Core–Shell Latex Containing Fluorinated Polymer Rich in Shell

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ABSTRACT: Core–shell latex with polyacrylate rich in core and fluoropolymer rich in shell was prepared by semicontinuous emulsion polymerization in the presence of mixed emulsifiers. The solids content of the latex was about 25 wt %. The polymerization conditions for the latex were discussed. The morphology of latex particles was characterized by transmission electron microscopy and the surface properties were determined by the Wilhelmy method. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1147–1153, 2002

Key words: fluoropolymer; core–shell acrylate latex; dynamic contact angle

INTRODUCTION

In recent years, polyacrylate modified by introducing fluorine-containing groups into the polymer chain[1] has attracted the increasing attention of many investigators. The film of fluorinated polyacrylate not only keeps the original properties of polyacrylate film, such as good adhesion to matrices, but also has better durability and both antifouling and self-cleaning properties. Thus, fluorinated acrylate polymers have been used to a progressively greater extent in surface coatings, such as for water and oil repellency for textile, paper, and leather. However, the prices of the fluorinated acrylate monomers are very high. Increased use of this kind of monomers will increase the prices of fluorinated polyacrylate coatings, so the relatively high market prices of fluorinated acrylate polymers are the biggest drawback to their increased use. The reported studies[2–6] indicate that the special surface properties of fluorinated polyacrylate, such as their water resistance, oil resistance, and self-cleaning character, are attributed to the fact that the perfluoroalkyl side chains $[-(CF_2)_nCF_3,\ n = 2-15)$ of polymers expand to the air and occupy the polymer/air interface. The low intermolecular force between fluorinated side chains and air significantly lessens the surface energy of the polymer film. Moreover, given that the stable C—F bond has high bond energy and perfluoroalkyl side chains pack the main chains of polymers, the inside molecules are protected. These structural characteristics also impart good weatherability to fluorinated polyacrylate. Thus, if most of the perfluoroalkyl side chains can be made to occupy the surface of the film, by adopting suitable polymerization techniques, we will resolve the dilemma and obtain fluorinated acrylate polymers with good surface properties, using only a minimum amount of fluoromonomers.

Compared to general emulsion, the core–shell latex has special particle morphology. The core–shell structure can provide some good properties for latex films, when polymers forming the core and the shell phase disperse totally or partially in film. Because of differences in hydrophobicity and in surface tension, one of the polymers might

preferentially migrate to the surface during film formation, which presents an economical value to the manufacturer of fluorinated polyacrylate coatings with low fluorine content. For example, Marion et al.[7,8] designed core–shell latex particles containing a fluorinated polymer in the shell and investigated the core–shell structure. In fact, although the synthesis method of this kind of fluoropolymer is very important, it has scarcely been reported. Thus, in this study, we focused more attention on the polymerization condition and the properties of the final latex.

In this work, core–shell latex with polyacrylate rich in core and fluoropolymer rich in shell was prepared by semicontinuous emulsion polymerization in the presence of mixed emulsifying agents. The solids content of latex was about 25 wt % and had good stability. The latex particle morphology was characterized by transmission electron microscopy (TEM) and the surface properties were determined by the Wilhelmy method.[9]

EXPERIMENTAL

Materials

Perfluoroalkylethyl methacrylate (Zonyl TM) samples and fluorinated acrylate monomers were obtained from Aldrich (Milwaukee, WI) and used without further purification. The value of n in the C_nF_{2n+1} group ranged from 6 to 8 and the fluorine-containing content was 60 wt %. Butyl acrylate (BA) and methyl methacrylate (MMA) were washed by 5 wt % sodium hydroxide solution to delete inhibitions. The initiator, ammonium persulfate, was purified by recrystallization. The mixed surfactant systems were composed of sodium dodecyl sulfate (SDS), OS-15, OP-10, or hexadecyl-trimethylammonium bromide (C_{16}TAB). The deionized water was obtained by ion exchange.

Emulsion Polymerization

The core–shell emulsion was synthesized by semicontinuous seed emulsion polymerization using mixed emulsifying agents and ammonium persulfate as initiator. For synthesis of the homogenous particles, a latex seed composed of polyacrylate was prepared first and the remaining components, including FMA, were next slowly added to the seed.

