



Fabrication of self-cross-linking fluorinated polyacrylate latex particles with core-shell structure and film properties



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ABSTRACT

A series of self-cross-linking fluorinated polyacrylate latex particles with core-shell structure were successfully prepared by one-step miniemulsion polymerization of methyl methacrylate (MMA), butyl acrylate (BA), dodecafluoroheptyl methacrylate (DFMA), and γ -methacryloxypropyl triisopropoxidesilane (MPS). The core-shell structure of the latex particles was confirmed and the latex films were characterized. Results showed that the latex films not only showed enhanced thermostability but also exhibited good hydrophobic property with the incorporation of a small amount of MPS (below 5 wt% of monomers). This core-shell fluorine/silicone-containing polyacrylate latex could potentially be used for developing advanced multifunctional protective coatings such as antiwetting, anti-icing, antifogging, and anticorrosion.

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1. Introduction

Recently, fluoropolymers have attracted considerable attention because of their unique properties [1–6] such as superior surface hydrophobicity; good chemical, thermal, and photochemical stability; low flammability; and high electron affinity. Fluoroacrylate copolymers with excellent film-forming capabilities have been used in biomaterials, microelectronics, antifogging, and anticorrosion applications, as well as surface coatings for textile, paper, and leather [7–8]. However, the application of fluoroacrylate copolymers is limited mainly due to the high cost of fluorinated monomers. One strategy to overcome this limit is to prepare core-shell fluorine-containing polyacrylate latexes composed of a fluorine-free core and fluorine-containing shell [9–14]. However, the performance of core-shell fluorine-containing polyacrylate latex is still poor because of its poor cold tolerance and adhesion to inorganic substrates [15–18]. Moreover, although fluorinated groups have the tendency to locate at the interface to minimize the interfacial energy during film formation process, the fluorinated groups may remigrate to the inside of films when the environment surrounding the film changes, that is, when being immersed in water [19].

One approach to overcome the aforementioned drawbacks is to introduce functional groups in polymers during synthesis, which can form cross-links under an appropriate cure condition and form thermosetting films [19–23]. For example, alkoxy silanes, such as γ -methacryloxypropyl triisopropoxidesilane (MPS) and vinyltriethoxysilane (VTES), were

commonly used for this purpose, because hydrolysis and condensation of $\text{Si}(\text{OR})_3$ groups in MPS or VETS can construct a cross-linked network. The introduction of alkoxy silanes could not only enhance the adhesion to inorganic substrates and improve the stability of films, but also immobilize the fluorinated polymer tightly on the surface of films. Numerous studies have been reported using semicontinuous seed emulsion polymerization to fabricate the core-shell polyacrylate latex containing fluorine and silicone in the shell [19–22]. In general, fluorine-free polyacrylate seed latex was first prepared, and then the shell layer containing fluorine and silicon was formed by adding fluorinated monomer and alkoxy silane monomer dropwise to the polymerization system containing seed latex.

However, studies on seed emulsion copolymerization of vinyl alkoxy silanes and organic monomers have shown that it is quite challenging to avoid premature hydrolysis and cross-linking of the silane moiety during synthesis, because of the transport of alkoxy silane monomer in water phase [24]. Because no mass transport process takes place among the droplets during the miniemulsion polymerization and the nucleation and propagation processes mainly occur inside the monomer droplets, miniemulsion polymerization has been suggested as a promising alternative method due to the following advantages: (1) Alkoxy silane monomers can be protected from the aqueous phase by the waterproof oil droplets and the hydrolysis and condensation reactions can be better controlled [25–27]. As a result, premature hydrolysis and cross-linking of the silane moiety during synthesis could be significantly restrained, thereby favoring the self-segregation of fluorine from the bulk to the surface during film formation. (2) Without undergoing the transport of monomer in water phase, the extremely

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hydrophobic fluorinated monomers can also easily polymerize in the monomer droplet during miniemulsion polymerization [28–31], even when the fluorinated monomer concentration is high.

However, to our best knowledge, there are few reports on the fabrication of self-cross-linking fluorinated polyacrylate latex particles with core-shell structure by simultaneously incorporating fluorine and silicone monomers in one-step miniemulsion polymerization. Therefore, the main objective of this study was to synthesize the core-shell polyacrylate latex containing both fluorine and silicon via a facile approach (one-step miniemulsion polymerization) and further assess the performance of corresponding latex films. In this study, dodecafluoroheptyl methacrylate (DFMA) and γ -methacryloxypropyl triisopropoxidesilane (MPS) were chosen as the fluorine monomer and silicone monomer, respectively. Methyl methacrylate (MMA), butyl acrylate (BA), and the functional monomers DFMA and MPS were simultaneously introduced into the miniemulsion polymerization system, and a series of core-shell fluorinated polyacrylate latexes containing various amounts of MPS unit were successfully synthesized; meanwhile, the resulting latex films were also characterized by various analytical techniques.

2. Experimental

2.1. Materials

MMA (99 wt%) and BA (99 wt%) were purchased from Sigma-Aldrich and distilled under a reduced pressure before polymerization study. DFMA (96 wt%) was obtained from Harbin XEOGIA Fluorine-Silicon Chemical Co., Ltd, China, and used as received. Silicon monomer MPS (97 wt%), anionic emulsifier sodium dodecyl sulfate (SDS, 99 wt%), costabilizer hexadecane (HD, 98 wt%), and azodiisobutyronitrile (AIBN, 99 wt%) were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China) and used without further purification. Deionized water was used throughout this experiment.

