

Study of Self-Crosslinking Acrylate Latex Containing Fluorine

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ABSTRACT: Self-crosslinking acrylate latices containing fluorine were prepared by the batch method, with *N*-hydroxymethyl acrylamide (NMA) as a crosslinking agent. The structure and component of latex polymers were studied by FTIR, ion-selective electrode analysis, and DSC. The stabilities of latices, such as storage stability, centrifugal stability, and electrolyte-resistant stability, were examined. The morphology of the latex particles was characterized by TEM and

the surface properties were determined by the Wilhelmy method. The effects of NMA on T_g of the latex polymers, the average particle size of the latices, and the surface properties of the latex films were discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3609–3616, 2003

Key words: latices; fluorine-containing acrylate; self-crosslinking; surfaces; films

INTRODUCTION

Since the late 1950s and 1960s fluorinated or partially fluorinated polymers were discovered to exhibit the characteristic of low surface energy.^{1,2} Because of their unique characteristics of thermal and photochemical stability, water and oil repellency, and self-cleaning property, fluorinated polymers have been widely studied for applications in recent years.^{3,4} Moreover, acrylate polymers containing fluorine have been the focus of a number of studies by many investigators who demonstrated useful and wide-ranging applications, such as oleophobic and hydrophobic coating for textiles,⁵ leather,⁶ stone,⁷ for optical fibers,⁸ and photoresisters.⁹ Acrylate polymers containing perfluoroalkyl side chains have three main advantages: (1) fluorinated acrylates have a good reactivity with fluorine-free acrylates; (2) the low intermolecular force between perfluoroalkyl side chains and the air lowers the surface free energy of polymers; and (3) the acrylic main chains ensure that polymers can adhere well to many kinds of matrices. With respect to surface property, the efficiency increases when the weight ratio of the fluoro-components in the polymer increases. However, the relatively high market price of fluorinated acrylate monomers limits their use, unless their weight ratios can be minimized while maintaining a reasonably good surface property.

Fluorinated acrylate copolymers are typically systems that contain the perfluoroalkyl group $[-(CF_2)_nF]$. The $-CF_3$ terminus on the pendant perfluoroalkyl chain provides much lower surface free energies than typical poly(tetrafluoroethylene)-like materials containing the $-CF_2-$ moiety in the polymer backbone.^{10,11} Thus it is the key to achieving low surface free energy that the surface of a material is covered with as many perfluoroalkyl groups as possible. Four approaches may be used to achieve this aim: (1) to synthesize block or graft fluorinated copolymers^{12,13}; (2) to prepare latices with special structures^{14–16}; (3) to blend¹⁷; and (4) to enhance the homogeneity of fluoromonomers by random polymerization.¹⁸

Acrylate latices containing fluorine continue to attract the increasing attention of many investigators because of their characteristically good surface and environmentally friendly properties. In 1997 Chen et al.¹⁸ reported a self-crosslinking latex system with fluorinated acrylate and stearyl acrylate as monomers and with *N*-hydroxymethyl acrylamide (NMA) as a crosslinking agent. Their research focused on the water/oil repellency of latex films. However, studies on the effect of crosslinking agents on the properties of acrylate latex films containing fluorine have scarcely been reported.

In our recent work,¹⁹ we succeeded in preparing an acrylate terpolymer latex with a low fluorine content by a fluorinated acrylate monomer (Zonyl TM), butyl acrylate (BA), and methyl methacrylate (MMA) as monomers, and studied the properties of these latices and their films, especially the surface property. We found that the films of these latices containing fluorine

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had good wetting resistance and water repellency when the amount of Zonyl TM was no more than 4 wt %. The aim of the present study was to increase the solvent resistance of these latex films and to investigate the effects of crosslinking agents on the properties of their films. Self-crosslinking acrylate latices containing fluorine were prepared by the batch method, with NMA as the crosslinking agent. The structure and components of latex polymers were studied by FTIR, ion-selective electrode analysis, and DSC analysis. The stabilities of latices, such as storage stability, centrifugal stability, and electrolyte-resistant stability, were examined. The effects of NMA on the glass-transition temperature (T_g) of the latex polymers, the average particle size of the latices, the solvent resistance, and the surface property of the latex films, were discussed.