The reaction was carried out in a 250-mL four-neck flask equipped with a stirrer, a condensation

tube, and a centigrade thermometer. Oxygen in the flask and monomers was removed by sparging nitrogen at first. BA, mixed emulsifying agents, and deionized water were all added to the flask in proportion. The mixture was stirred to be completely preemulsified, and then the solution was heated by water bath after adding the initiator. When the temperature inside the flask reached about 70°C, the polymerization reaction started. After the self-heating process finished, the reaction temperature was kept at about 78°C for 10 min so that the polymers of the core phase formed completely. Then the preemulsified mixture, composed of MMA, Zonyl TM, the remaining BA, initiator, mixed emulsifying agents, and deionized water, was slowly dropped into the reaction system. This slow step was performed for at least 4 h. After the dropping step was complete, the reaction continued at about 80°C for 1 h. After the reaction was over, the temperature was lowered to room temperature. Finally, $NaHCO_3$ was added to control the pH value of the final latex at the range of 6 to 7. The solids content of the final latex was about 25 wt %.

Solids Content and Final Conversion

The solids content and final conversion were measured by gravimetric analysis. A certain quantity of emulsion was cast onto a petri dish and dried to a constant weight in a dry oven at 75–85°C. The solids content and final conversion, respectively, were calculated by the following formulas:

$$\text{Solids content (\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\%$$

where W_0 is the weight of the petri dish, and W_1 and W_2 are the weight of emulsion before and after drying to constant weight, respectively.

$$\text{Conversion (\%)} = \frac{[W_3 \times \text{solids content (\%)}] - W_4}{W_5}$$
$$\times 100\%$$

where W_3 is the total weight of all the materials put in the flask in each polymerization, W_4 is the weight of materials that cannot volatilize when drying, and W_5 is the weight of total monomers.

Stability of Latex

The formula, $\sigma = (W_c/W_m) \times 100\%$, was used to show the polymerization stability. The latex's co-

Table I   Effects of Different Emulsifying Systems on the Preemulsifying Effect and Polymerization Stability (σ)

	Emulsifying System			
	OS-15/SDS	OP-10/SDS	OS-15/C_{16}TAB	OP-10/C_{16}TAB
Preemulsifying effect	Demix after storing 10 min	Demix after storing 10 min	Demix at once after storing	Demix at once after storing
σ (wt %)	1.5	2.0	—[a]	—[a]

[a] No data because of poor polymerization stability.

agulate was filtered by filter cloth, washed by deionized water, and dried to constant weight at 60°C. The weight of dried coagulate was recorded as W_c (g) and the total weight of monomers was recorded as W_m. Thus, the larger the value of σ, the worse the polymerization stability.

A 20-mL sample of latex was sealed in a test tube with tap, then stored at 50 and −5°C, respectively. The changes in the latex, such as precipitation and breaking, showed the heat stability and freezing stability, respectively.

The final latex was stored at room temperature for 3 months under a sealing condition. The changes in emulsion showed the storage stability.

Latex Particle Morphology

Latex particle morphology was observed by TEM. First a certain quantity of final emulsion was diluted properly by distilled water, and then dyed by phosphotungstic acid solution (pH = 6.4). After filming on copper, photos were taken to observe the particle morphology by TEM-100SX (JEOL LTD., Tokyo, Japan).

Dynamic Contact Angle of Latex Film

The dynamic contact angles of the latex films were measured by the Wilhelmy method using a Krüss interface tension meter (Krüss GmbH., Hamburg, Germany). The latex film sample was cut into squares, held in a microbalance, and progressively immersed into water at a constant rate, then, conversely, receded to its original position. The analysis of the wetting force data yielded low contact angles, which were an advancing contact angle and a receding contact angle. The plates were immersed into water at a speed of 0.5 mm/s.

