

Colloidal and Polymer Properties Difference of Fluorinated Acrylate Latex Prepared with Different Fluorinated Monomers

Lijun Chen,¹ Fengqin Wu²

¹School of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310032, People's Republic of China

²Intertek Testing Services, Hangzhou 310052, People's Republic of China

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ABSTRACT: Fluorinated acrylate latex was prepared by copolymerizing fluorinated monomer, butyl acrylate, and methyl methacrylate, which was initiated by potassium persulfate in the water. The resultant fluorinated latex and its film were characterized with contact angle determinator, dynamic light scattering detector, and differential scanning calorimetry, respectively. Influence of type of fluorinated monomers on colloidal and polymer properties of fluorinated acrylate latex was studied. Results show that

the coagulation rate, particle size, contact angle, glass transition temperature, and chemical resistance are increased with the increase of the number of fluorine atom in the fluorinated monomer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 376–381, 2012

Key words: fluorinated monomer; fluorinated acrylate latex; colloids; properties

INTRODUCTION

Fluorinated acrylate latexes, which are widely used as adhesives, paints, and coating industries,^{1–4} are produced with acrylic monomers and fluorinated monomers via emulsion polymerization to provide latexes with desirable properties, are becoming increasingly important due to their environmental compliance. Many researchers are focused on the preparation and properties of the fluorinated acrylate latex, which are presented in Table I. The emphasis in above researches on fluorinated acrylate latex was mainly focused on influence of monomer composition, cross-linking and polymerization process on the colloidal and polymer properties. However, the type of the fluorinated monomer has been strongly neglected. The comparative study of influence of different types of fluorinated monomer on

the colloidal and polymer properties has been not reported. The aim of this work is to examine how different types of fluorinated monomers (See Scheme 1) affect the colloidal and polymer properties.

In this study, three types of fluorinated monomers such as hexafluorobutyl acrylate (HFBA), dodecafluoroheptyl methacrylate (DFMA), and perfluorononoxylene ethanyl acrylate (PFEA) were used to prepare the fluorinated acrylate latex. For the sake of uniform conditions, fluorinated acrylate latexes, comprising primarily poly (methyl methacrylate-*co*-butyl acrylate) (MMA-*co*-BA) (Seen Scheme 2) were prepared via semi-continuous seeded emulsion polymerization with the same recipe. In this paper, A denotes the latex comprising primarily poly(methyl methacrylate-*co*-butyl acrylate-*co*-hexafluorobutyl acrylate) (MMA-*co*-BA-*co*-HFBA); B denotes the latex comprising primarily poly(methyl methacrylate-*co*-butyl acrylate-*co*-dodecafluoroheptyl methacrylate) (MMA-*co*-BA-*co*-DFMA); C denotes the latex comprising primarily poly (methyl methacrylate-*co*-butyl acrylate-*co*-perfluorononoxylene ethanyl acrylate) (MMA-*co*-BA-*co*-PFEA).

Correspondence to: L. Chen (chenlj@zjut.edu.cn).

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EXPERIMENTAL

Materials

BA and MMA were obtained from Shanghai Chemical Reagents Supply Procurement of Five Chemical

TABLE I
Research Focuses on Fluorinated Acrylate Latex

Researchers	Research focuses
Gao et al. ⁵	Preparing a novel fluorinated polymer emulsion with core/shell structure.
Cui et al. ⁶	Preparing the emulsifier-free core-shell interpenetrating polymer network (IPN) fluorinated polyacrylate latex particles
Xiong et al. ⁷	Preparing core-shell fluorinated acrylic copolymer latexes with silicon monomer cross-linking.
Cheng et al. ⁸	Synthesizing IPN fluorinated polyacrylate latex with core-shell structure.
Chen et al. ⁹	Preparing emulsifier-free latices of fluorinated acrylate copolymers by semicontinuous polymerization method
Our research group ¹⁰⁻¹⁴	Preparing a series of fluorinated acrylic polymers via different polymerization technologies.

