

BA-MMA-POMA Copolymer Latexes Prepared by Using HMPS Polymerizable Emulsifier

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ABSTRACT: BA-MMA-POMA copolymer latex was successfully prepared by soap-free emulsion polymerization of 2-(perfluoro-(1,1-bis(isopropyl)-2-propenyl)oxyethyl methacrylate(POMA) with butyl acrylate(BA), methyl methacrylate (MMA) initiated by $K_2S_2O_8$ in the water. POMA was synthesized from the intermediate perfluoro nonene and 2-hydroxyethyl methacrylate as the starting reactants. The structure of BA-MMA-POMA copolymer latex was investigated by Fourier transform infrared (FTIR). The characteristics of the film such as hydrophobicity and glass transition temperature were characterized with the contact angle and differential scanning calorimetry respectively. The influences of the amount of the fluorinated monomer and the initiator on the soap-free emulsion polymerization and performance of the latex were studied. In addition,

comparison with the latex prepared by the conventional emulsifier SDBS is investigated. Results show that the hydrophobicity and glass transition temperature (T_g) of the latex are increased when the fluorinated monomer is introduced to copolymerize with other monomers. The hydrophobicity can be improved further with heating. Compared with the latices prepared by using SDBS emulsifier, the latices prepared by using HMPS emulsifier have larger particle size, higher surface tension. However, the difference of their T_g is extremely minute. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 819–826, 2011

Key words: polymerizable emulsifier; emulsion polymerization; HMPS; copolymer latex

INTRODUCTION

Polymer latex produced by emulsion polymerization of acrylates such as methyl methacrylate(MMA), *n*-butyl acrylate(BA) is mainly used as binder for coatings. Anionic emulsifier such as sodium dodecyl benzene sulfonate(SDBS) is widely used in industrial emulsion polymerization. Conventional emulsifier adsorbed onto the latex particle surface may desorb, resulting in latex destabilization. Moreover the presence of adsorbed emulsifiers inside of the polymer film can confer water sensitivity, which is a major drawback during application such as paints and other protective coatings.^{1–3} A simple, promising way to overcome such a drawback can be realized

by using polymerizable emulsifier.^{4–9} These polymerizable emulsifiers can copolymerize with the main monomer and become covalently bound to form an integral polymeric material. The polymerizable emulsifiers for emulsion polymerization have been examined recently, and the reports have highlighted two advantages of polymerizable emulsifiers: (a) hydrophobicity of the film of the latex is improved^{10,11} (b) polymerizable emulsifiers exhibit an efficient steric hindrance.^{12–14} Thus, the polymerizable emulsifiers will be important emulsifiers in the field of emulsion polymerization. Polymerizable emulsifiers can copolymerize with the adsorbed matrix and be bonded onto the surface of the matrix permanently. They can emulsify the matrix and be a part of the matrix.

Sodium 2-hydroxy-3-(methacryloyloxy) prop- ane-1-sulfonate (HMPS), which is a copolymerized stabilizer with good properties, can be copolymerized with other vinyl group monomers e.g., acrylate, vinyl acetate and styrene because the C=C bond in the HMPS has high reactivity. In this article, using the intermediate perfluoro nonene and 2-hydroxyethyl methacrylate as the starting reactants, we would like to report the convenient method to synthesize new copolymer latex by the soap-free emulsion polymerization technique. The emphasis is put in the present work on the different parameters of the

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polymerization and the properties of the latices films formed before and after annealing. In addition, comparison with the latex prepared with the conventional emulsifier SDBS is investigated.

EXPERIMENTAL

Materials

Butyl acrylate (BA) and methyl methacrylate (MMA) were distilled under reduced pressure prior to polymerization. 2-(perfluoro-(1,1-bis(isopropyl)-2-propenyl)oxyethyl methacrylate (POMA) was prepared in our laboratory, which was based on our previous work,¹⁵ and used as received. HMPS and SDBS were industrial grade. Potassium persulfate ($K_2S_2O_8$) is obtained from the Second Chemical Reagent Factory in Yixin (China). Sodium bicarbonate ($NaHCO_3$) is purchased from Hongguang Chemical Plant Co., Ltd in Shanghai (China). The water used in this experiment was distilled followed by deionization.

