Cationic Fluorinated Polyacrylate Core-Shell Latex with Pendant Long Chain Alkyl: Synthesis, Film morphology, and Its Performance on Cotton Substrates

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ABSTRACT: We synthesized a novel cationic fluorinated polyacrylate latex (FLDH) with pendant long chain alkyl by copolymerization of perfluoroalkyl ethyl acrylate, lauryl methacrylate, dimethylaminoethyl methacrylate, and 2-hydroxypropyl acrylate. FTIR, ^{1}H-NMR, TEM, DSC, and TGA were used to characterize the as-prepared FLDH. Then fine morphology, components, and hydrophobicity of films on silicon wafer and cotton substrates were investigated by scanning electron microscope, field emission scanning electronic microscope, atomic force microscope, X-ray photoelectron spectroscopy (XPS), contact angle meter, etc. Results showed that the FLDH particles had quasi-spherical core-shell structure with an average diameter of 144 nm. The core-shell FLDH film thus had two T_g and its thermal property was improved compared to fluorine-free acrylate latex. FLDH could form a film on both the cotton fiber and silicon wafer substrate. At an amplification of <60,000 (of the original fiber) and the observation rule (working distance) of >100 nm, FLDH showed a smooth resin film on the treated fabric/fiber surface. However, as the observation rule decreased to 2 nm-almost a molecular lever-the FLDH film mostly exhibited an inhomogeneous structure and uneven morphology in its atomic force microscope images. There were many low or high peaks in FLDH topography. Consequently, in 5 μm^2 scanning field, the root mean square roughness of FLDH film reached to 0.506 nm. XPS analysis indicated the perfluoroalkyl groups had the tendency to enrich at the surface. In addition, water contact angle of the treated fabric could attain 146.2°. FLDH do not influence whiteness of the treated fabric but will make it slightly stiff at high doses. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Fluorinated acrylate copolymers possess both the inherent characteristics of fluorine-containing polymers, such as high thermal, chemical, aging and weather resistance; low surface energy; excellent oil and water repellency, etc., and favorable adhesion property of acrylate resin to various substrates.[1,2] Hence, it has been widely used in the field of coatings, fabric finish, leather, and packing.[3–5] Among them, textiles are probably the largest category in which they are used, due to their optimum performance in terms of both hydrophobicity and oleophobicity without impairing the textile's permeability to air and vapor or modifying the handle of the fabrics.[6]

In recent years, many researchers have devoted themselves to investigating and developing the fluorinated polyacrylate latexes

(FLDH) because of their special surface property and especially economical, low-toxic characteristics compared with fluorinated polyacrylate solutions. For this reason, various kinds of fluorinated polyacrylate emulsions, such as graft,[7] random,[8] hybrid nanocomposites,[9] core-shell,[3,10–12] etc., have been developed via diverse emulsion polymerization methods. Fluorinated polyacrylate latices with core-shell structure were paid much attention due to their typical advantage in film formation compared with common emulsions, especially the latex consisting of fluorine-free acrylic core and fluorine-containing acrylic shell. During film-forming process, its shell preferentially migrated to the surface and endowed the materials with excellent surface properties. By comparison, its core assembled in the bulk and provided the materials with good adhesion towards substrate.

Anionic fluorinated polyacrylate core-shell emulsions are often encountered in literatures[3,10–14]; however, little work has been focused on the cationic fluorinated acrylic core-shell latexes, which show very high adhesion to different ionic substrates, especially anionic substrates such as textile, paper, leather, and glass. In our previous work,[15] a novel cationic fluorinated polyacrylate core-shell emulsion (CFBDH) was synthesized and used to treated the cotton fabrics, then, its film morphology on cotton fabrics or imitated cellulose substrate and hydrophobicity of the treated cotton fabrics were investigated. The CFBDH film on imitated cellulose substrate, silicon wafer surface, presented an inhomogeneous pattern and had many low or high peaks resulting from fluoroalkyl groups by atomic force microscope (AFM) detection. At 2 nm data scale and in 1 μm^2 scanning field, Rq of CFBDH film reached to 0.205 nm. Finally, water contact angle of the treated cotton fabric could attain 134.2°.

Hence, in this work, to further improve the water repellency of cationic fluorinated polyacrylate core-shell latex, lauryl methacrylate (LMA) segment was introduced into the polymers to acquire a cationic FLDH with pendant long chain alkyl, which was prepared through semi-continuous seed emulsion polymerization of perfluoroalkyl ethyl acrylate (FA), LMA, dimethylaminoethyl methacrylate (DM), and 2-hydroxypropyl acrylate (HPA), are used to treat the cotton fabrics. Then, its film morphology and microstructure on cotton fabrics or silicon wafer surface, as well as its performance were investigated by field emission scanning electronic microscope (FESEM), AFM, contact angle meter, X-ray photoelectron spectroscopy (XPS), and other instruments.

EXPERIMENTAL

Materials

DM and HPA were purchased from Shanghai Chemical Auxiliary, China and used as received. LMA was purchased from Tianjin Tianjiao Chemical, China, and used with no treatment. FA was kindly provided by Anhui Lixing Chemical, China and used as received. The initiator ammonium persulfate (APS) was purchased from Shanxi Baohua Technology, China and used without further purification.