RESULTS AND DISCUSSION

Emulsion Polymerization Condition

Although emulsifying agents do not take part in polymerization, they exert a significant effect on the stability of emulsion polymerization. Thus, a suitable emulsifying system is an important factor for emulsion polymerization. According to previous reports[10], mixed emulsifying agents have a superior emulsifying effect. In our work, the mixed emulsifying systems were obtained by mixing OS-15 or OP-10 with SDS or C_{16}TAB. Under the conditions that the total concentration of emulsifying agents and the ratio of nonionic to ion emulsifying agents were all fixed, the relationships between the emulsifying systems and preemulsifying effect or polymerization stability were investigated, the results of which are listed in Table I. Using the mixed emulsifying system composed of C_{16}TAB and nonionic emulsifying agents, the reaction mixture still demixed after being stirred for 30 min at 400 rpm/min, so this emulsifying system clearly is not efficient. Compared to the cationic/nonionic emulsifying system, the anionic/nonionic emulsifying system composed of SDS and OP-10 or OS-15 caused monomers to be well emulsified and well dispersed in water, and the reaction mixture became a white emulsion and was stable after stirring ceased. Moreover, concerning the polymerization stability in anionic/nonionic emulsifying systems, the value of σ is less when using SDS/OS-15 than that when using SDS/OP-10. The larger the value of σ, the worse the polymerization stability. Thus all these data in Table I illustrate that the mixed emulsifying system, which was composed of OS-15 and SDS, had the best emulsifying effect. In the reaction system, no more than 6 wt % Zonyl TM was used. Consequently, the emulsifying agents, which were used in the polymerization of normal acrylates, can also be used in the fluorine-containing acrylates polymerization system.

The effects of ratio of OS-15 to SDS on emulsion polymerization stabilities are shown in Table II. When the ratio value changed from 2 to 4, the emulsifying effect exerted no obvious change, although the value of σ increased from 2.04 to 4.53

Table II Effects of the Ratio of OS-15 to SDS on Polymerization Stability (σ) and Final Conversion (%)

	Ratio of OS-15 to SDS		
	2 : 1	3 : 1	4 : 1
σ (wt %)	2.04	3.20	4.53
Final conversion (wt %)	94.22	93.65	88.86

and the final conversion decreased rapidly. These outcomes indicate that the greater the quantity of OS-15, the more difficult the polymerization process. In this system, OS-15 is a kind of nonionic emulsifying agent and its emulsifying capability is less than that of SDS; thus, the greater the quantity of OS-15, the fewer micelles (which were polymerization positions) were formed. The final conversion decreased correspondingly. Moreover, coagulates were easily formed when a greater quantity of OS-15 was used, so the value of σ increased with the increasing concentration of OS-15.

Figure 1 shows the effect of the concentration of mixed emulsifying agents on polymerization conversion. The curve shows an increasing trend, which indicates that the final conversion increased concomitantly with an increase in the total concentration of mixed emulsifying agents. An increase in the amount of emulsifying agents, which could generate more micelles, increases the possibility of polymerization, further leading to increased conversion.

Concerning the OS-15/SDS emulsifying system, the suitable ratio of OS-15 to SDS is 2 to 1, and the optimum total concentration is 3.7–4.5 wt %.
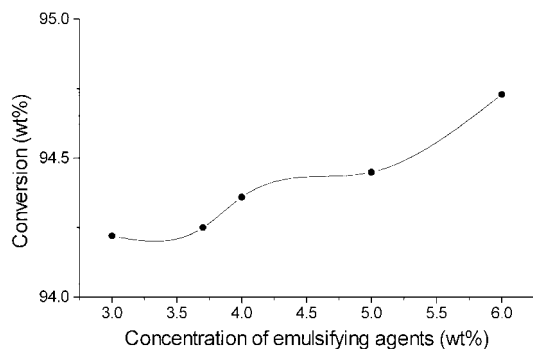
Figure 1 Conversion versus concentration of mixed emulsifying agents.
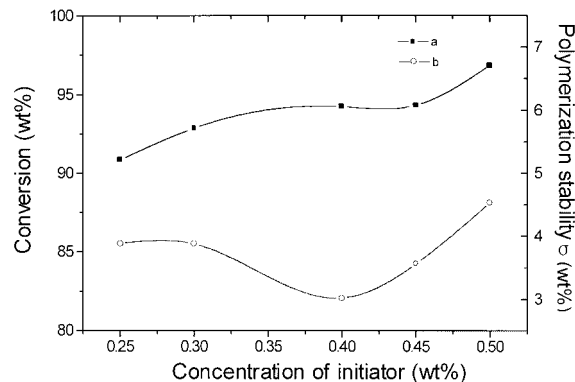
Figure 2 (a) Conversion versus concentration of initiator; (b) emulsion stability versus concentration of initiator.