EXPERIMENTAL

Materials

Perfluoroalkylethyl methacrylate (Zonyl TM) samples were obtained from Aldrich (Milwaukee, WI) and used without further purification. The value of n in their C_nF_{2n+1} groups ranged from 6 to 8 and the fluorine content was 60 wt %. BA and MMA were washed by 5 wt % sodium hydroxide solution to delete inhibitions. The crosslinking agent (NMA), the initiator (ammonium persulfate), and the surfactant [sodium dodecyl sulfate (SDS)] were all purified by recrystallization. 1,1,2-Trifluorotrichloroethane was used as the solvent for selective extraction. NaF was dried before use. The deionized water was obtained by ion exchange.

Emulsion preparation

Emulsion polymerization was carried out at 72°C under nitrogen atmosphere in a 250-mL four-neck flask equipped with a Teflon stirrer, a condensation tube, and a centigrade thermometer. Oxygen in the monomers and the flask was at first removed by purging nitrogen. Next, monomers (containing 18.0 g BA, 12.0 g MMA, 1.3 g Zonyl TM, and 1.0 g NMA), SDS, and deionized water were added to the flask and the mixture was preemulsified for 20 min at 45°C. Ammonium persulfate was then added and the mixture was heated to 72°C by water bath. The polymerization started and continued for at least 4 h at 72°C. Finally, $NaHCO_3$ was added to control the pH value of latices in the range 5 to 6 and the final latex was obtained.

Polymer characterization

The fluorine content of polymer was determined by ion-selective electrode analysis. A standard curve was created through examining standard NaF solutions in

different concentrations (from 10^{-2} to 10^{-5} mol/L). According to the mathematical analysis of the standard curve, a linear regression [eq. (1)] was obtained, as follows:

$$E \text{ (mV)} = -5.1 - 58.1 \log[F^-] \text{ (mol/L)} \quad (1)$$

A latex film was extracted for 24 h at 40°C, using 1,1,2-trifluorotrichloroethane as the solvent. The residual film was dried in a vacuum oven at room temperature. Next, a certain amount of the residual film was burned in an oxygen bomb with 50 mL 0.1 mol/L NaOH solution as the absorbing medium. The absorbing solution was then diluted 1.25 times and determined by fluorine ion-selective electrode analysis to obtain a response E . According to the linear regression eq. (1) and the response E , the concentration of fluorine ion in the solution could be calculated. The fluorine content of the copolymer was calculated by the following formula:

$$C_F \text{ (wt \%)} = \frac{1.25[F^-] \times 0.05 \times M_F}{W} \times 100\% \quad (2)$$

where $[F^-]$ is the concentration of fluorine ion in the absorbing solution, M_F is the molar mass of F element, and W is the weight of the film before burning.

Infrared spectra of the latex films were recorded with Perkin-Elmer Spectrum One FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) in the range 4000 to 400 cm^{-1} . The glass-transition and thermal decomposition temperatures of polymers were measured with a Perkin-Elmer DSC7 differential scanning calorimeter and TGA7 thermogravimeter, respectively, under nitrogen atmosphere at the heating rate of 20°C/min.

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

$$\text{Solid content (wt \%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100\% \quad (3)$$

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

Conversion (wt %)

$$= \frac{\text{Solid content (wt \%)} \times (W_3 - W_4)}{W_5} \times 100\% \quad (4)$$

where W_3 is the total weight of all the materials put in the flask before polymerization, W_4 is the weight of

materials that could not volatilize during the drying period, and W_5 is the total weight of monomers.

The latices were diluted, after which their particle sizes were characterized directly by PCS particle size and distribution meter (produced by Malvern Co., UK) at a fixed scattering angle of 90° . The morphology of latex particles was investigated by TEM. The latices were diluted and stained by phosphotungstic acid solution (pH = 6.4). The stained samples were applied to a 200-mesh copper grid and allowed to dry. TEM micrographs were obtained by TEM-100SX transmission electron microscopy (JEOL Co., Tokyo, Japan) at 60 kV.

The centrifugal stability and electrolyte-resistant stability of latices were determined by the centrifugal method and adding electrolyte solutions to latices, respectively. The higher the sedimentation ratio, the less were these two stabilities. The sedimentation ratio was calculated by the following formula:

$$\text{Sedimentation ratio (wt \%)} = \frac{W_1}{W_0} \times 100\% \quad (5)$$

where W_1 is the weight of the sedimentation and W_0 is the weight of the original latex samples.