Owing to wide differences of surface energy and relative density between fluorinated acrylate monomer and other fluorine-free monomers, it would be best to choose the complex emulsifier systems for stabilities of emulsion polymerization and the final emulsion. So the mixed emulsifier systems in this work were composed of Gemini surfactant N,N′-dihexadecyl-N,N,N′,N′-tetramethyl ethyl diamide bromide (21631, HLB value = 14) and fluorinated fatty alcohol polyoxyethylene ether (S-200, HLB value = 17), which were purchased from Henan Daochun Chemical, China and Harbin XEOGIA Fluorine-Silicon Chemical, China, respectively and used as received.

A cotton fabric with a density of 133 × 72 (the counts of warp × fill yarns; 10 × 10 cm^2) was purchased from Huarun textile manufacture company, Shaanxi, China. Prior to finishing treatment, a piece of cotton fabric was successively ultrasonicated using deionized water and acetone at 25°C for 30 min, respectively, and then dried at 100°C for 5 min. This process was to remove the slurry and contaminants on the fiber/fabric substrates. Silicon wafers, kindly provided by Songjiang Silicon Material, Shanghai, China, were cleaned and dried based on our previous works.[16–18]

Synthesis of FLDH Core-Shell Latex

The core-shell FA/LMA/DM/HPA latex was synthesized by semi-continuous seed emulsion polymerization. All the polymerization steps were conducted under the protection of nitrogen gas in a 250 mL four-neck flask equipped with reflux condenser, mechanical stirrer, dropping funnel, and a nitrogen inlet. The first step was to obtain the seed latex. Ten grams LMA and 1 g HPA were pre-emulsified at 50°C for 0.5 h in the flask containing 60 g deionized water and 1.41 g mixed emulsifiers of 21631 and S-200 (at the optimized weight ratio of 21631/S-200 = 1 : 2 based on conversion and coagulation ratio of emulsion polymerization). When the flask was heated to 80°C, 0.055 g of initiator (APS) was added to prepare the seed latex for 0.5 h. The second step was to synthesis the core-shell copolymer as follows. The mixture monomers of 5 g LMA, 15 g FA, 1.5 g DM, and 0.108 g APS were added drop-by-drop during 3–4 h. After the addition of all these materials, the reaction temperature was held at 85°C for another 0.5 h. The latex was obtained eventually by adjusting its pH value to 3–4 with NaHCO$_3$ solution at room temperature and the total conversion rate was 80.66%. Meanwhile, fluorine-free polyacrylate emulsion was also synthesized by copolymerization of LMA, DM, and HPA according to aforementioned procedure and noted as LDH.

Application of the FLDH Latex on Silicon Wafer and Cotton Fabric Substrates

FLDH was dissolved with deionized water to form a 0.03 wt % polyacrylate aqueous solution. A prepared silicone wafer was impregnated into the above FLDH aqueous solution and kept for several seconds, then dried at 80°C for 5 min and cured at 170°C for 3 min. Finally, the sample was kept in a desiccator to balance for 24 h and noted as FLDH/Sil (for the silicon wafer substrate).

As for the treatment of cotton fabrics, 0–3.5 wt % FLDH aqueous solutions were first prepared and then fabric samples were impregnated in those aforesaid aqueous solutions and kept for several seconds, padded to wet pick-up at about 70% on the weight of the dry fabrics. Then the padded fabrics were dried at 100–105°C for 10 min, cured at 160°C for 30 s, finally kept in a drier overnight, and noted as FLDH/cotton (for the cotton fiber/fabric substrate).

Characterization of the FLDH Latex and Its Film

FTIR spectra of samples were recorded between 4000 and 500 cm^{-1} on a Bruker VECTOR-22 spectrophotometer using KBr pellet technique. ^{1}H-NMR analysis was performed with INOVA-400 spectrometer using CDCl$_3$ as solvent and tetramethylsilane (TMS) as an internal standard.

The particle size and its distribution of the FLDH latex were measured by Nano-ZS particle sizer (Malvern Instruments Company, UK). Transmission electron microscopy (TEM) micrographs of the FLDH particles were taken with H-600 transmission electron microscope (Hitachi Company, Japan)
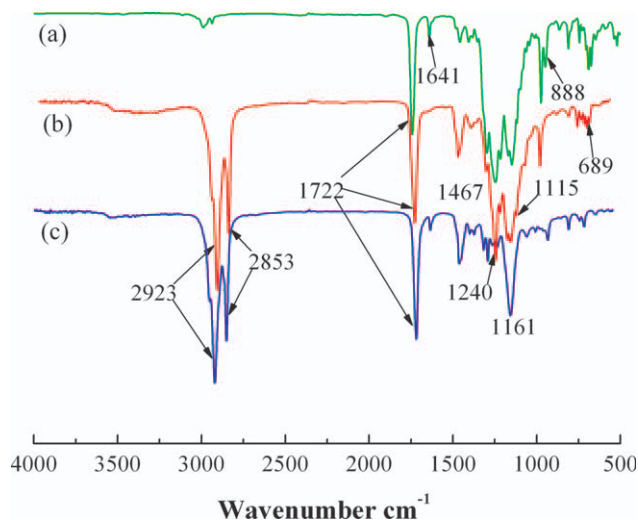
Figure 1. FTIR spectra of (a) monomer FA, (b) FLDH, and (c) LDH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with an acceleration voltage of 200 kV. The samples were stained with 2% phosphotungstic acid solution.