The relationships between the concentration of initiator and final conversion or polymerization stability, are shown in Figure 2(a) and (b), respectively. The curve in Figure 2(a) shows that the final conversion increased with increasing initiator concentration. The curve of polymerization stability versus concentration of initiator, as shown in Figure 2(b), had the lowest point when the concentration was 0.40 wt %. An increase in the concentration of initiator would promote faster creation of radicals, and thus the concentration of radical in water would increase. Thus, increased radical diffusion into the micelles would be accompanied by an increase in the nucleation rate, thus leading to an increase in the final conversion. However, this initiator reaction is an exothermal reaction. The heat of decomposition of the initiator accelerated Brownian motion of latex particles, thus increasing the rate of collision and, in turn, decreasing polymerization stability. Clearly, too high a concentration of initiator did not benefit the emulsion polymerization. Thus, the concentration of initiator was optimal at about 0.40 wt % for this system.

Figure 3 shows the effect of dropping time on the final conversion. The increasing slope of the curve illustrates that prolonging the dropping time could raise the final conversion. In our work, semicontinuous emulsion polymerization was used. Part of the reaction mixture, composed of monomers, initiator, and water, was added slowly into the reaction system during the reaction process. This feeding method could generate monomers under starved conditions and lessen the loss of monomers caused by volatilization. Thus, the slower the rate of addition, the higher the final conversion. Compared to the following TEM re-
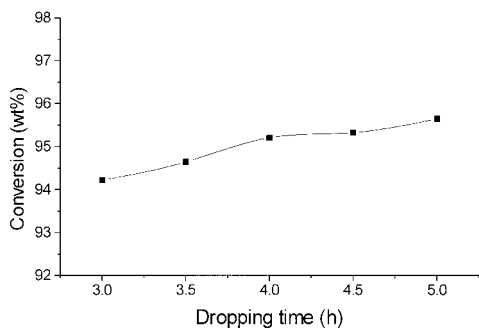
Figure 3 Conversion versus dropping time (h).

sults, when the dropping time was 4 h, the latex particles formed a clear and orbicular core–shell structure; thus, a dropping time of 4 h was found to be optimal.

Latex Particle Morphology

The morphology and structure of latex particles obtained under different polymerization conditions were characterized by TEM and are shown in Figure 4. As seen in Figure 4, the core–shell structure of latex can be clearly distinguished.

The latex particles of Figure 4(a) and (b) were synthesized at different total concentrations of emulsifiers, whereas other polymerization conditions were fixed. By comparison of Figure 4(a) to Figure 4(b), it was found that the latex dispersed well when the total concentration of emulsifying agents reached 3.7 wt % and the sizes of latex particles became smaller with an increase in the concentration of emulsifying agents. These phenomena agree with traditional emulsion polymerization theory.

Figure 4(c) and (d) show that the latex particles were better dispersed and the particle sizes were larger when the ratio of OS-15 to SDS was 2 to 1 and the concentration of emulsifying agents was fixed. This result was consistent with the effect of the ratios of OS-15 to SDS on final conversion.

The effect of dropping time on latex particle morphology can be found from Figure 4(e) and (f), in which latex particles were prepared under different dropping times, whereas other polymerization conditions were the same. When the dropping time reached 4 h or more, the core–shell structure formed completely and was clear. This was the result of lower polymerization activity of fluorinated acrylate monomers, compared to that of nonfluorinated acrylate monomers. Only by slow dropping can the contents of the fluoromono-

mer inside the emulsion and on the surface of the core phase be kept so low that they are under starved conditions, thus promoting the formation of core–shell latex.