The weighed latex films were dipped in distilled water for 48 h. Then the water on the surface of the films was removed and the films were weighed again. The water absorption ratio of the films was calculated by the following formula:

$$\text{Water absorption ratio (wt \%)} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (6)$$

where W_0 and W_1 are the weight of the films before and after the films absorb water, respectively.

The weighed films were dipped in different organic solvents for 48 h. Then the solvents on the surface of the films were cleaned off and the films were weighed again. The swelling ratio of the films was calculated by the following formula:

$$\text{Swelling ratio (wt \%)} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (7)$$

where W_1 and W_2 are the weight of the films before and after the films are swollen, respectively.

The dynamic contact angles of latex films were measured by the Wilhelmy method²⁰ using a Krüss II interface tension meter (Krüss Co., Hamburg, Germany). The latex films were cut into squares, held in a microbalance, and progressively immersed into water at a speed of 0.5 mm/s, then, conversely, allowed to recede to the original position. Analysis of the wetting

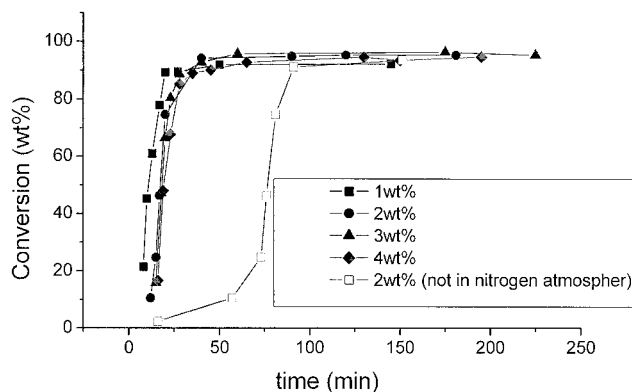


Figure 1 Effects of the amount of NMA on the curves of conversion versus time.

force data yielded both an advancing contact angle and a receding contact angle.

RESULTS AND DISCUSSION

Effect of the amount of NMA on emulsion polymerization

To investigate the change of the conversion during the whole emulsion polymerization process, we removed about 1 mL emulsion each time at short intervals, added a drop of inhibition solution into the emulsion as quickly as possible, and then determined the conversion. Figure 1 shows the relationship between the conversion and time under different amounts of NMA, confirming that the conversion slightly increased with the increase in the amount of NMA. It is worth mentioning that oxygen would evidently elongate the induction time in this system.

Structure and composition of polymers

From the IR spectrum of the latex film (BA : MMA : NMA : Zonyl TM = 18.0 : 12.0 : 1.0 : 1.3 g) shown in Figure 2(a), the characteristic absorption of the C=C bond at 1640 cm^{-1} disappeared, indicating that the monomers had polymerized. Compared to the IR spectrum of P(BA-*co*-MMA) latex film [Fig. 2(b), BA : MMA = 18.0 : 12.0 g], the IR absorption peak at $1000\text{--}1260 \text{ cm}^{-1}$ became wider and blunter, attributed to the stretching vibration absorption of the C—F bond at $1100\text{--}1240 \text{ cm}^{-1}$, overlapping with the stretching vibration absorption of the C—O—C bond of ester groups at 1250 cm^{-1} . The characteristic absorption of the N—H bond appeared at 1539 cm^{-1} [Fig. 2(a)]. These two results further proved that Zonyl TM and NMA participated in the polymerization.

To study whether Zonyl TM took part in the copolymerization reaction, the latex film (BA : MMA : NMA : Zonyl TM = 18.0 : 12.0 : 1.0 : 1.3 g) was ex-