2.2. Synthesis of core-shell polyacrylate latex via miniemulsion polymerization

A certain amount of SDS was added to deionized water and stirred at 200 rpm for 10 min. The initiator AIBN and costabilizer HD were dissolved in the monomer mixture (MMA, BA, DFMA, and MPS), and the oil phase was then added to the aqueous solution containing emulsifier. The oil and aqueous phases were further mixed using a mechanical agitator at 500 rpm for 30 min to form a homogeneous emulsion. Subsequently, the resultant emulsion was homogenized by ultrasonication for 10 min using a pulsed sequence (5-s sonication followed by 5-s break) with a 60% duty cycle under magnetic agitation in an ice bath. A miniemulsion was then introduced into a 500-mL glass jacket reactor, which had been prepurged with nitrogen for 30 min, and subsequently the temperature was rapidly increased to 65 °C. Nitrogen was used throughout the reaction, while the stirring speed was maintained at 200 rpm. The polymerization reaction lasted for 5 h for a high monomer conversion, and the temperature was kept constant at 65 °C. The reaction details and the monomer conversion degree of every polymerization reaction are presented in Table 1.

2.3. Characterization of latex particle and its film

The monomer conversion was measured by gravimetric analysis. The latex particle size was monitored by dynamic light scattering (DLS) using a Zetasizer Nano ZS90 particle size analyzer (Malvern Instruments Company, UK). The latex particle morphology was observed by transmission electron microscopy (TEM) (JEOL JSM-1200EX, Tokyo, Japan) with an acceleration voltage of 80 kV. The latex particles were stained with 2% phosphotungstic acid solution before TEM examination. Fourier transform infrared spectra (FTIR) were recorded between 4000

Table 1
Reaction recipes of the one-step miniemulsion polymerization.

Sample	MMA (g)	BA (g)	DFMA		MPS		Conversion (%)	Particle size (nm)	PDI
			(g)	(wt%)*	(g)	(wt%)*			
0F0Si	15	5	0	0	0	0	96.0	118	0.067
4F0Si	12	4	4	20.0	0	0	97.3	106	0.030
4F0·5Si	12	4	4	20.0	0.5	2.5	95.3	108	0.036
4F1·0Si	12	4	4	20.0	1.0	5.0	96.2	107	0.053
4F1·5Si	12	4	4	20.0	1.5	7.5	95.7	110	0.064
4F2·0Si	12	4	4	20.0	2.0	10.0	95.8	112	0.089

Reaction condition: HD 0.4 g, SDS, 0.4 g, AIBN 0.05 g, H₂O 80 g, temperature 65 °C

*Mass ratio of DFMA or MPS to total monomer mass of MMA, BA, and DFMA.

*The number in the sample name refers to the content of DFMA and MPS, for example, 4F1·0Si indicates that 4 g of DFMA and 1.0 g of MPS take part in the copolymerization reactions, respectively.

and 400 cm⁻¹ with a Fourier transform infrared spectrometer (Nicolet 6700, ThermoFisher Scientific, Boston, MA, USA) using KBr pellet technique. The latex particles were centrifuged and redispersed in deionized water thrice and the resulting latex was dried under vacuum at 50 °C for 24 h before FTIR analysis. The latex films were prepared by the following method: glass slides were cleaned in an ultrasonic bath with ethanol at 40 °C for 1 h and rinsed with deionized water thrice, and subsequently they were dried under vacuum at 60 °C for further use. The synthesized latex was directly dropped onto the clean glass slides and the thin films were prepared by the spin coating method (3000 rpm for 60 s). Finally, the films were dried at 80 °C under vacuum for 10 h and used for thermal and surface property characterization. The glass transition temperature (T_g) of latex film was measured by a differential scanning calorimeter (DSC, TA Instruments, Model DSC Q2000). In order to eliminate thermal history, two scanning cycles of heating-cooling were performed for each sample at a heating rate of 10 °C min⁻¹ in the temperature range of -20 to 150 °C under nitrogen atmosphere. The second heating run was used to determine the T_g. Thermogravimetric analysis (TGA) was performed using a thermal analyzer (TGA-Q500, Waters, Milford, MA, USA) under nitrogen atmosphere at a heating rate of 10 °C/min to 700 °C. Water contact angle (WCA) measurements were performed on a DSA-20 contact angle goniometer (Kruss, Germany) by the sessile drop method with a microsyringe at room temperature. The initial WCA was measured soon after the water being dropped onto the latex film. Typically, six water drops were placed on the surface of the latex films and the average of six readings of contact angles was taken for each sample. Moreover, the WCA of the films was also recorded as a function of time. The chemical composition of the latex film surface was determined by an X-ray photoelectron spectrum (XPS) analyzer (K-Alpha, ThermoFisher Scientific, USA) with a takeoff angle of 90° and the film thickness analyzed was approximately 10 nm. Atomic force microscopy (AFM, XE-100E, Park Systems, South Korea) was used to investigate the film surface morphology in a tapping mode at ambient temperature by maintaining a scan size of 2 × 2 μm.

3. Results and discussions

3.1. Size and morphology of the latex particle

Fig. 1 shows the evolution of the latex particle size during the miniemulsion polymerization. It could be seen that the average particle size remains almost constant in the progress of polymerization. It should be noted that the particle size evolution in this study does not exhibit significant difference between the polymerization with or without the presence of MPS. While in conventional seed emulsion polymerization, previous studies have shown that the particle size increases markedly with the increase in the amount of MPS [19], attributable to the existence of "bridged" particles formed by coagulation resulting from the hydrolytic condensation of alkoxy silane groups [26]. However,

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