Stability of Latex

There were few coagulates in the final latex. The storage, heat, and freezing stabilities of latex with different fluorine-containing contents are listed in Table III. When the latex was stored under a sealing condition at room temperature for 3 months, at either 50 or $-5°C$ for 12 h, the latex did not demix.
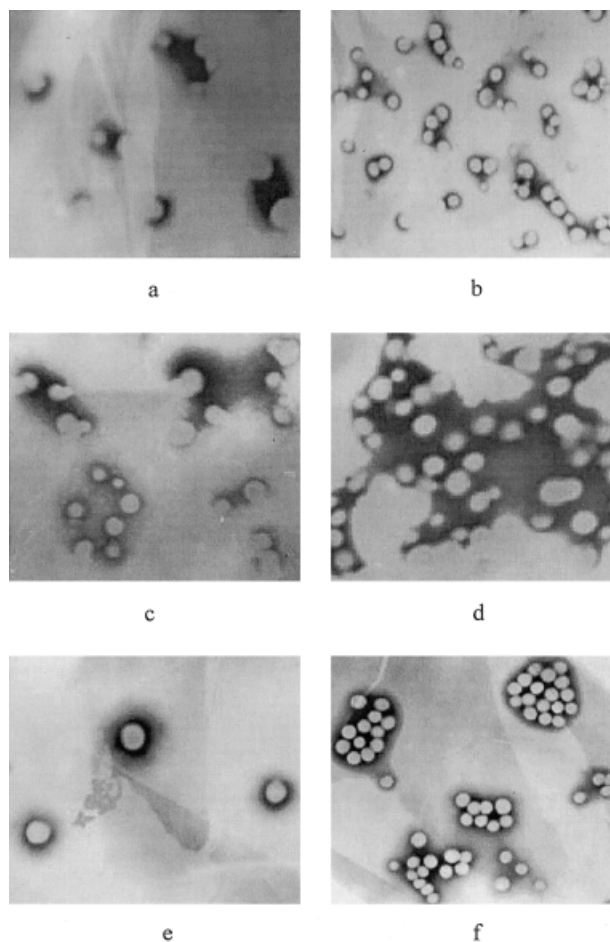

Figure 4 Morphology of latex particles under different conditions: (a) $x = 4 \times 10^4$, $C_e = 3.7$ wt %; (b) $x = 4 \times 10^4$, $C_e = 6.0$ wt %, and other conditions were the same as in a; (c) $x = 4 \times 10^4$, OS-15/SDS = 2; and (d) $x = 4 \times 10^4$, OS-15/SDS = 4, and other conditions were the same as in c; (e) $x = 4 \times 10^4$, $t_{dropping} = 4$ h; (f) $x = 4 \times 10^4$, $t_{dropping} = 5$ h, and other conditions were the same as in e.

Table III   Stabilities of Emulsions with Different Concentrations of Fluoromonomer (Zonyl TM)

	Fluoromonomer Concentration (wt %)					
	0.0	0.5	1.0	2.0	3.0	4.0
Room temperature, for 3 months	No change	No change	No change	No change	No change	No change
50°C, for 12 h	No change	No change	No change	No change	No change	No change
−5°C, for 12 h	No change	No change	No change	No change	No change	No change

Dynamic Contact Angle of Latex Film

Figure 5 illustrates the relationships between the dynamic contact angles of latex films and water under different polymerization conditions.

The advancing angles are all above 90°, whereas the receding angles are about 30°. These indicate that the fluorine-containing polyacrylate latex films could be wetted by water only with difficulty, and that the surface structure might