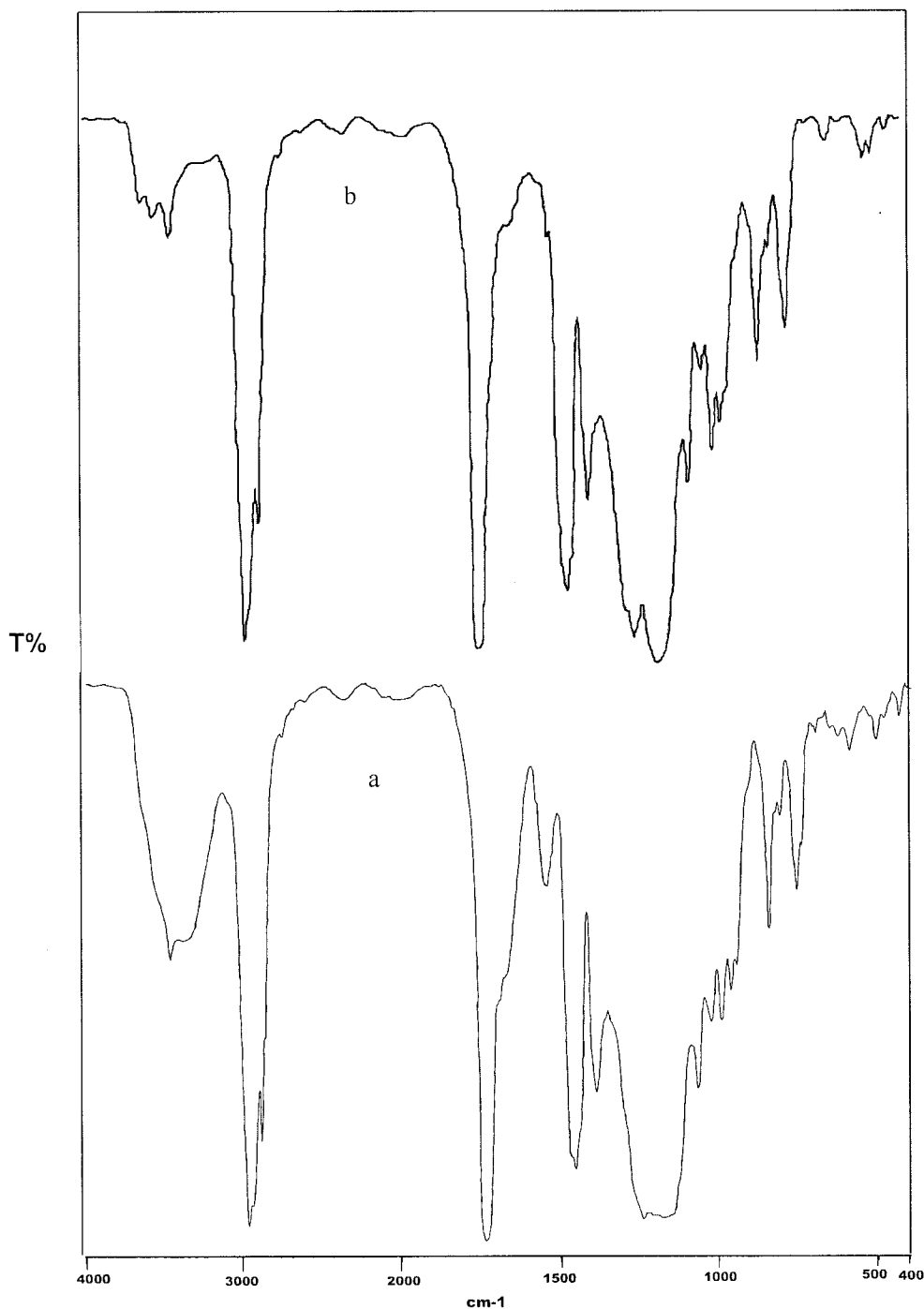


Figure 2 IR of the latex films: (a) P(BA-MMA-NMA-Zonyl TM) films; (b) P(BA-MMA) films.

tracted first by 1,1,2-trifluorotrichloroethane to remove the residual Zonyl TM and fluorinated acrylate homopolymers. Because Zonyl TM and fluorinated acrylate homopolymers could dissolve in 1,1,2-trifluorotrichloroethane, the main component of the residual film consisted of the copolymers containing BA, MMA, NMA, and Zonyl TM. Next, 0.0104 g residual film was burned, changing the fluorine in the copolymer to the fluorine ion in the absorbing solution. Then,

the absorbing solution was diluted and determined by fluorine ion-selective electrode analysis. The response E was 222 mV; thus the concentration of the fluorine ion in solution was 1.23×10^{-4} mol/L according to eq. (1) and the fluorine content of the film was 1.40 wt % according to eq. (2). This result proved that Zonyl TM took part in the copolymerization. However, the fluorine content of the film in theory was 2.4 wt %, higher than the experimental value, which could be attrib-