Plants (Shanghai, China) and were distilled under reduced pressure before polymerization. Fluorinated monomers such as DFMA and HFBA were purchased from Harbin Xeogia Fluorine-silicon Material (Harbin, China). PFEA was prepared in our laboratory. The prepared method was based on our previous research results.¹¹ Potassium persulfate (KPS) was obtained from the Second Chemical Reagent Factory in Yixin (China). Sodium bicarbonate (NaHCO₃) is purchased from Shanghai Hongguang Chemical Plant (Shanghai, China). Sodium dodecyl benzene sulfonate (SDBS) was supplied by Shanghai Yingpeng Chemical Reagent (Shanghai, China). Polyethylene glycol mono-pnonyl phenyl ether (OP-10) was obtained from Shanghai Minchen Chemical (Shanghai, China). The water used in this experiment was distilled followed by deionization.

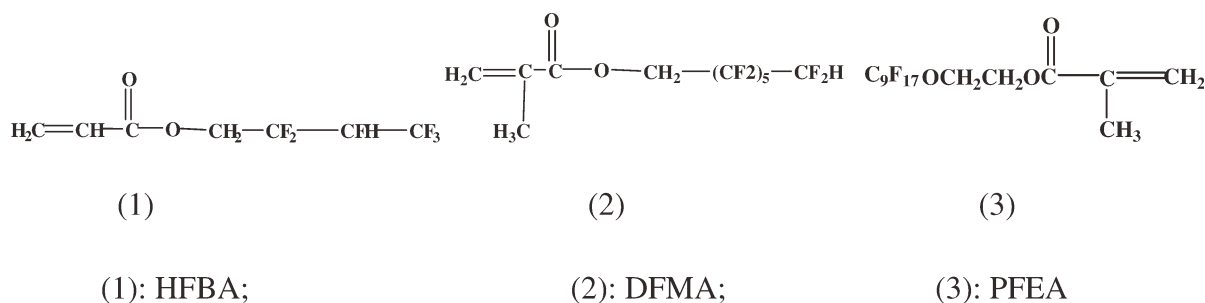
Preparation of fluorinated acrylate latex

The mixed monomers consisted of 30.00 g BA, 20.00 g MMA, and 10.00 g fluorinated monomer such as HFBA, DFMA, or PFEA. A homogeneous aqueous solution containing 90.00 g deionized water, 0.90 g NaHCO₃, and mixed emulsifiers composed of 0.60 g SDBS and 1.20 g OP-10 was charged into a 250 ml four-neck flask equipped with reflux condenser, mechanical stirrer, dropping funnels, and heated with the water bath. The stirring speed was maintained at 200 rpm throughout the runs. The reaction temperature was increased to 80°C within 30 min. An initia-

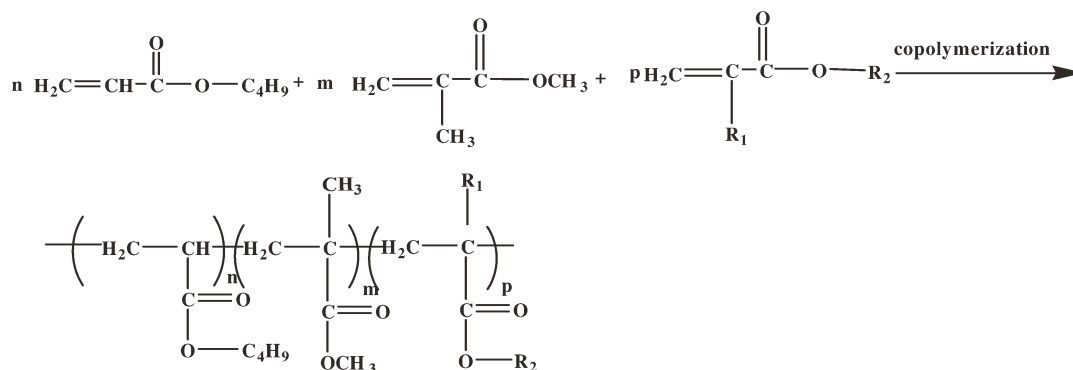
tor solution containing 0.12 g K₂S₂O₈ and 6.00 g deionized water and 20% mixed monomers were charged to the reactor to form the seed latex within 15 min. The seeded polymerization was continued for an additional 10 min. At that point, the initiator solution composed of 0.48 g KPS and 24.00 g deionized water and the rest of the mixed monomers were added slowly to the reactor using two separate dropping funnels. The feeding time for the initiator and the rest of mixed monomers were 3.5 and 3.0 h, respectively. After the feed was completed, the temperature was raised to 90°C and maintained for another 30 min to increase monomer conversion. The latex was then cooled to below 40°C, and NH₄OH (25 wt %) was added to increase the pH to about 8.0. Finally, the mixture in the flask was cooled and filtered. Thus, the fluorinated acrylate latex was obtained.