The glass transition temperature (T_g) of polymer samples was measured by a NETZCH DSC-200. The scanning rate was 10°C/min from −80 to 100°C under nitrogen atmosphere. Thermogravimetry analysis (TGA) was performed on a Q500 thermogravimeter (TA Instruments Company) under the nitrogen atmosphere at a heating rate of 10°C/min from ambient temperature to 800°C.

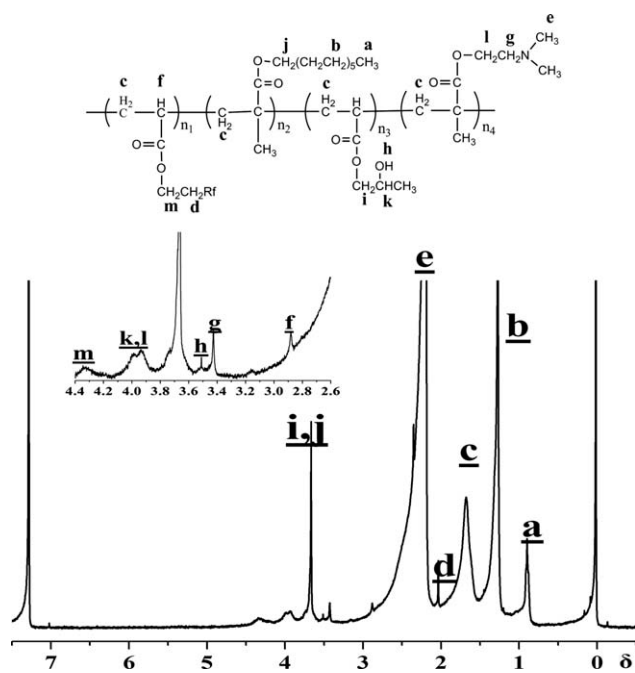The surface morphology of the cotton fibers/textiles or silicon wafer treated by FLDH were observed by scanning electron microscope (SEM), FESEM, and AFM. SEM and FESEM measurement were carried out on S-570 scanning electron microscope (Hitachi) and a SIRION 200 field emission scanning electron microscope after the fiber samples were coated with gold in vacuum, the morphologic photographs were taken at magnification of 5000, 20,000, and 60,000 times. AFM images were obtained with a Nanoscope IIIA AFM (Digital Instruments) in tapping mode. All the scanning was performed at 22°C and in air of relative humidity of 48%.

The surface chemical compositions of the treated textiles were analyzed by XPS instruments. XPS analysis were performed on a Physical Electronics Model 5700 X-ray photoelectron spectrometer equipped with monochromatic Al Kα source (150 W, 15 KV, and KE = 1486.6 eV). Three take-off angles (30°, 60°, and 90°) were adopted and the vacuum degree of analysis chamber was 6.7×10^{-8} Pa. In the XPS measurement, the deviation of the binding energy was corrected by the C1s photoelectron emission signal occurring at 284.8 eV due to hydrocarbon contamination on the sample surface.

Static contact angles (CAs) of water on the air-exposed film surface were performed by the sessile drop method on a JC2000A contact angle goniometer (Shanghai Zhong Chen Powereach, China) at 20°C. The injection volume of liquid was 5 μL and
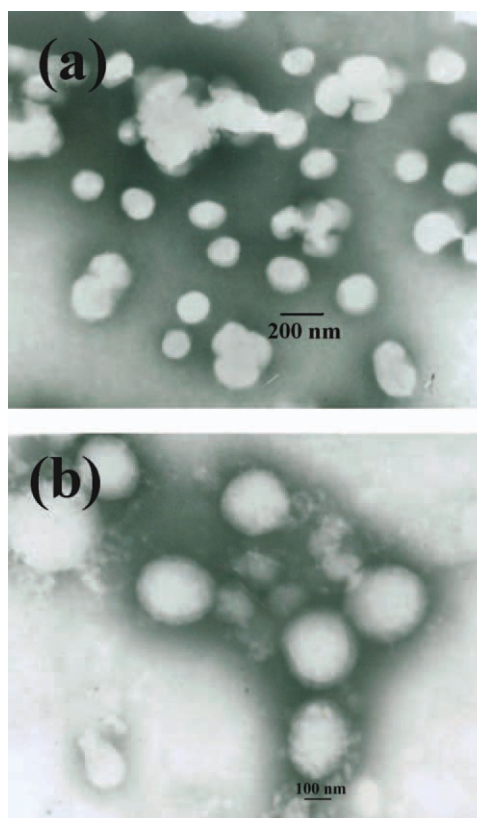

Figure 2. ^{1}H-NMR Spectrum of FLDH.

