Miniemulsion Polymerization of a Fluorinated Acrylate Copolymer: Kinetic Studies and Nanolatex Morphology Characterization

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ABSTRACT: A stable fluoroacrylate copolymer emulsion was successfully prepared by miniemulsion polymerization with fluoroacrylate, lauryl methylacrylate, and methyl methacrylate as monomers. Extremely hydrophobic fluoroacrylate, instead of conventional cosurfactants, was used as a reactive cosurfactant to stabilize the miniemulsions. The results indicated that fluoroacrylate retarded Ostwald ripening and allowed the production of stable miniemulsions. The chemical compositions of the copolymer were studied with Fourier transform infrared and ^{1}H-NMR. The average composition of the copolymers prepared with miniemulsions was in good agreement with the feed ratio according to ^{1}H-NMR from the integration ratios corresponding to typical protons of the individual monomers. The particle size distribution and morphology of the latex particles were determined with laser particle analysis and transmission electron microscopy. The particle size of the latex underwent no change in the process of miniemulsion polymerization, but the particle size distributions were broader than those of conventional emulsion polymerization. The effects of various reaction parameters, including the temperature and concentrations of the emulsifier and initiator, on the miniemulsion polymerization were also investigated, and the polymerization rate and conversion increased with increasing concentrations of nonylphenol polyethoxylate (with an average of 40 ethylene oxide units per molecule), cetyltrimethylammonium, and 2,2′-azobisisobutyronitrile. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 641–647, 2007

Key words: emulsion polymerization; fluoropolymers; kinetics (polym.); microstructure; surfactants

INTRODUCTION

Low-surface-energy coatings play essential roles in microelectronics, antifogging and antifouling applications, and even medical applications.[1,2] Perfluoroalkyl-substituted acrylate copolymers have emerged as the most widely used low-surface-energy polymer coatings of substrates such as textiles, paper, leather, and wood because their presence can introduce a number of unique physical and chemical surface properties.[3,4] In addition, polymers with fluorinated functional groups at the surface can be envisioned to convey other properties such as resistance to corrosive chemicals and organic solvents, flame resistance, water and oil repellency, and low coefficients of friction.[5,6] Fluorine-containing copolymers can be easily prepared by the radical copolymerization of fluoroacrylate (FA) with common vinyl monomers in solutions or in aqueous emulsions.[7–13] Making a fluorinated dispersion by classical emulsion polymerization is difficult because this technique relies on monomer transport from the droplets to the growing particles, and the solubility of fluorinated monomers in water is very low.[9,14–16] Therefore, FA-containing copolymer latexes are usually synthesized by the addition of a large amounts of an organic solvent to the continuous phase.[9,10,15]

Because of its unique features, miniemulsion polymerization is a good method for preparing fluorinated acrylate copolymers. In the miniemulsion polymerization, both the particle nucleation and subsequent propagation reaction occur primarily in submicrometer monomer droplets of 50–500 nm.[17–20] This polymerization technique involves droplets in water at the reaction temperature with the aid of a surfactant/cosurfactant, followed by the addition of the initiator. Furthermore, the kinetics of miniemulsion polymerization are very different from those of conventional emulsion polymerization.[21–23] In this system, each miniemulsion droplet can be perceived as a separate nanoreactor that does not interact with the others. Each is independent of the amount of the initiator as well as the particle size. Polymerization in a miniemulsion does not rely on monomer transport through the water phase, but droplet nucleation of the small droplets is the predominant initiation mechanism. This enables the polymerization of the miniemulsions, and the problem of the

polymerization of extremely hydrophobic FA is reduced to the question of the preparation of stable miniemulsions, whereas solubility questions are avoided. There are only a few researchers[10–14] who have reported work on the miniemulsion polymerization of FA with hexadecane as a cosurfactant or dimethyl phthalate as a cosolvent. The properties of fluorocopolymers are affected by the presence of this low-molecular-weight, organic substance.

In this work, we focused on the kinetic study of miniemulsion copolymerization and the morphology characterization of the obtained copolymer emulsions. Extremely hydrophobic FA was used as a reactive cosurfactant during the subsequent miniemulsion polymerization. The particle morphology and the change in the particle size during miniemulsion polymerization were investigated in detail, and the effects of operation variables such as the reaction temperature, concentrations of the initiator, emulsifier, and cosurfactant, and monomer ratios were studied.