Characterizations

The amount of coagulum was measured by collecting the solid deposited on the reactor walls and stirrer, and by the residual of filtered latex. It is expressed as the weight of coagulum per total weight of monomer added. The particle size of the latexes was determined by Zetatrac dynamic light scattering detector (Microtrac Limited Corporation) at 25°C. The power and the wavelength of the diode laser used in the dynamic light scattering measures were 3 mW and 780 nm, respectively. The film of



Scheme 1 Structural formula of fluorinated monomer used in the experiment.



Scheme 2 Synthesis pathway of the fluorinated polyacrylate latex (R_1 is $-\text{H}$ or $-\text{CH}_3$; R_2 is $\text{C}_4\text{F}_6\text{H}_3-$, $\text{C}_6\text{F}_{12}\text{H}_3-$ or $\text{C}_{11}\text{F}_{17}\text{H}_4\text{O}-$).

latex is obtained from coating the latex on the clean glass and drying at 80°C for 2 h in the bake oven. Contact angle (CA) between film and water was determined with the DataPhysics contact angle meter (OCA-20, Germany) at room temperature. The differential scanning calorimetry (DSC Q100) was applied to determine T_g of the film. The heating temperature was in the range from -40°C to 100°C . The heat rate was $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Coagulation percentage

Effect of the different fluorinated monomers on the coagulation percentage is given in Table II. Table II indicates that the coagulation percentage is increased with the increase of the number of fluorine atom in the fluorinated monomer. This can be explained via the stability mechanism of the polymer latex. The hydrophobic latex particles, which are stable in the water phase, are dependent on the absorption or combination of the hydrophilic substance on the surface of the particles. The surface of the latex particles can not be coated completely by sufficient emulsifiers when the number of fluorine atom in the fluorinated monomer is increased further. The collision among the latex particles leads to the coagulation. In addition, the formed hydrated layer on the surface of the latex particles is decreased obviously because of the hydrophobicity of the latex particles, which results in the increase of the coagulation.

Particle size

Change of particle size of the latex with different fluorinated monomers is shown in Figure 1. Figure 1 indicates that the particle size of three latexes is unimodal distribution and the particle size of the latex is increased with the increase of the number of fluorine atom in the fluorinated monomer. This phe-

nomenon may be caused by the fact that strong hydrophobicity of fluorine segment leads to the aggregation of the particles. Accordingly, the particle size of the latex is increased. In addition, it is easy to aggregate among the latex particles because of the obvious decrease of the hydrated layer. Thus, the stability of the latex particles is decreased, and the aggregated particles in the system are more, which cause the particle size of latex to increase.