Synthesis of fluorinated monomer POMA

2-hydroxyethyl methacrylate and triethylamine were introduced into a three-necked flask with the stirrer. *N,N*-dimethylformamide (DMF) was then added into the flask and the stirrer was agitated for 5 min. Perfluoro nonene was added dropwise within 3 h at room temperature. The reaction continued for 4 h after perfluoro nonene was dripped completely. The resulting mixture was dissolved in 2.5% HCl solution to separate the mixture. The lower liquid was washed with 5% HCl solution and then with the distilled water. The obtained liquid was dried with Na_2SO_4 . Thus, POMA was obtained for next soap-free emulsion polymerization.

Preparation of latices

All runs were performed as seeded semibatch emulsion polymerizations in three stages. The first stage was a batch seed production step, the second was a continuous stage involving feeding a monomer mixture and initiator stock solution, and the third stage was a batch finishing stage to increase the monomer conversion to completion. The mixed monomers consisted of BA, MMA, and POMA. A homogeneous aqueous solution containing de-ionized water, $NaHCO_3$, and HMPS (or SDBS) 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 reactor temperature was increased to 80°C within 30 min. An initiator solution containing $K_2S_2O_8$ and deionized water and a monomer mixture containing

BA, MMA, and POMA 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 and monomer emulsion stock solutions were added slowly to the reactor using two separate dropping funnels. The feeding time for the initiator and the monomer emulsion stock solutions 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 NH_4OH (25 wt %) was added to increase the pH to about 8.0. Finally, the mixture in the flask was cooled and filtered. Thus, the latex was obtained.

Characterization

Fourier transform infrared (FTIR) spectrometric analyzer (Thermo Nicolet AVATAR370, USA) was used to analyze the chemical structures of the latex films. The contact angle between film and water was determined with the DataPhysics contact angle meter (OCA-20, Germany) at room temperature. The particle size of the latices was determined by Zetatract dynamic light scattering detector (Microtrac Limited Corp., USA) 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 surface tension of latex was measured with contact angle-surface tension determinator (DCA-315, Thermo Cahn, USA) at 25°C. TEM photographs of the latex were obtained at 60 kV using a TEM-100SX (JEOL, Japan). The latices were negatively stained with an aqueous solution of 2% uranyl acetate. 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. Conversion rate was determined by the mass difference of a sample taken before and after evaporation of the liquid phase. The sample was dried completely, and the residual polymer was weighed. Conversion rate of the monomer was calculated according to the following equation¹⁶:

$$X\% = \frac{(W_2 - W_0)/(W_1 - W_0) - A}{B} \times 100\%$$

where X is the conversion ratio; W_0 is the weight of the weighing bottle; W_1 is the weight of the latex and bottle; W_2 is the weight of the dried latex and bottle; A is the weight percent of the total nonvolatile ingredients in the recipe. B is the weight percent of the total monomer in the recipe. The differential scanning calorimetry (DSC Q100, TA, USA) was applied to determine the glass transition temperature (T_g) of the film of the latex. The raised

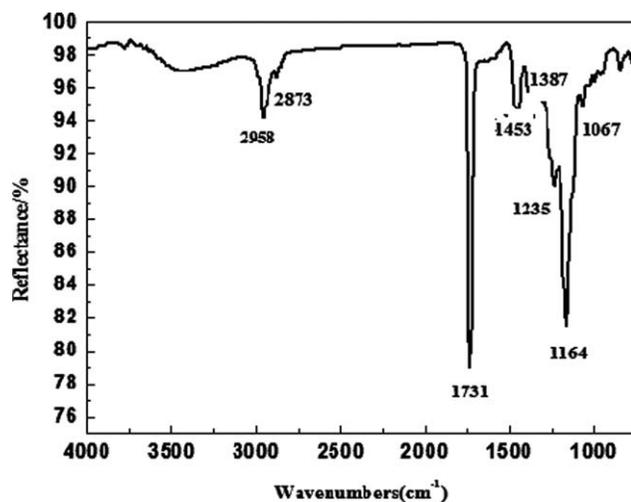


Figure 1 FTIR spectrum of the film of the prepared latex.

