide with the variational diameter from 50 to 170 nm.

With the further increasing D_4^V content up to 10 wt %, the noticeable variation of particle morphology was found as indicated by the TEM image in Figure 3(c). However, the distribution of latex particle size was improved and almost all of the particles behaved as the uniform core-shell structure with the dark core matrix and the gray shell coronal. It is expected that the phase separation between core and shell phases in the latex would be attributed to the increase of crosslinking densities, which was also due to a side effect of the redundant vinyl groups of D_4^V as mentioned by Bourgeat-Lami et al. [18].

The depressed phase separation can be further proved by the DSC results. During the second heating process of DSC measurement, the thermograms of the as-synthesized latexes with different D_4^V content at 0, 5, and 10 wt % are shown in Figure 4 by the blue, black, and red line in part (a), (b), and (c), respectively. For the latex without the introduction of D_4^V as shown by the blue line in Figure 4(a), a melting peak at -46.3°C due to PDMS can be obviously seen. Besides, the glass transition process with T_g at 13.9°C is found, which is attributed to the fluorinated polyacrylate molecular chains. However, for the FA-g-PVMS latex with the D_4^V content at 5 wt % as shown by the black line in Figure 4(b), the melting peak was much weaker than that of the latex without D_4^V (blue line), and the low-temperature shift of T_g to -18.1°C was observed. The lessened melting peak and the low-temperature-shifted T_g indicated the increasing phase compatibility between the polysiloxane and fluorinated polyacrylate phase. For the FA-g-PVMS latex with the D_4^V content at 10 wt % as shown by the red line in Figure 4(c), the melting peak of PDMS totally disappeared, which was attributed to that the regularity of polysiloxane chains have been interrupted by the grafted side chains of fluorinated polyacrylate. Meanwhile, the T_g of the FA-g-PVMS latex with the D_4^V content at 10 wt % was at a higher temperature around -10.7°C than that of the FA-g-PVMS latex with the D_4^V content at 5 wt %, indicating the increasing intermolecular crosslinking densities.

The properties of the as-synthesized latexes with different amount of D_4^V are listed in Table III. With the increase of the D_4^V content from 0 to 10 wt %, even through the stable polymer latexes can be obtained, the appearance of the isolated copolymers from the emulsions changed from the sticky oil state to rubbery form. The textile softness of the fabrics after the treatment using the as-synthesized latexes also changed

from grades 4 to 1. The depressed textile softness is expected to be caused by the increasing amount of grafted fluorinated polyacrylate side-chains, which behave as the negative influence on the flexibility of the main chain of PDMS. Moreover, the additional crosslinking reaction caused by the graft reactions also shows the contribution on the rigidity of the latex performance. The variational performance of the latex finishing agents with the increasing D_4^V content is also consistent with the DSC results. When the content of D_4^V was increased to above 10 wt %, the corresponding polymers were almost lost their functionality on soft finishing. Therefore, the content of D_4^V was controlled at 5 wt % for the further investigation in the following part.

Influence of DFMA Content on Latex Properties

The textile softness of the finished fabrics using the as-synthesized latex was evaluated. In addition, the water contact angles on the latex films and the finished fabrics were respectively measured. Moreover, the water repellent and the antimoisture properties of the as-synthesized latexes with the different DFMA content were also characterized. These results are listed in Table IV. It can be seen that the water contact angles on the latex films and the finished fabrics by using the as-synthesized latexes obviously increased with the increasing DFMA content from 0 to 10%, and respectively kept constant at 115° and 145° with DFMA content at 20 and 40%. Correspondingly, the water repellent and antimoisture properties of the fabrics after treatment by the synthesized latexes were also much improved with the increasing content of fluoro components. Accompanied with the DFMA content increased from 0 to 40%, the water-repellent grade of the fabrics treated by the corresponding copolymer latexes increased from grades 2 to 6, meanwhile, the antimoisture grade increased from grade 1 with whole the surface wetted by water to grade 4 with only small drops of water sustained on. However, the textile softness of finished fabric was kept on 3, which was not sacrificed with the increasing water-resistant properties. Therefore, the increase of DFMA content in the FA-g-PVMS latexes can effectively improve the hydrophobic property of finished fabrics, although the textile softness of them is not changed.

CONCLUSION

The fluorinated acrylate grafted silicone latexes were successfully synthesized via a pseudo one-step method. The D_4^V monomer provided the binding points for the graft of fluorinated acrylate on to the PVMS chains, which can effectively depress the phase

separation of the latex particles. In addition, the results of TEM images indicated that the latex particles with homogeneous structures can be produced with the controllable D_4^V content above 5 wt %. The synthesized latexes were further applied as textile finishing agent for cotton fabrics. The results show that the textile softness of the finished fabrics would totally depressed with the D_4^V content up to 10 wt %, due to the increasing density of side chains on to the polysiloxane chains. However, the content of the side chains, such as the DFMA content, did not show the obvious influence on the softness of the finished fabrics. In contrast, the water repellent and the antimoisture properties show the sensitive dependence on the DFMA content. Through the controlling on the D_4^V and DFMA content in the latex (e.g., 5 wt % of D_4^V and 40 wt % of DFMA), this work provided an efficient way to synthesis waterborne textile finishing agent, which can endow the fabrics both desirable softness and excellent water resistances.

ACKNOWLEDGMENTS

This work was financially supported by National Science Foundation of P. R. China (Grant No. 21304007), the Scientific and Technological Project of Beijing (Grand No. Z131103002813071), and Fundamental Research Funds for the Central University at Beijing University of Chemical Technology.

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