Contact angle

CA is a typical property to understand the surface energy of materials. The hydrophobic property of a polymeric material can be estimated in terms of CA measurement by depositing a water drop on the surface of film and the value of CA depends on the chemical compositions of film surface.^{15,16} The higher the wetting resistance of film surface, the higher CA is. Because the fluorinated polymers have good hydrophobic property and fluorine atom tends to locate on the film surface during the film formation. The CAs of the latex with different fluorinated monomers are shown in Figure 2. Figure 2 shows that the contact of the film of latex is increased with the increase of the fluorine atom number in the molecule of the fluorinated monomer. The increase of the CA is caused by the fact that more fluorine atom is introduced into a single polymer, and fluorine atom tends to locate on the film surface during the

TABLE II
Effect of the Different Fluorinated Monomers on Coagulation Percentage

Sample	% Coagulum
A	0.57
B	1.68
C	2.86
D	0.25

Sample D was prepared with the same recipe without the fluorinated monomer.

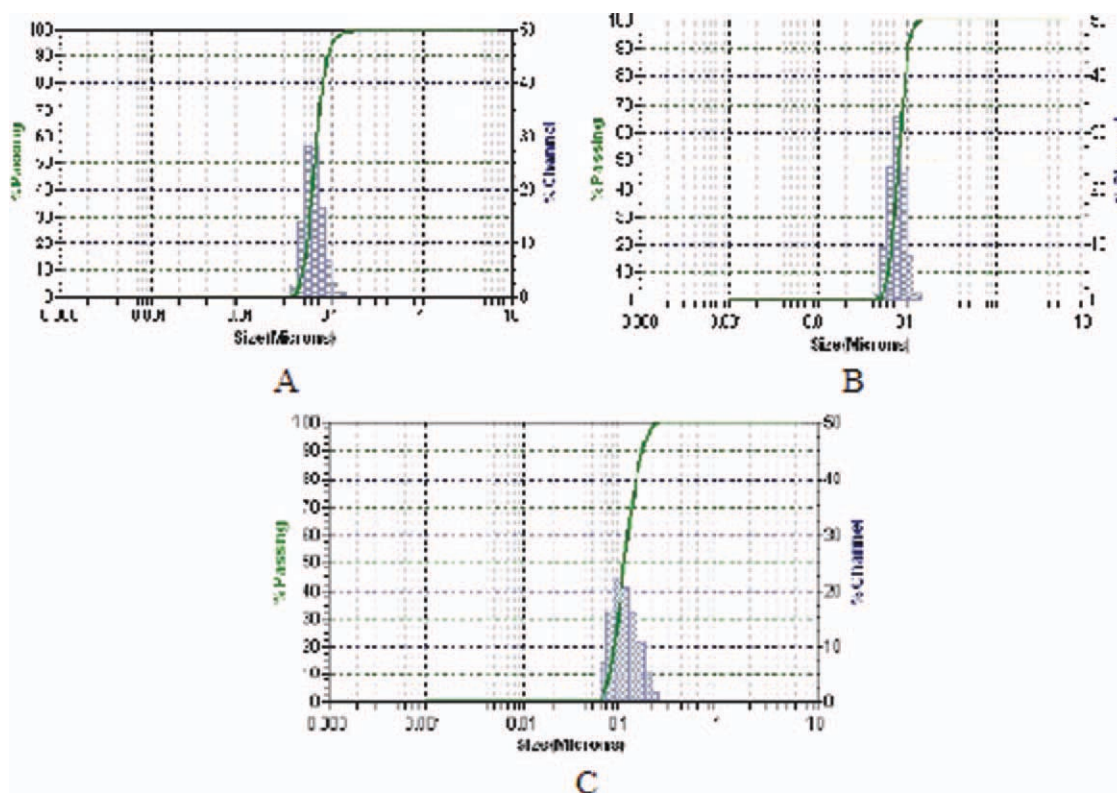


Figure 1 Change of particle size of latex with different fluorinated monomers (A: $M_v = 0.0662 \mu\text{m}$; B: $M_v = 0.080 \mu\text{m}$; C: $M_v = 0.1132 \mu\text{m}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

film formation to minimize the interfacial energy, which can increase the hydrophobic property of polymer. The lower the surface energy is, the larger the CA. Therefore, it is expected that introducing fluorinated monomer with more fluorine atom into a single polymer can increase the hydrophobic property of polymer.