temperature was in the range from -40 to 100°C . The velocity of the raised temperature was $10^{\circ}\text{C}/\text{min}$. The film of latex is obtained from coating the latex on the clean glass and drying at room temperature. The purification method of the latex was that the coated film on the clean glass was dried for 2 h at 80°C in the bake oven. In the case, the water and un-reacted monomers were removed completely.

RESULTS AND DISCUSSION

FTIR of the film of the latex

Figure 1 is FTIR spectrum of the latex film. In Figure 1, 2958 cm^{-1} and 2873 cm^{-1} are the characteristic stretching peaks of C–H (CH_3, CH_2), 1731 cm^{-1} is stretching vibration of C=O, 1453 cm^{-1} is distortion vibration of $-\text{COO}-$, 1387 cm^{-1} is the wagging vibration of CH_3 , 1235 cm^{-1} is the stretching vibration of C–F bonds. $1164\text{--}1067\text{ cm}^{-1}$ is the character-

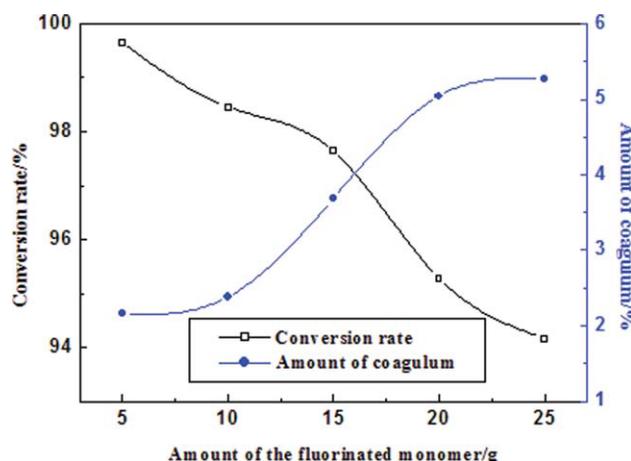


Figure 2 Effect of the amount of the fluorinated monomer on the soap-free emulsion polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

istic absorption peak of SO_3Na . FTIR spectrum of the latex film confirms that four kinds of BA, MMA, POMA, and HMPS all take part in the copolymerization reaction and the latex is prepared.

Amount of coagulum and conversion rate

Effect of the fluorinated monomer content on the amount of coagulum and conversion rate is shown in Figure 2. Figure 2 indicates that the amount of coagulum is increased but the conversion rate is decreased when the fluorinated monomer content is increased. This phenomenon can be explained by the following fact. The adsorptive capacity of the fluorinated acrylate latex to the polymerizable emulsifier becomes weaker because of its lower surface energy although the reaction enthalpy and Q-e value of the fluorinated monomer are similar to those of the acrylate monomer.¹⁷ Thus the stability of the emulsion polymerization is decreased, i.e., the amount of coagulum is increased. In addition, the amphiphilic properties of the formed latex make it difficult to come closer for the fluorinated monomer, thus causing the decrease of the conversion rate. In a word, it is beneficial to the soap-free emulsion polymerization of copolymerized monomer when the fluorinated monomer content is fewer.