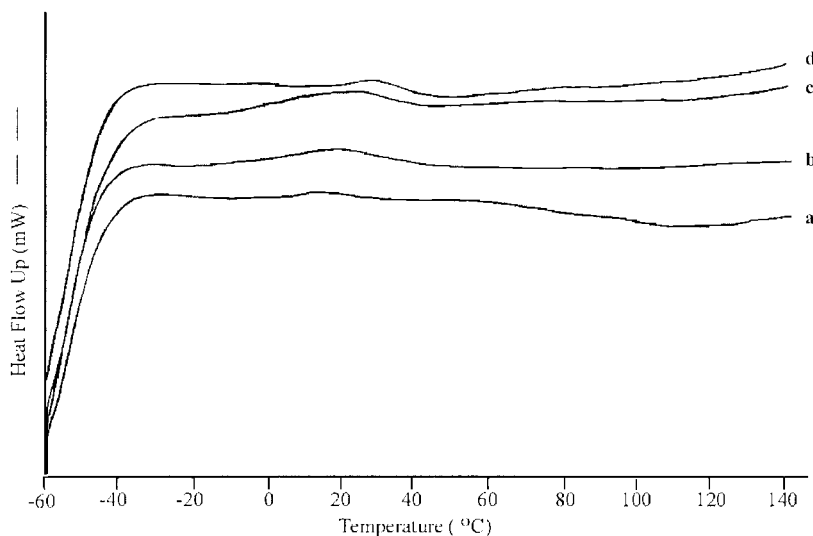


Figure 3 DSC curves of the latex films formed at room temperature with different amounts of NMA: (a) 1.0 wt %; (b) 2.0 wt %; (c) 3.0 wt %; (d) 4.0 wt %.

uted to two reasons. One reason was the loss of fluorine during the burning process because the oxygen bomb was made of glass; the other possible reason was the existence of Zonyl TM homopolymer trace.

Figure 3 shows the DSC curves of the latex polymers containing 18.0 g BA, 12.0 g MMA, 1.3 g Zonyl TM, and different amounts of NMA. There was only one obvious temperature transform on each of the DSC curves, indicating that there was one T_g in all the latex polymers, for example, 18.3°C for the latex polymer containing 4.0 wt % NMA. Figure 3 also shows the effects of the amount of NMA on the polymer's T_g . The polymer's T_g became increasingly higher when the amount of NMA increased.

Latex particle size and morphology

Table I lists the average particle size of the latices prepared under different amounts of NMA. The data show that the latex particle sizes increased with the increase of the amount of NMA. Because of the existence of NMA, the crosslinking reaction occurred during the emulsion polymerization, allowing some linear macromolecules to link and form networks between molecule chains. Moreover, the crosslinking density increased with increasing the amount of NMA, so the average particle size of latices increased correspondingly.

TABLE I
Average Particle Sizes of Latices with Different Amounts of NMA

Amount of NMA (wt %)	0.0	1.0	2.0	3.0	4.0
Average size (nm)	63.2	73.2	73.7	75.9	86.5

From the TEM micrographs of latices (Fig. 4), one may observe that many latex particles aggregated and formed groups, and also that the group sizes increased with increased amounts of NMA, indicating both intraparticle and interparticle crosslinking.

Stabilities of latex

There were few coagulates in the final latices. When the latices were stored under a sealing condition at room temperature for 1 month, at either 50 or -5°C for 24 h, the latices did not demix. Table II indicates the effects of the amount of NMA on the centrifugal stability and electrolyte-resistant stability of latices. The higher the sedimentation ratio, the less were the