Glass transition temperature

T_g of the latex can be preliminarily estimated from Fox equation:

$$\frac{1}{t_g} = \frac{m_1}{t_{g1}} + \frac{m_2}{t_{g2}} + \dots + \frac{m_i}{t_{gi}} \quad (1)$$

where m_i is the mass fraction of copolymerized monomer; t_{gi} is the value of t_g of homopolymer. The determination of t_g is related to other components of polymer, the tested method and instrument, and the velocity of raised temperature. However, Fox equation neglects the influence of relative molecular mass of polymer on t_g . Therefore, there is some difference between the theoretical value and the measured value of t_g .¹⁷ Figure 3 shows that t_{gB} and t_{gC} of the latexes are higher than t_{gA} of the latex. This phenomenon can be explained by the fact the carbon chains of HFBA are the same with the ones of BA, and the carbon chains of DFMA or PFEA are also the same with the ones of MMA. T_g of the homopolymer of HFBA is lower than the one of the homopolymer of DFMA or PFEA because BA and MMA

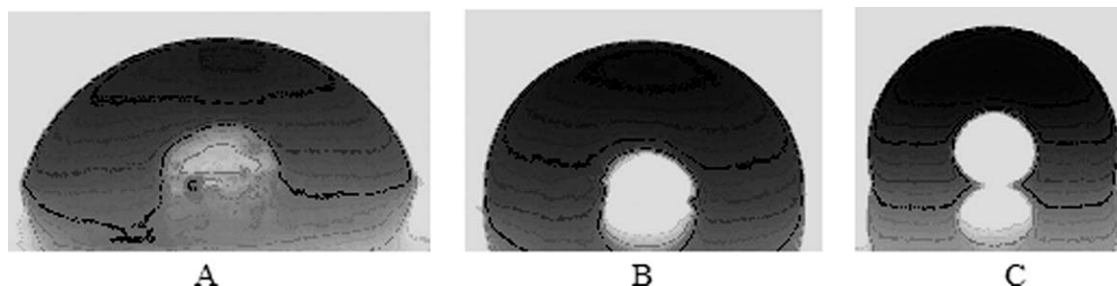


Figure 2 Contact angle of film (A: 79.0° ; B: 97.5° ; C: 108.7°).

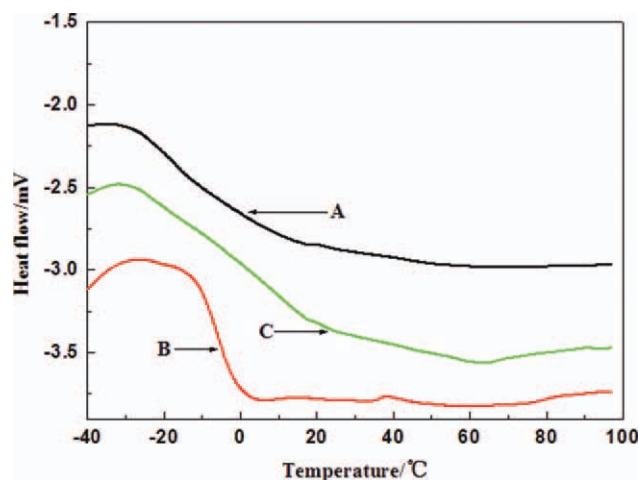


Figure 3 DSC curves of fluorinated acrylate latex ($t_{gA} = -15.23^{\circ}\text{C}$; $t_{gB} = -7.16^{\circ}\text{C}$; $t_{gC} = 8.06^{\circ}\text{C}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are the soft monomer and hard monomer, respectively. For two kinds of copolymerized monomer, e.g., MMA and BA, Fox equation can be turned into

$$\frac{1}{t_g} = \frac{m_1}{t_{g1}} + \frac{m_2}{t_{g2}} \quad (2)$$

where m_1 is the mass fraction of MMA; m_2 is the mass fraction of BA; t_{g1} is t_g of MMA homopolymer; t_{g2} is t_g of homopolymer BA. The following equation can be obtained via differentiating eq. (2):

$$\frac{dt_g}{dm_1} = \left(\frac{1}{t_{g2}} - \frac{1}{t_{g1}} \right) \cdot t_g^2 \quad (3)$$