EXPERIMENTAL

Materials

The FA monomers [$CH_2=CH-COOCH_2CH_2C_nF_{2n+1}$ ($n = 6$, 8, or 10; average $n = 8.2$)], purchased from DuPont (Wilmington, DE), were used as received. The monomers lauryl methylacrylate (LMA) and methyl methacrylate (MMA) were freshly distilled under reduced pressure and stored at $-5°C$. The initiator 2,2′-azobisisobutyronitrile (AIBN) was recrystallized in ethanol. The surfactants, nonylphenol polyethoxylate with an average of 40 ethylene oxide units per molecule (NP-40) and cetyltrimethylammonium (CTAB), were used as received.

Miniemulsion copolymerization

The miniemulsion was prepared by the dissolution of NP-40 and CTAB in deionized water and stirred at 300 rpm for 10 min. A monomer mixture containing AIBN and an aqueous solution were mixed with a mechanical agitator at 500 rpm for 30 min. The resultant emulsion was then homogenized by ultrasonication for 120 s at a 60% amplitude at 0°C to prevent polymerization. The miniemulsion polymerization was charged into a 100-mL glass reactor equipped with a mechanical stirrer, a thermometer, and a reflux condenser and then purged with nitrogen for 10 min. Although the reactor temperature was raised to 70°C, the latex was synthesized after polymerization for 6 h at this temperature (70°C). A typical miniemulsion charge comprised 40 g of water, 0.12 g of CTAB, 0.08 g of NP-40, 4 g of FA, 3 g of MMA, 3 g of LMA, and 0.08 g of AIBN. In that case, the solid content was close to the expected 20.4%.

Conventional emulsion polymerization

Batch conventional emulsion polymerization was performed by batch emulsion polymerization in a 100-mL glass reactor with AIBN as an initiator and CTAB and NP-40 as complex surfactants. Typically, the reactor was charged with an emulsified mixture containing 10 g of the monomers (4 g of FA, 3 g of MMA, 3 g of LMA), 40 g of deionized water, and 0.20 g of emulsifiers (CTAB/NP-40 = 3 : 2) purged with nitrogen gas and then heated to 70°C. At that point, the initiator AIBN (0.08 g), dissolved in a small amount of ethanol (3 mL), was added. The polymerization was allowed to proceed for 6 h.

Analysis and characterization

The conversion of the monomers during the progress of the polymerization was determined gravimetrically.

The data for the average monomer droplet and latex particle size during polymerization were obtained by the dynamic light scattering method with a Malvern Sizer 2000 (Malvern, Worcestershire, UK).

Electron microscopy was performed with a JEM 1200EX transmission electron microscope (JEOL, Tokyo, Japan) operating at 100 kV. The latex particles were diluted to 0.3‰, applied to a 400-mesh, carbon-coated copper grid, and left to dry at room temperature.

Dried samples of the latexes were obtained from precipitation in ethanol. The filtered latexes were washed several times with water and ethanol to remove emulsifiers and then dried in a vacuum oven at an elevated temperature. ^{1}H-NMR analysis was conducted with a Bruker 500-MHz Avance DMX500 NMR spectrometer (Bruker, Faellanden, Switzerland) and was carried out with a 5 wt % solution in $CDCl_3$ at room temperature. The compositions of the copolymers were calculated from the characteristic proton integrals. IR spectra of the FA copolymers were recorded on a Nicolet 5700 Fourier transform infrared (FTIR) instrument (Thermo Electro, Madison, WI). The polymer films were cast onto KBr disks from tetrahydrofuran solutions.

RESULTS AND DISCUSSION

Synthesis and characterization of the copolymer latexes

It is difficult to prepare fluorine-containing colloidal dispersions with high FA contents by conventional emulsion polymerization because the solubility of fluorinated monomers in water is very low.[13,14] To overcome this difficulty, we adopted a miniemulsion polymerization to synthesize fluorocarbon copolymers with reactive FA as a cosurfactant. In miniemulsion polymerization, the initiation and propagation reactions of monomers take place in monomer droplets, and there-
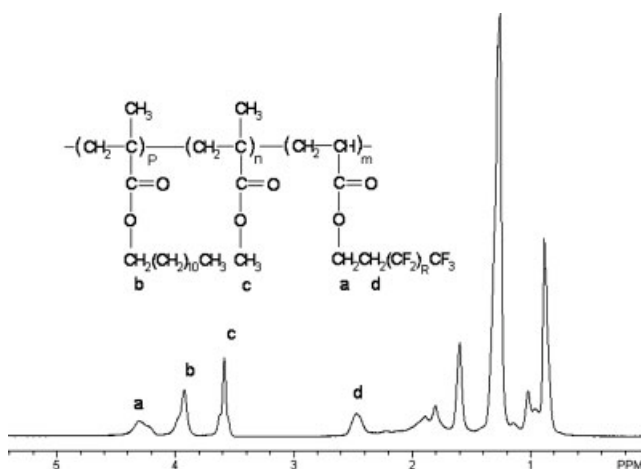
Figure 1 ^{1}H-NMR spectrum of the FA–LMA–MMA copolymer.