Figure 3. TEM photographs of the FLDH: (a) ×100,000 and (b) ×200,000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
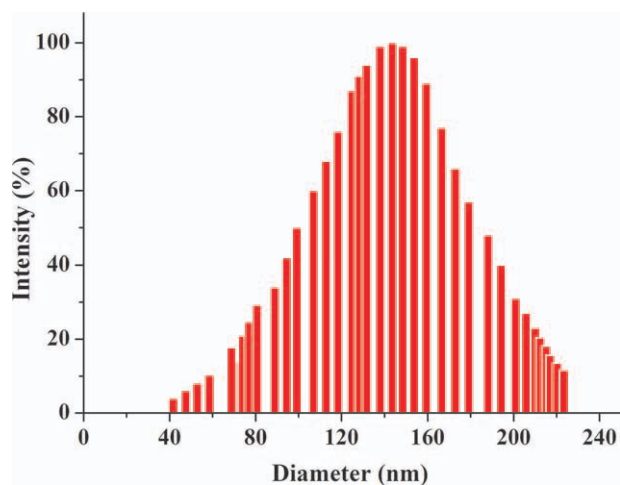
Figure 4. Particle size distribution of FLDH emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. DSC thermograms of the FLDH.

the average of five readings was used as the final contact angle of each sample.

Bending rigidity (BR) and whiteness of the treated fabrics by FLDH were measured with a Kawabata Evaluation System (KES) instrument and an YQ-Z-48B fluorescent whiteness tester, respectively.

RESULTS AND DISCUSSION

Characterization of the Resultants

FTIR spectra of the monomer FA [Figure 1(a)], fluorinated polyacrylate latex FLDH [Figure 1(b)] and fluorine-free polyacrylate latex LDH [Figure 1(c)] are compared and shown in Figure 1. All of the three spectra exhibited the characteristic stretching and distortion vibration peaks of C—H (CH$_2$) at 2923, 2853, and 1467 cm^{-1}, stretching vibration of C=O at 1722 cm^{-1}, asymmetrical and symmetrical stretching vibration of C—O at 1240 cm^{-1} and 1161 cm^{-1}, respectively. The absorption at 1641 and 888 cm^{-1} in Figure 1(a) should be attributed to the characteristic of C=C bonds of FA.[14] However, there were neither of the above two absorption peaks in Figure 1(b), which indicated C=C bonds of FA participated in polymerization.

It was also shown that the outline of fluorine-containing latex FLDH was similar to that of polyacrylate latex LDH in Figure 1(b,c). But the stretching vibration of —CF$_2$ and —CF$_3$ groups at about 1289–1100 cm^{-1} and asymmetrical stretching vibration of C—O at 1240 cm^{-1} overlapped each other,[9,19–21]

which resulted in broadening of absorption peaks at 1240–1100 cm^{-1} compared with that of LDH. Furthermore, strong signal at 1115 cm^{-1} and weak absorption band at 689 cm^{-1} should be assigned to the stretching vibration of —CF$_2$ and —CF$_3$ groups and the wagging vibration of CF$_2$ groups, respectively.[19–21]

^{1}H-NMR spectrum of the FLDH is presented in Figure 2. The δ_H of O—CH$_2$CH$_2$R$_f$ in FA were found at 4.36 ppm (mH) and 2.01 ppm (dH). Peaks at δ0.88 ppm (aH), δ1.29 ppm (bH), δ3.65 ppm (jH), and δ1.79 ppm (cH) belonged to the δ_H in LMA and the δ_H of main chain, respectively. Peaks at δ3.99 ppm (lH), δ3.43 ppm (gH), and δ3.58 ppm (hH) were assigned to the δ_H of O—CH$_2$CH$_2$ in DM and the δ_H of —OH in HPA, respectively.

In conclusion, both FTIR spectra and ^{1}H-NMR spectrum indicated that the monomers were polymerized together through seed emulsion polymerization. The deduced chemical structure is also given in Figure 2.
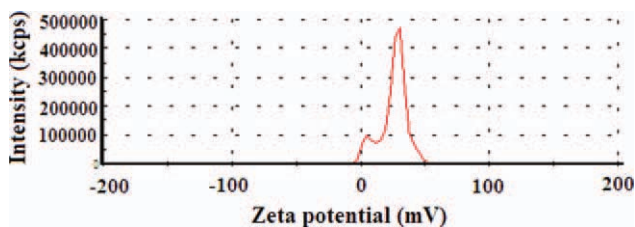