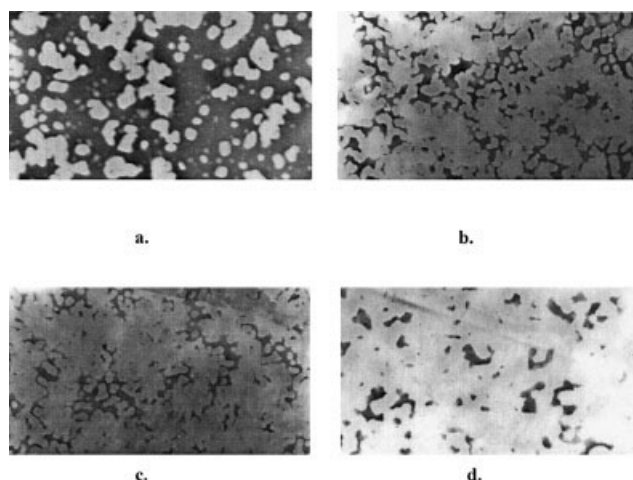


Figure 4 Morphology of the latex particles: (a) $x = 2 \times 10^4$, 1.0 wt % NMA; (b) $x = 2 \times 10^4$, 2.0 wt % NMA; (c) $x = 2 \times 10^4$, 3.0 wt % NMA; (d) $x = 2 \times 10^4$, 4.0 wt % NMA.

TABLE II
Effects of the Amount of NMA on the Centrifugal Stability and Electrolyte-Resistant Stability of the Latices

Amount of NMA (wt %)	1.0	2.0	3.0	4.0
Centrifugal stability (wt %) ^a	4.28	2.73	3.19	4.87
Electrolyte-resistant stability (wt %) ^b	14.63	6.04	16.19	17.51

^a Centrifugal rate is 12,000 rpm, and centrifugal time is 120 min.

^b Using 1.0 mol/L Na₂SO₄ as electrolyte and placed for 72 h.

centrifugal stability and electrolyte-resistant stability. With increased amounts of NMA, both the centrifugal stability and electrolyte stability of latex showed a decreasing trend. Because the amount of SDS was fixed in this system, it became more difficult to stabilize the latices when the particle size and the crosslinking density of the latices increased. When the amount of NMA was 2.0 wt %, the latex exhibited the best centrifugal stability and electrolyte stability.

Properties of latex films

The latex films were immersed in methanol, ethanol, acetone, and THF for 48 h, respectively. Table III lists the swelling degrees of the latices with different amounts of NMA in these solvents. Our previous research results¹⁹ indicated that P(BA-MMA-Zonyl TM) latex films without crosslinking structures could be dissolved in acetone and THF, although Table III also shows that the films with crosslinking structures could swell only in acetone and THF, but not be dissolved in them, indicating that the solvent resistance of the latex films was enhanced. The fluorine content was low in this system, so the protecting effect of perfluoroalkyl groups on the main chains was limited. After the solvent swelled the polymers, the solvent molecules could not break the crosslinking molecules because of the network of crosslinking bonds. Moreover, the crosslinking reaction increased the molecular weight; thus the solvent resistance of the latex

TABLE III
Swelling Degrees of Latex Films with Different Amounts of NMA in Different Solvents

Solvent	Swelling degrees on different amounts of crosslinking agent (wt %)			
	1.0 wt %	2.0 wt %	3.0 wt %	4.0 wt %
Methanol	78.4	63.0	57.8	54.8
Ethanol	66.4	61.5	54.9	52.7
Acetone	— ^a	— ^a	980.5	700.8
THF	— ^a	— ^a	1674.9	1108.0

^a No data because of low accuracy.

TABLE IV
Water Contact Angles of Latex Films Formed at Room Temperature with Different Amounts of NMA

	Amount of NMA (wt %)			
	1.0	2.0	3.0	4.0
Advancing water contact angle of films	96.8°	95.9°	93.9°	90.3°
Receding water contact angle of films	35.1°	30.5°	27.6°	24.3°

films was successfully enhanced. The greater the amount of NMA, the higher the crosslinking degree and molecular weight, and thus the solvent resistance of the latex films improved.

Data on the water contact angles of latex films with different amounts of NMA are listed in Table IV. The advancing angles of films were all above 90°, indicating that it was difficult to wet the latex films containing fluorine and that the films had the characteristic surface property of fluorochemicals. Because of high hydrophobicity and low surface tension, the fluorinated chains could accumulate at the surface during the latex film formation, and thus the surface free energy of the latex films was greatly diminished and it was difficult to wet the latex films. However, water contact angles of the latex films obviously decreased with the increase in the amount of NMA, indicating that the wetting resistance of the films decreased with the increase of NMA content. When the amount of NMA reached 4.0 wt %, the advancing contact angle of the latex film was just only 90.3°, probably because the crosslinking density was low and the mobility of fluorinated side chains was limited; thus some NMA side chains with high surface free energy were exposed to the surface of the films, increasing the surface free energy of the films. However, the receding angles of the films were much lower than the advancing angles, attributed to several possible reasons: (1) the surface of latex films was not smooth enough; (2) the fluorinated groups would migrate to the inside of the films and hydrophilic groups would migrate to the surface under low crosslinking density, when the environment surrounding the latex films changed, say, by being immersed in water. In this system, the value of *n* in the