Influence of the amount of the initiator

Influences of the amount of the initiator on the conversion rate and the amount of coagulum are shown in Figure 3. In Figure 3, it is found that the conversion rate of monomers is gradually increased with the increase of the amount of initiator. However, the amount of coagulum is decreased firstly, and then is increased with the increase of the amount of initiator. According to kinetic equation of polymerization

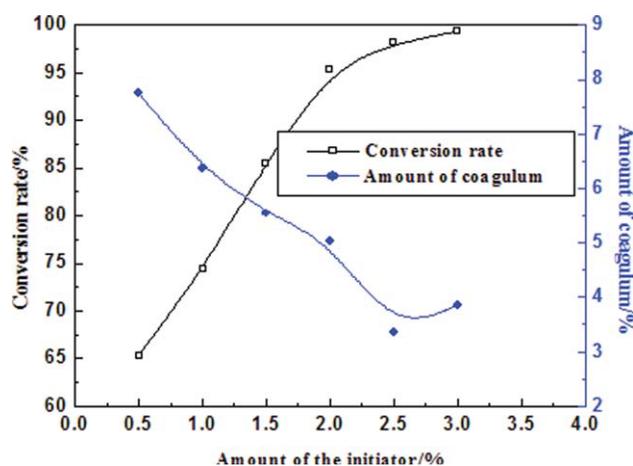


Figure 3 Influence of the amount of the initiator on the conversion rate and amount of coagulum. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

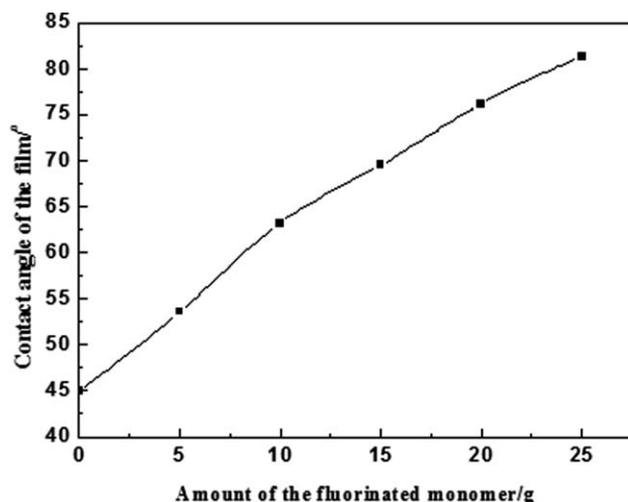


Figure 4 Effect of the amount of the fluorinated monomer on the contact angle of the film.

reaction, when the amount of initiator is small, the probability that the latex particles obtain free radicals is fewer. Therefore, the number of effective latex particles, which takes part in the polymerization reaction, is fewer, and the polymerization rate is fewer. The ultimate conversion rate is lower after the specific reaction time. When the amount of initiator is increased, the probability that the particles of the polymer obtain free radicals is increased. Thus the reaction rate is quickened, and the ultimate conversion rate is raised. In addition, $K_2S_2O_8$ belongs to the electrolyte. Part of $K_2S_2O_8$ will act as the electrolyte if the amount of $K_2S_2O_8$ is excessively large. The concentration of the electrolyte in the system is increased. However, the increase of concentration of K^+ has a negative effect on the stability of the emulsion polymerization. The amount of coagulum is increased. Thus, the stability of the emulsion polymerization is decreased. Therefore, initiator is continuously dripped into the reaction system and the dripping rate is strictly controlled to keep the polymerization rate constant besides that the overall amount of initiator is strictly controlled.

Measurement of contact angle

Contact angle is a typical property to understand the surface energy of materials. The hydrophobic property of a polymeric material can be estimated in terms of contact angle measurement by depositing a water drop on the surface of film and the value of contact angle depends on the chemical compositions of film surface.^{18,19} The higher the wetting resistance of film surface, the higher contact angle is. Because the fluorinated polymers have good hydrophobic property and fluorine atom tends to locate on the film surface during the film formation. It is expected that introducing more fluorinated monomers into a single polymer can increase the hydrophobic property of polymer. The contact angles of the latex with various fluorinated monomer contents are shown in Figure 4. One can see that when the fluorinated monomer is introduced into the polymer chains, the films of latex show higher contact angle compared with the latex without fluorine as expected. In addition, in the case of fixing the content of other monomer, the contact angles of the latex films are increased with the increase of the fluorinated monomer content. The increase of the contact angle is caused by the fact that the fluorinated groups have the tendency to migrate toward interface and preferentially locate at the interface to minimize the interfacial energy. The lower the surface energy is, the larger the contact angle.