Figure 5. Zeta potential graph of the FLDH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
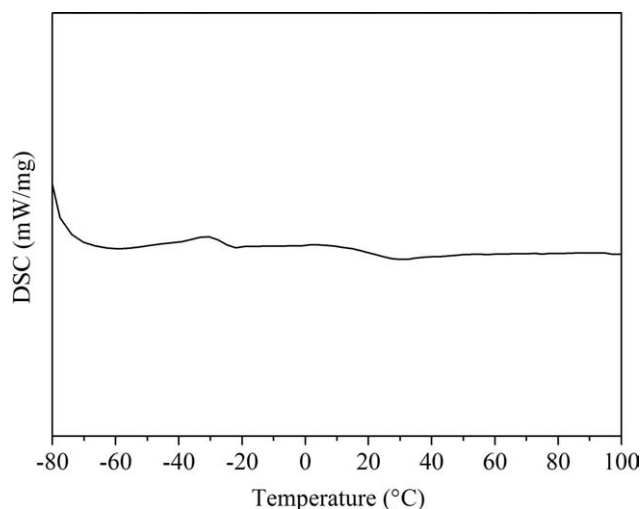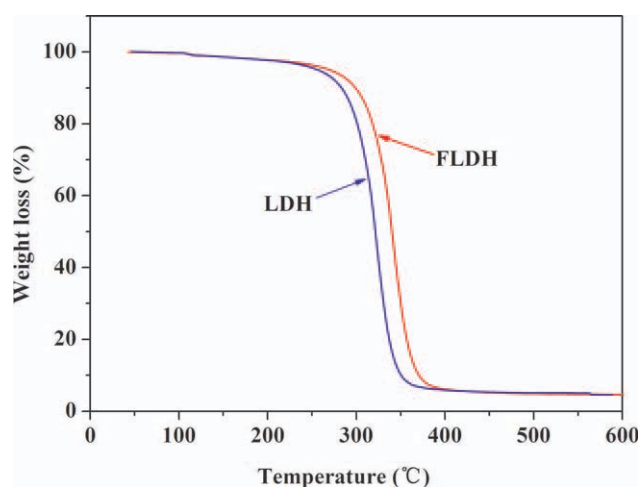

Figure 7. TGA curves of the LDH and the FLDH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
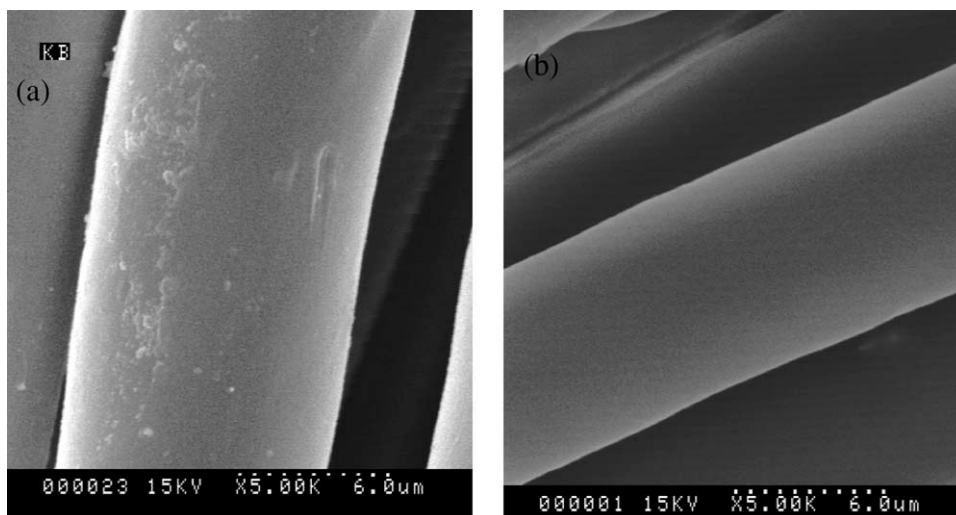
Figure 8. SEM photographs of the blank cotton fabrics (a) 5000× and ones treated by FLDH (b) 5000×.

Morphology and Size of the FLDH Particles

TEM photograph of FLDH is presented in Figure 3. It could be seen that the latex particles existed with relative clear and quasi-spherical core-shell structure because of the difference of electron penetrability to the core phase and the shell phase. The light and dark regions in the particles corresponded to the polyacrylate core phase and the fluorinated polyacrylate shell phase, respectively.[3,12] The particles were spheres with an average diameter of about 140 nm, obtained by calculating the diameter from the TEM photograph.

Particle size distribution (PSD) and zeta potential graph of the FLDH emulsion are also shown in Figures 4 and 5, respectively.

As seen from Figure 4, PSD of the FLDH was about 40–250 nm and the average particle size was 144 nm, which accorded well with the above TEM result. Besides, the FLDH latex possessed two zeta potentials of +25.78 and +10.41 mV from Figure 5, which demonstrated that the latex particles carried positive charges and this would improve not only stability of the latex but adhesion of the latex particles to anionic matrices such as textile.