TABLE V
Water Absorption Ratio of Latex Films Formed at Room Temperature with Different Amounts of NMA

	Amount of NMA (wt %)				
	0.0	1.0	2.0	3.0	4.0
Water absorption ratio (wt %)	15.7	23.5	26.0	29.1	36.9

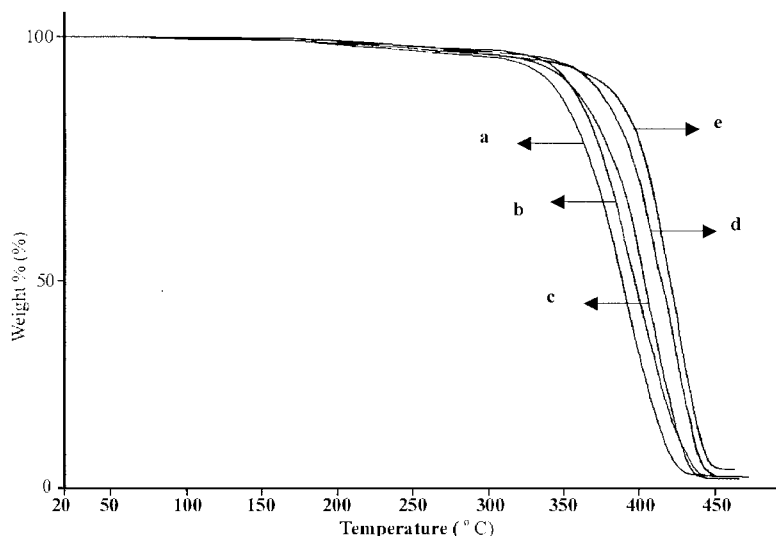


Figure 5 TGA curves of the latex films formed at room temperature with different amounts of NMA: (a) 0.0 wt %; (b) 1.0 wt %; (c) 2.0 wt %; (d) 3.0 wt %; (e) 4.0 wt %.

C_nF_{2n+1} group of the fluoromonomer (Zonyl TM) was in the range 6 to 8. According to a recent research report,²¹ if n was less than 12, the fluorinated domains were in a random state of aggregation without a crystalline phase and the fluorinated chains would reorient and rearrange with the environmental change.

The data of Table V elucidate the effects of the amount of NMA on water absorption ratios of the latex films. The Zonyl TM content was fixed in this system. The water absorption ratio of the latex film without NMA was 15.7 wt %, whereas the water absorption of the latex film with 1.0 wt % NMA increased to 23.5 wt %. The higher the water absorption ratio, the less the water repellency of the films. Thus the water repellency of the films clearly decreased with use of NMA, attributed to the latex film's enhanced hydrophilicity after NMA, with good hydrophilicity, was introduced into the latex polymer chains in this system.

The results of water absorption and contact angles of latex films both indicated that NMA had a negative effect on the wetting resistance and water repellency of the latex films containing fluorine.

The thermogravimetric curves of the latex films with different amounts of NMA are shown in Figure 5. The crosslinking reaction caused linear polymer molecules to form network structures, and the crosslinking density increased with increasing amounts of NMA, such that the starting decomposition temperature of polymers increased and the decomposition temperature range expanded, indicating that the thermal stability of the latex films was enhanced.

CONCLUSIONS

Self-crosslinking acrylate latices containing fluorine were prepared by the batch method, with *N*-hydroxymethyl acrylamide (NMA) as the crosslinking agent. The stabilities of emulsion, such as storage stability, centrifugal stability, and electrolyte resistance, were all excellent. When the amount of NMA increased, the T_g of the latex polymers trended to the high temperature area, the average particle size of the latices increased, and the solvent resistance and thermal stability of the latex films were enhanced. The advancing contact angles of latex films were all above 90°, indicating that it was difficult to wet the latex films containing fluorine and that the films had the characteristic surface property of fluorochemicals. However, NMA had a negative effect on the wetting resistance and water repellency of the latex films containing fluorine.

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