Annealing

A physical treatment of annealing at 80°C for 1 h is accepted to modify the arrangement of perfluoroalkyl groups at the polymer-air interface. Contact angles of the polymer films with heating and without heating are shown in Figure 5. From the comparison of contact angle of the polymer film in, it can be seen that contact angle of film of the latex is increased after the heat treatment. That is to say the film becomes more repellent to both the water and the oil after heating. It might be caused that the solvent is polar, and polar segments are supposed to

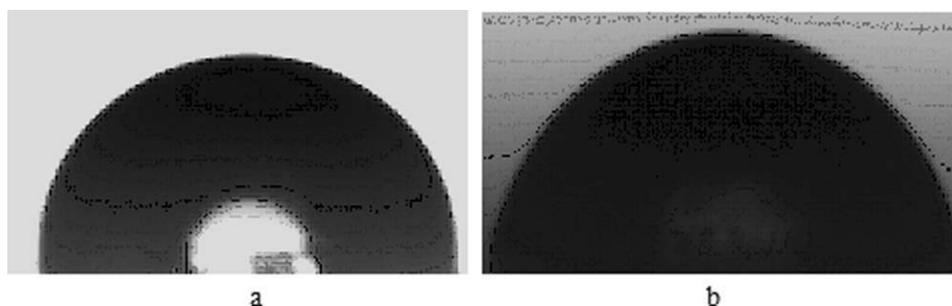


Figure 5 Contact angle of the film of the latex (Picture a is the contact angle of the film with heating, which contact angle is 102.8°; and picture b is the contact angle of the film without heating, which contact angle is 76.2°).

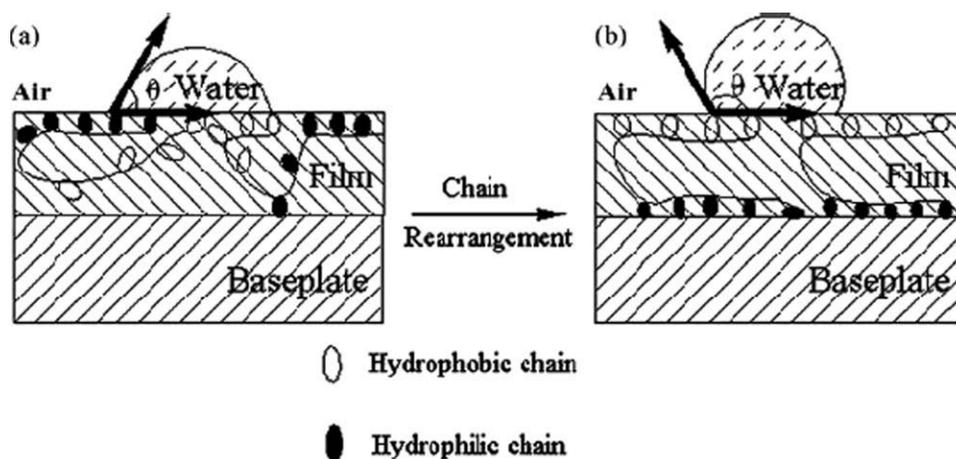


Figure 6 Schematic illustration of the rearrangement of the amphiphilic copolymer before and after the heating treatment and the influence on the contact angle. Picture (a) is the schematic illustration of the distribution of hydrophobic and hydrophilic segments in the film before heating treatment; and picture (b) is the schematic illustration of these segments after heating treatment and the influence on the contact angle.

be dissolved in it more easily.²⁰ When the solvent evaporated, part of hydroxyl groups in the macromolecule of the latex will be brought to the surface of the film. As a result, surface of the film is filled with hydrophilic groups before heating treatment as presented by Figure 6(a), and energy of the film is quite high. However, under high temperature, flexibility of the polymer chains will increase. As it is known that fluorinated groups have relatively low surface energy, and they have strong tendency to spread to the surface. As a result, after 1 h heating treatment, the fluorinated segments move to the interface, and form a hydrophobic surface, as shown in Figure 6(b). In addition, the crosslinking reaction occurs during annealing the latex, allowing some linear macromolecules to link and form networks among molecule chains.