Thermal Properties of the FLDH Film

To investigate thermal properties of the FLDH film, DSC and TGA were implemented in this article and are individually shown in Figures 6 and 7. Two glass transition temperatures
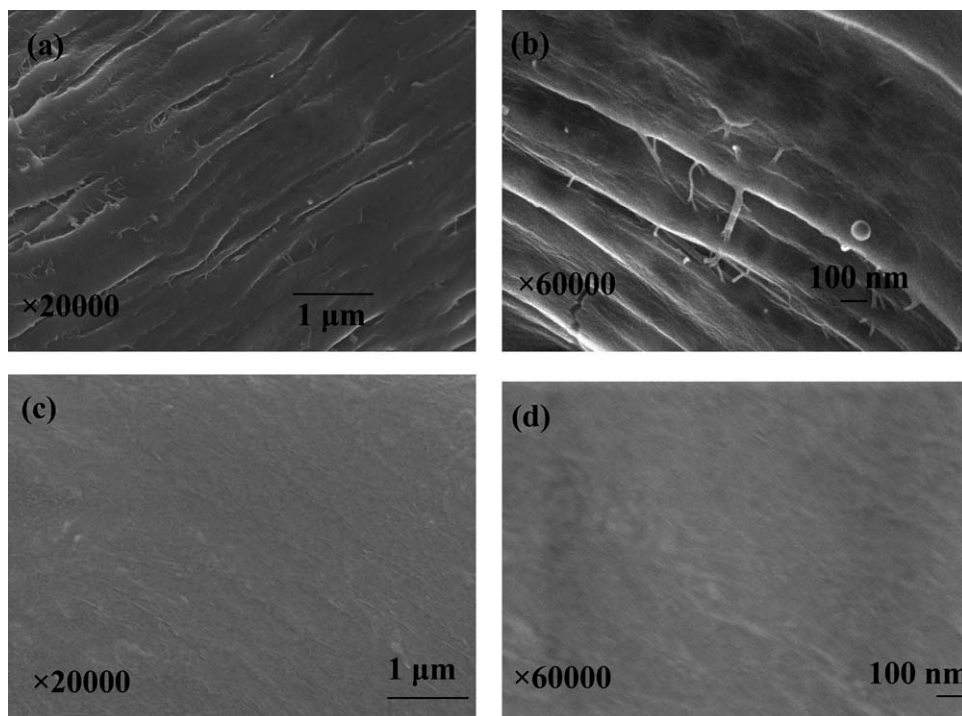

Figure 9. FESEM photographs of the blank cotton fabrics (a) 20,000×, (b) 60,000×, and treated ones by FLDH (c) 20,000×, and (d) 60,000×.
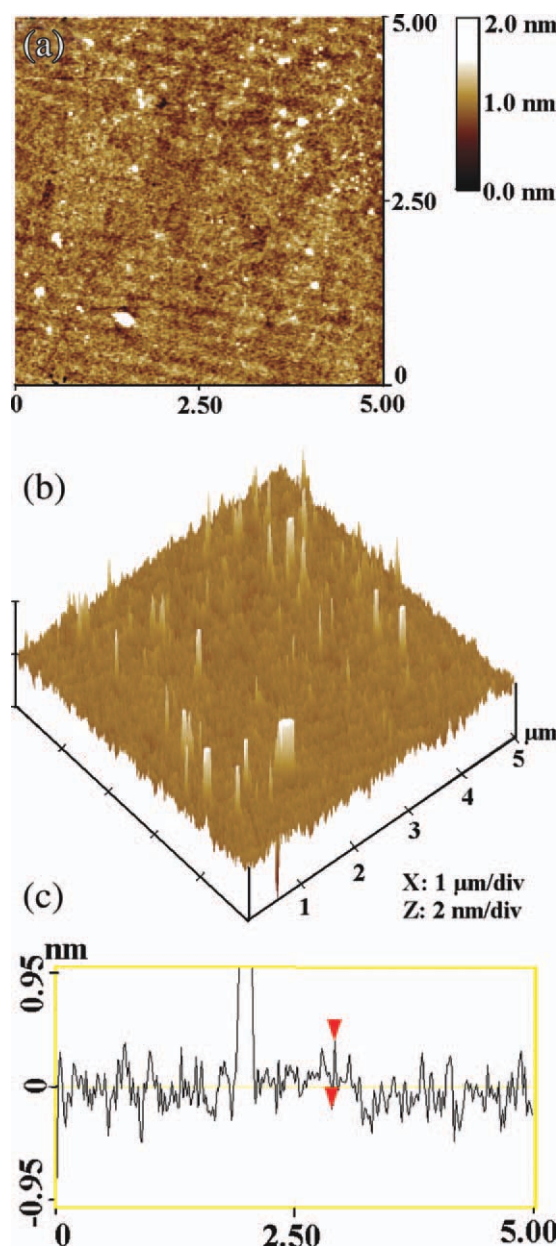
Figure 10. AFM images of FLDH film with a Rq of 0.506 nm. (a) Flatten, (b) three dimensional, and (c) the surface profile along a line. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(T_g), that is, −26.2 and 24.1°C, could be seen from Figure 6, which stood for T_g of the core phase and the shell phase, respectively. The DSC result also interpreted that the core-shell structure was formed, which also fitted well with the TEM image of the core-shell latex particles.