change when latex films were immersed in water. The fluoropolymer was in the shell phase by controlling the polymerization method. Because of fluoropolymer's high hydrophobicity and low surface tension, the fluoropolymer could accumulate at the surface during the film formation, thereby greatly lessening the surface energy, and thus latex film could not be wetted by water easily. On the other hand, the value of n in the C_nF_{2n+1}
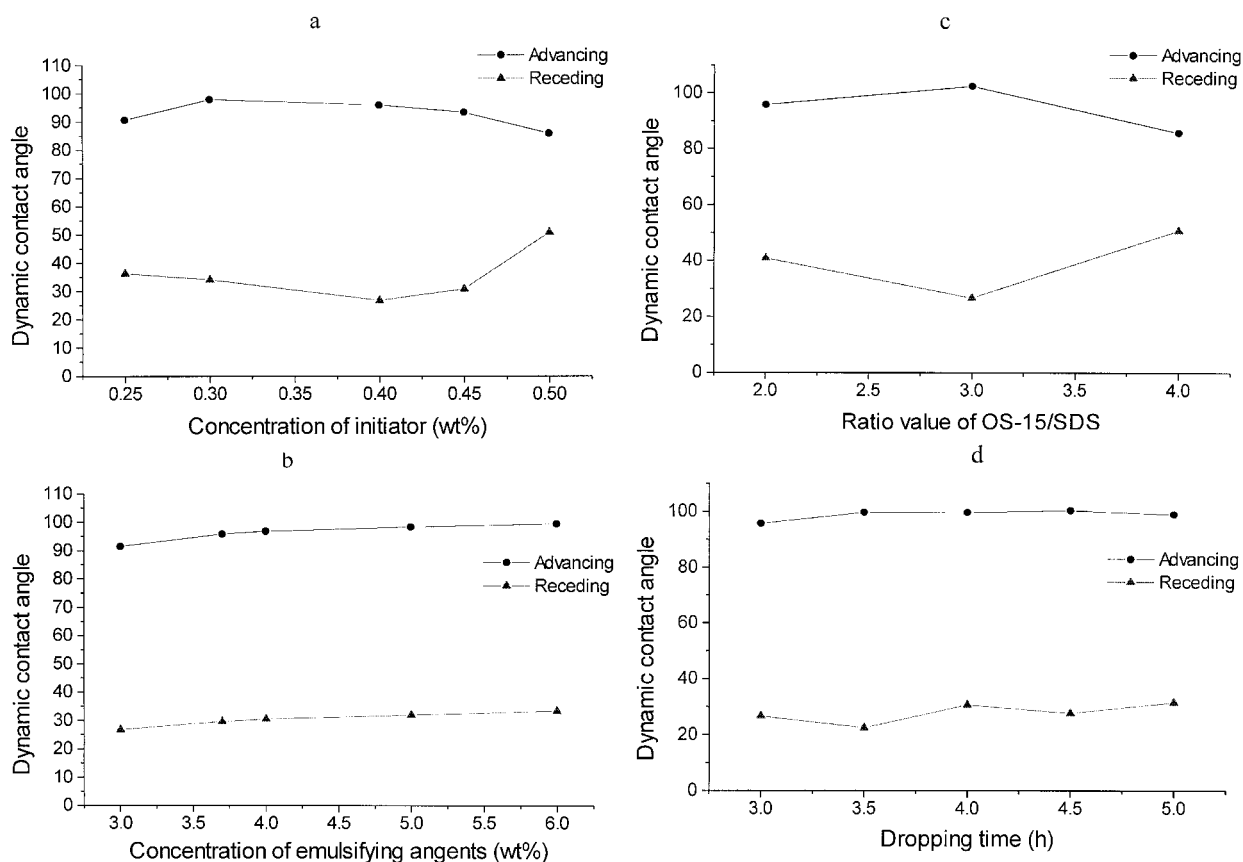

Figure 5   Effect of different polymerization conditions on advancing angles or receding angles of latex films and water: (a) effect of concentration of initiator; (b) effect of concentration of mixed emulsifying agents; (c) effect of the ratio of OD-15 to SDS; (d) effect of dropping time. ●, advancing angles; ▲, receding angles.

group of fluoromonomer (Zonyl TM) was in the range of 6 to 8. According to recent research reports,[11–13] when n was less than 12, the fluoropolymer was in a random state of aggregation with no crystal part. Thus the fluoro-groups with high hydrophobicity would migrate to the inside of the film and hydrophilic groups would migrate to the surface, when the environment surrounding the latex films changed, say, by being immersed in water. This may be the one reason for the significant difference between the advancing angles and the receding angles; the other reason may be that the film surface is not smooth enough. When analyzing the difference between the advancing angles and the receding angles under each polymerization condition, an interesting phenomenon was found: the larger the advancing angle, the smaller the receding angle. This may exert some influence on the group–migrating ratios. Further study is thus needed by other determinations.

CONCLUSIONS

Core–shell latex with polyacrylate rich in core and fluoropolymer rich in shell was prepared by semicontinuous emulsion polymerization in the presence of mixed emulsifying agents of OS-15 mixed with SDS. The polymerization temperature was about 70–80°C and the solids content of latex was about 25 wt %. The stability of the final latex was very good and the core–shell structure of latex particles can be clearly seen. The advanc-

ing angles of the film to water were all above 90°, so that the latex film could be wetted by water only with difficulty. By preparing core–shell emulsion with a fluoropolymer in the shell phase, we can efficiently modify the surface property of polyacrylate latex films by using only small amounts of fluorinated acrylate monomer.

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