Effect of the amount of the fluorinated monomer on T_g of the latex

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 .²¹ Figure 7 shows that T_g of the latex is increased with the increase in fluorine

content in the monomers. This phenomenon can be explained by the fact the carbon chains of POMA is the same with the ones of 2-hydroxyethyl methacrylate, whose hydrogen on the double bond is not replaced by other groups although the hydrogen on the hydroxyl group in 2-hydroxyethyl methacrylate is replaced by perfluoro nonene group. T_g of the homopolymer of POMA is higher than the one of the homopolymer of BA (soft monomer) because 2-hydroxyethyl methacrylate is the hard monomer. The amount of MMA is constant. For two kinds of copolymerized monomer, e.g., POMA and BA, FOX equation can be turned into

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

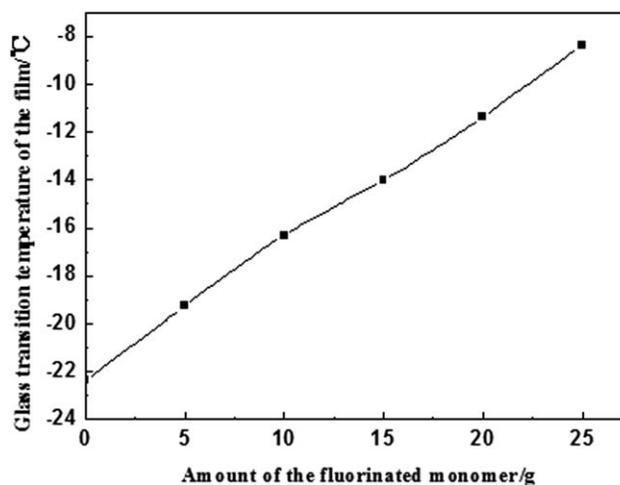


Figure 7 Influence of the amount of fluorinated monomer on the glass transition temperature of the film.

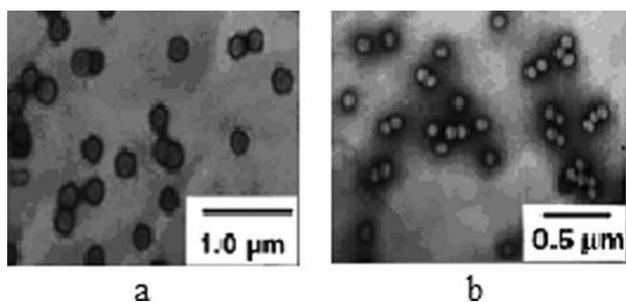


Figure 8 TEM of latices (Picture a is TEM of Sample P4; and picture b is TEM of Sample C4).

where m_1 is the mass fraction of POMA; m_2 is the mass fraction of BA; t_{g1} is T_g of POMA 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 $1/t_{g1}$, and dt_g/dm_1 is positive, i.e., t_g of polymer increases with the increase of the amount of POMA. Besides, in Figure 9, 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.

Comparison with the latex prepared by the conventional emulsifier SDBS

Recipes were presented in Table I. In this paper, P stands for the latex prepared with the polymerizable emulsifier HMPS; C stands for the latex prepared with conventional emulsifier SDBS.

Emulsion polymerization of the mixed monomers

Table II shows the emulsion polymerization of the mixed monomers results by using HMPS and SDBS emulsifier. It can be seen that the conversion ratio by using HMPS emulsifier is higher and has less coagulation than the one using SDBS emulsifier. The particle size is smaller for the emulsions prepared by using SDBS emulsifier. This phenomenon can be explained by the fact that the nucleation mechanism of the latex prepared with HMPS is different from the one of the latex prepared with SDBS during the course of the emulsion polymerization. The nucleation mechanism of the latex prepared with SDBS emulsifiers is the micelle nucleation, i.e., the emulsifier is formed to micelles and the site of the emulsion polymerization-reaction center is formed after the part of the micelles obtains the free radicals which are decomposed from the initiator. However,