Meanwhile, it could be seen from Figure 7 that the weight loss of core-shell fluorinated polyacrylate emulsion film began at around 246°C, which was higher about 16°C than that of fluorine-free polyacrylate emulsion film. This result indicated that thermal stability of the latex films was enhanced due to the introduction of FA. This could be illustrated that through seed
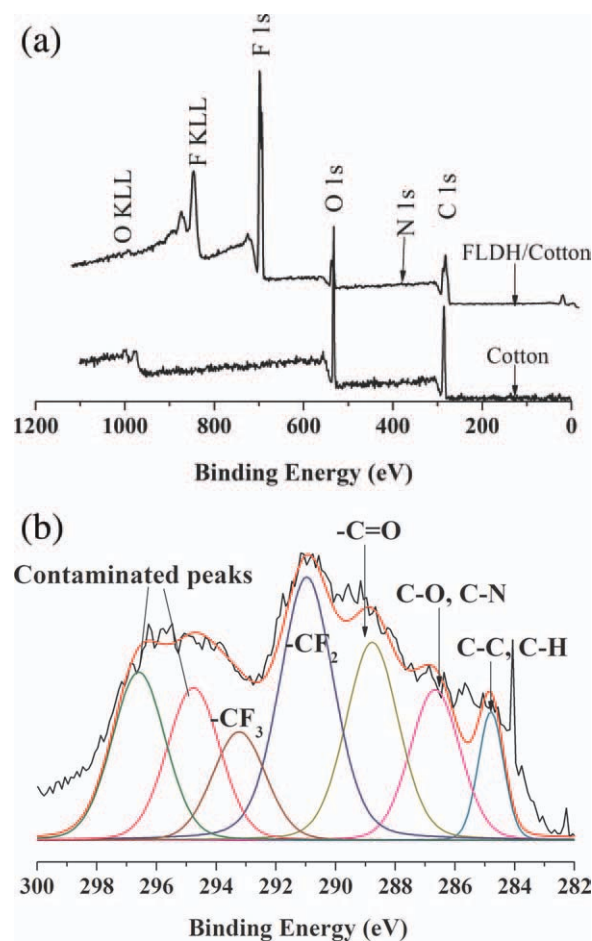

Figure 11. XPS spectra of the FLDH film: (a) on cotton surface (b) C1s signals with 30° take-off angle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

emulsion polymerization, fluorine containing acrylate monomer could be fixed in the shell of the latex particles and the per-fluoroalkyl groups containing C—F bonds has high bond energy. Thus, thermal stability of the copolymer is improved.[12]

Film Morphology of the FLDH on Substrates

It is well known that properties or application performances of a polymer depend largely on its structure or morphology on substrates. Thus exploration of its morphology on substrates is of great value. Fluorinated polyacrylates possess low surface tension. This property makes them outspread easily and adsorbed onto the surface of hydrophilic matrix (e.g., fabric), forming films of molecular dimensions. As such films sheath the fibers, more or less modified morphology of the treated fibers should

Table I. XPS Datum for Element Content of the FLDH Film-Air Surface

Take-off angle (°)	Element content (%)			
	F1s	O1s	N1s	C1s
30	48.18	6.45	0.84	44.53
60	46.32	7.53	0.92	45.23
90	43.56	8.41	0.98	47.05

Table II. Performance of the Cotton Fabric Treated by the FlDH

Dose of the FLDH latex (g/100 g H$_2$O)	WCA (°)	Static absorbing time (h)	Grade of oil repellent	Whiteness (°)	BR (mN)	
					w	f
0	0	<1 s	0	85.42	189	101
0.5	111.2	1.3	1	85.31	183	103
1	119.7	3.4	2	84.40	195	110
1.5	123.3	4.6	3	84.50	197	108
2	132.5	>6	4	84.40	209	114
2.5	146.1	>6	5	85.64	216	119
3	146.2	>6	5	84.81	225	125
3.5	146.2	>6	5	84.78	238	132

WCA, water contact angles; BR, bending rigidity; w, wrap; f, fill.

be observed in experiments. Thus, from observation of the treated fiber surface, we can get some information about morphology of fluorinated polyacrylate on the fiber substrate. Figures 8 and 9 are a series of SEM and FESEM photographs of pure cotton fabrics/fibers untreated or treated by FLDH. Figure 8 clearly showed that relatively smooth surfaces were observed on the treated fibers at a magnification of 5000 times (the observation rule = 6.0 μm), compared with the untreated fibers. In Figure 9, FESEM photographs demonstrated that a fluorinated polyacrylate resin film had been coated on the treated fiber surfaces. A majority of the grooves had disappeared on the treated fiber surface or become shallower; moreover, the edges of some fiber surface looked blunt and smoother. Although the amplification had already reached to 60,000 times (based on the original) and the observation rule working distance decreased to 100 nm, FESEM could not yet provide the precise structure of the FLDH film on the fiber surface, and hence the more powerful instrument is needed.