In eq. (3), t_{g2} is smaller than t_{g1} , so $1/t_{g2}$ is more than $1/t_{g1}$, i.e., t_g of polymer increases with the increase of the amount of MMA. The amount of the hard monomer is increased which leads to the increase of t_g of the film when DFMA or PFEA is added. However, the amount of the soft monomer is increased which leads to the decrease of t_g of the film when HFBA is added. Therefore, t_{gB} and t_{gC} of the latexes are higher than

t_{gA} of the latex. Figure 3 also shows that t_{gB} are higher than t_{gC} , which means that t_g of the homopolymer DFMA is higher than that of the homopolymer PFEA. Besides, in Figure 3, it can be seen that the latex has only one t_g , which shows that the latex is a kind of random copolymer and the consistency among the chain segment is fairly good.

Chemical resistance

The glass slides coated with polymer film were immersed into a solution of 5% H_2SO_4 at room temperature for 24 h. Then, the glass slides were washed with distilled water, and dried at 80°C . The CA of polymer film was examined and shown in Figure 4. In comparison with Figure 2, the results indicate that the reducing degree of the CA is decreased with the increase of the number of fluorine atom in the fluorinated monomer, implying the increased chemical resistance of polymer film. The increased chemical resistance is attributed to more fluorine atoms in the molecule of the latex. The long side chain of C—F bond makes the fluorinated moieties accede to the outermost layer because of its low surface energy. The fundamental chain of C—C is mostly enclosed with fluorine atom intensively and the closer spiral structure is formed to protect C—C against impacting when more fluorine atoms are combined with the fundamental chain of C—C in the latex molecule.

CONCLUSIONS

The type of fluorinated monomers has an influence on the colloidal and polymer properties of fluorinated acrylate latex. The stability of polymerization is decreased with the increased number of fluorine atom in the copolymerized monomer. The particle size of the fluorinated acrylate latex is increased with the increased number of fluorine atom in the copolymerized monomer. The glass transition temperature of film of the fluorinated acrylate latex is increased with the increased number of fluorine atom in the copolymerized monomer. Both the water resistance and chemical resistance of the film of the fluorinated

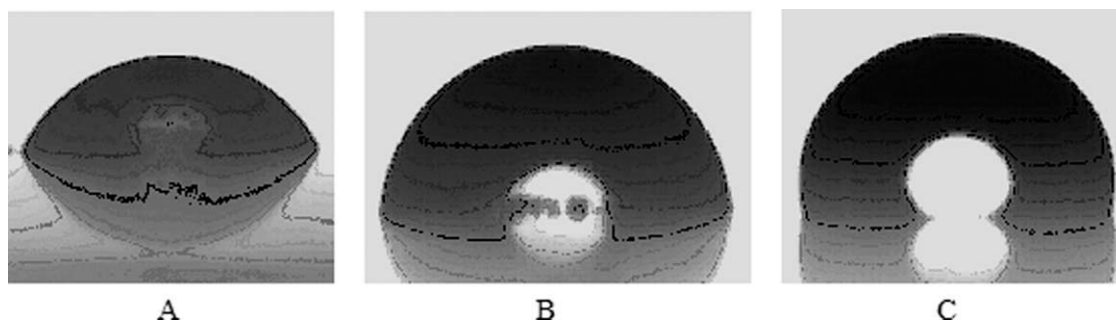


Figure 4 Contact angle of film (A: 63.7° ; B: 88.0° ; C: 106.7°).

acrylate latex are improved with the increased number of fluorine atom in the copolymerized monomer.

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