HMPS has good hydrophilicity but bad lipophilicity. It is difficult to form the micelles in the aqueous solution. Thus, the nucleation mechanism of the latex prepared with HMPS is homogeneous nucleation, i.e., a small amount of monomers dissolved in the water is copolymerized with HMPS to precipitate the high molecular polymers, which is not dissolved in the water. They collide with the precipitated polymers around to form the reaction center. They collide and grow to form the particle of the latex.^{22,23} The proportion of homogeneous nucleation of the latex is bigger because of the smaller proportion of the micelles nucleation of the latex. Therefore, the number of particles of the latex is fewer and the particle size of the latex is larger.

TEM of latices

TEM photographs of the latices prepared by HMPS and SDBS are shown in Figure 8. It can be seen that the particles prepared by HMPS are larger than the ones prepared by SDBS emulsifier. This is well accord with the dynamic light scattering characterization results. From Figure 8, it also can be found that TEM of sample C4 has a penetrating stain and the other does not. This can be related to the anchoring of HMPS to the particles.

Difference of T_g of the film

The DSC curves of sample P4 and sample C4 are shown in Figure 9. From Figure 9, it can be found that the T_g (P4) prepared by HMPS and the T_g (C4) prepared by SDBS are -11.35°C and -11.47°C ,

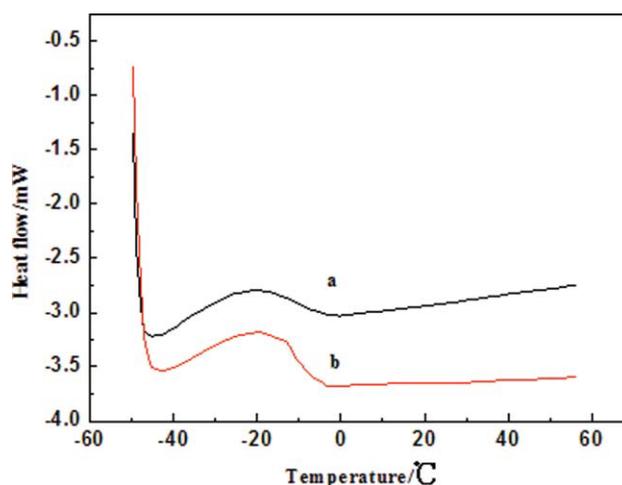


Figure 9 DSC curve of the film of latex (Curve a is the glass transition temperature of sample P4, and the glass transition temperature is -11.35°C ; and curve b is the glass transition temperature of sample C4, and the glass transition temperature is -11.47°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Recipes of Semicontinuous Seeded Emulsion Polymerization by Using Different Emulsifiers

Sample No.	Monomers	Weight of monomers/g	Weight of emulsifier/g	Weight of initiator/g
C1	BA+MAA+POMA	20+10+5	0.5	0.6
C2	BA+MAA+POMA	20+10+5	1.0	0.6
C3	BA+MAA+POMA	20+10+10	1.5	0.8
C4	BA+MAA+POMA	20+10+10	2.0	0.8
C5	BA+MAA+POMA	20+10+15	2.5	0.9
C6	BA+MAA+POMA	20+10+15	3.0	0.9
P1	BA+MAA+POMA	20+10+5	0.5	0.8
P2	BA+MAA+POMA	20+10+5	1.0	0.8
P3	BA+MAA+POMA	20+10+10	1.5	0.9
P4	BA+MAA+POMA	20+10+10	2.0	0.9
P5	BA+MAA+POMA	20+10+15	2.5	1.0
P6	BA+MAA+POMA	20+10+15	3.0	1.0

respectively. Their difference is extremely minute. This indicates that using the HMPS emulsifier in the considered emulsion polymerization has nearly no effect on T_g of the prepared latex because only a small amount of HMPS has been used; this will not largely change the copolymer characteristic temperature.