AFM is a newly developed instrument, which is widely used for detecting the morphology of polymer films on a nanometer scale.[22] Since natural fabrics or fibers are easily deformed during AFM observation, a polished and rigid silicon wafer is usually replaced as substrate to research film morphology and microstructures of functional polymer.[16–18] Therefore, the precise morphology of the FLDH film on the silicon wafer matrix was studied by AFM in this work and the result is shown in Figure 10. It was distinctly discovered that when the observation rule decreased to 2 nm, the macroscopic relative smooth FLDH film substantially exhibited an inhomogeneous structure on the silicon surface. There were some higher bright peaks resulting from fluoroalkyl groups and many lower dark peaks belonging to the softer nonfluorinated acrylate in its three dimensional topography (Figure 9).[21,23] This is the results of phase separation of the fluoroalkyl segments.[24] Basically, the interaction between acrylate polymers and the polar silicon wafer substrate is smaller than that between fluorine-containing groups and silicon surface, and it is easier for fluorine-containing segments to erect on a silicon surface than acrylate polymers. Therefore, in the annealing process the fluoroalkyl groups preferred to migrate to the air/polymer interface and occupy the outmost surface.[21] In

5 μm^2 scanning field, the average roughness of FLDH film (expressed by the root mean square roughness, Rq.) reached to 0.506 nm, which was larger than that of CFBDH film, 0.205 nm, prepared in our previous work.[15] This result was probably arose from the replacement of butyl acrylate segment in CFBDH by LMA segment in FLDH preparation, which was in favor of generation of much rougher fluorinated acrylate polymer film with low surface free energy and next possibly engendered better water repellency of cationic fluorinated polyacrylate film.

XPS Analysis of the FLDH Film

The XPS analysis gives some insight into the chemical compositions of the film-air interface of core-shell fluorinated acrylic latex film on cotton surface and the results are shown in Figure 11. The survey spectrum seen in Figure 11(a) revealed the characteristic signal of carbon, oxygen (O1s at 532.2 and 533.8 eV) and fluorine (F1s at 688.4 and 690.2 eV) as well as a weak nitrogen (N1s at 403.4 eV) signal as expected. In the C1s spectrum, shown in Figure 11(b), it was resolved into a series of Gaussian curve-fitted peaks: —CF$_3$ around 293.2 eV, —CF$_2$— around 290.9 eV, —C=O around 288.7 eV, —C—O—C=O and —C—N around 286.6 eV, and hydrocarbon (—CH$_n$: n = 0–3) around 284.8 eV, from high to low binding energy. However, two peaks at larger than 293.2 eV are likely originated from a certain contaminated source.

At the same time, the changes of the orientation of fluorine on the film surface were analyzed by XPS spectrum, and the elements on different layers of the film surface are given in Table I. Analysis performed at various take-off angles of 30°, 60°, and 90° provided a means to probe both the surface and deeper features of this FLDH/cotton film. As could be seen from Table I, changing from a take-off angle of 90°, 60°, and 30°, the fluorine concentration increased from 43.56 to 48.18%, while those of oxygen, nitrogen, and carbon decreased. This implied that the outmost layer of the dried film was composed of mainly perfluoroalkyl groups and some ester groups.[25] Besides, owing to hydrophilicity and cationic charge of nitrogen-containing acrylate segment, it is susceptible to be absorbed onto the anionic cotton substrate. Then this leads to decrease of the nitrogen content at the interface of air-film. In one word,

XPS analysis indicates the perfluoroalkyl groups have the tendency to enrich at the film-air interface, which are consistent with previously mentioned AFM morphology of the FLDH film.

Application Performance of the FLDH

Morphology will influence the performance of a functional polymer. Fluorinated polyacrylate latex has favorable film-forming ability, low surface free energy property, which is often used as water and oil repellent finish to treat textile.[6,26,27] While the core-shell FLDH possessing inhomogenous, phase-separated morphology aggregates and sheathes on the cotton surface, surface properties of the treated fabrics will be changed. Hence, the performances of the cotton fabrics treated or untreated with FLDH was determined and are shown in Table II.

As expected, along with the increase of the FLDH dose to 2.5 g, the hydrophobicity of the treated fabric, such as WCA, static absorbing time and grade of oil repellent, gradually attained the best values, which should be resulted from the equilibrium of absorption and rearrangement of perfluoroalkyl groups on the cotton surface. At last water contact angle, static absorbing time, and grade of oil repellent of the treated fabric were 146.2°, larger than 6 and 5 h, respectively. The whiteness of the treated fabrics changed little compared to the untreated fabric; however, BR of the treated fabrics will increase compared to the blank while dose of the FLDH latex is more than 1 g in 100 g aqueous solution. This result implies that hand feel of the treated fabrics by great dose of the FLDH latex will change stiff, which is also accordant with T_g of the FLDH shell phase, 24.1°C, exceeding the ambient temperature.

CONCLUSIONS

Cationic FLDH with pendant long chain alkyl had been successfully synthesized via semicontinuous seed emulsion polymerization. TEM observation demonstrated it possessed quasi-spherical core-shell structure with an average diameter of 144 nm. DSC and TGA analyses illustrated that the FLDH had two T_g and its thermal stability was thus enhanced by introduction of fluorine-containing monomer.

SEM, FESEM, and AFM detections demonstrated that FLDH was a good film-forming material. Although the macroscopic FLDH/cotton film seemed to be smooth, the microscopic morphology of the FLDH/Sil film was inhomogeneous and existed in a phase-separated state in fact. In addition, FLDH could provide good hydrophobicity for the treated fabric and water contact angle of this fabric could attain 146.2°. FLDH do not influence whiteness of the treated fabric. However, it will make the treated fabric slightly stiff at high doses.

ACKNOWLEDGMENTS

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