Surface tension of latices

Usually, the surface tension of HMPS and SDBS at 20°C is 54.0 mN/m and 34.2 mN/m, respectively. Surface tension of the latices is shown in Figure 10. Compared with the surface tension of latices prepared with the SDBS emulsifier, the surface tension of latices prepared by HMPS emulsifier is very high and closes to that of water (72.0 mN/m), indicating a low concentration of HMPS in the aqueous phase. The reason for this low concentration may be the chemical anchoring of HMPS to the particles. In contrast, the surface tension of all latices prepared by SDBS emulsifier is close to that of SDBS emulsifier

itself surface tension. This indicates an extremely high concentration of SDBS emulsifier in the aqueous phase due to the SDBS emulsifier anchors onto the particle surface. Surface tension value can be used to judge whether the emulsifier has joined to polymerization with monomer or not. According to Uaulina et al.²⁴ and Abele et al.²⁵ work, if the surface tension of the prepared emulsion is close to water (72.0 mN/m), the polymerizable emulsifier has completely joined to polymerization with the monomer; otherwise, the emulsifier is only anchoring on the surface of the emulsion particles. Because the surface tensions of the latex prepared with HMPS emulsifier are 61.5–65.2 mN/m, which is not far from the surface tension of water, it can be said that large part of HMPS emulsifier is joined polymerization with monomer, only small part anchored on the surface of the latex particles. Whereas the surface tension of the latices using SDBS is much lower than that of water, it can be said that SDBS emulsifier is completely anchored on the surface of the latex particles.

TABLE II
Results of Semicontinuous Seeded Emulsion Polymerization by Using Different Emulsifiers

Sample No.	Conversion/%	Particle size/nm	Coagulation/%	Solid content/%
C1	78.25	95.4	8.26	18.27
C2	82.53	89.6	5.35	18.85
C3	92.56	85.3	6.52	21.53
C4	95.28	82.2	5.04	22.87
C5	97.15	81.5	4.86	23.15
C6	98.58	78.6	4.63	23.68
P1	82.21	142.7	4.05	20.03
P2	85.75	195.3	4.37	21.16
P3	95.46	220.6	3.42	23.21
P4	97.61	235.7	3.24	23.78
P5	98.83	262.3	2.57	24.13
P6	99.70	270.8	1.68	24.35

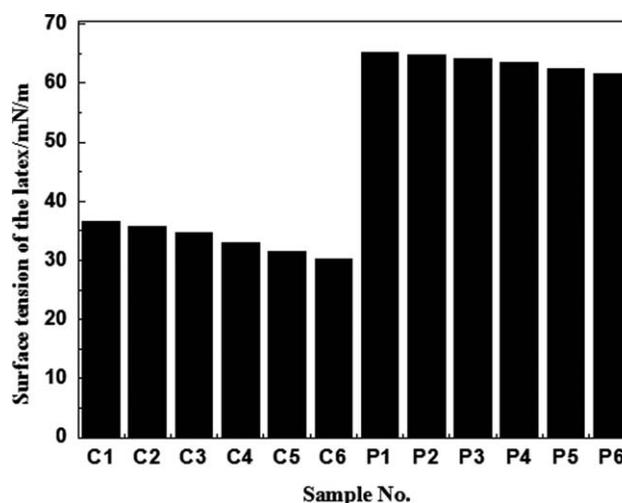


Figure 10 Surface tension of the prepared latices.

CONCLUSIONS

BA-MMA-POMA copolymer latices have been prepared successfully prepared by soap-free emulsion polymerization of 2-(perfluoro-(1,1-bis(isopropyl)-2-propenyl)oxyethyl methacrylate (POMA) with butyl acrylate (BA), methyl methacrylate (MMA) initiated by $K_2S_2O_8$ in the water, which can be confirmed with FTIR. The hydrophobicity and T_g of the latex are increased when the fluorinated monomer is introduced to copolymerize with other monomers. The hydrophobicity can be improved further with heating. Compared with the latices prepared by using SDBS emulsifier, the latices prepared by using HMPS emulsifier have larger particle size, higher surface tension. However, the difference of their T_g is extremely minute.

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