fore the mass transport of monomers through the aqueous phase can be avoided. In comparison with conventional emulsion polymerization, both the stability and conversion of FAs in miniemulsion copolymerization are greatly improved.

Composition analysis of the copolymers

The chemical structure of the FA–LMA–MMA copolymer was identified by ^{1}H-NMR (Fig. 1). The peaks at 2.5 and 4.3 ppm represent the CH_2 group of FA in the side chain, and the peak at 3.7 ppm is indicative of the $OOCH_3$ group of MMA. The peak at 3.9 ppm represents another typical band of the CH_2 group in $OOCH_2$ protons of LMA. Figure 2 shows the FTIR spectra of the MMA–FA copolymer and FA–MMA–LMA copolymer. In these two spectra, the peaks at 2850 and 2920 cm^{-1} are attributable to the characteristic bands of the long CH_2 in the LMA side chain. The region of interest lies at 1200 cm^{-1} in the FTIR spectrum [Fig. 2(B)], which is dominated by bands associated with motions of the CF_2 group at 1260 and 1160 cm^{-1}.
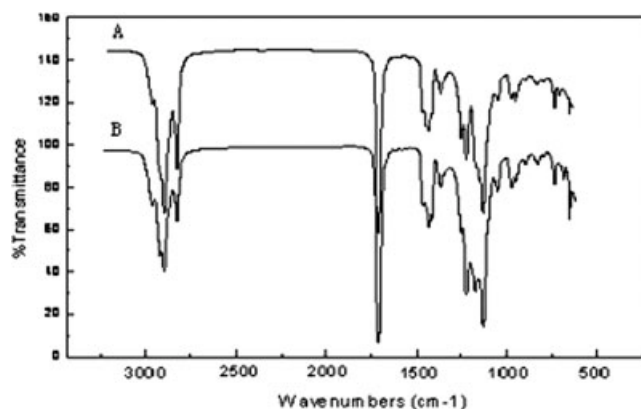

Figure 2 FTIR spectra of (A) the LMA–MMA copolymer and (B) the FA–LMA–MMA copolymer.

Two medium bands at 660 and 710 cm^{-1} stem from a combination of rocks and wagging vibrations of CF_2CF_3 groups. In addition, the peaks at 1450, 1385, and 960 cm^{-1} are the three characteristic bands of C—H in —OCH$_3$ of MMA, and the peaks at 1240 cm^{-1} result from O—C of MMA and LMA. Thus, the composition analysis based on FTIR and ^{1}H-NMR spectra confirms the formation of fluorinated copolymers in miniemulsion polymerization.

The molar compositions of poly(methyl methacrylate)/poly(lauryl methylacrylate)/polyfluoroacrylate copolymers prepared by miniemulsion polymerization and conventional emulsion polymerization are compared in Table I. The copolymer compositions were calculated by the ^{1}H-NMR analysis of OOCH$_2$ protons in LMA, OOCH$_3$ protons in MMA, and OOCH$_2$ protons in FA. The FA/LMA/MMA compositions of the copolymers prepared by miniemulsion polymerization are in good agreement with the feed ratios (Table I). However, for the conventional emulsion polymerization system, even for a very low feed ratio of the FA monomer, there is a significant difference between the calculated data and the corresponding theoretical values. In emulsion polymerization, the mass transport of FA from the monomer droplets into micelles or growing latex particles is seriously limited by the low solubility of FA in water. Only a small amount of FA is transported into growing particles and forms stable copolymer particles. Most of the fluorine-containing acrylate is lost during the emulsion polymerization because of severe coagulation.

Size and morphology of the latex particles

Figure 3 shows the average particle size as a function of the reaction time. The value of the average particle size remains almost constant, and therefore the resultant polymer particles are found in the manner of a one-to-one copy of the monomer droplets, which is a major feature of miniemulsion polymerization.[20] As shown in Figure 3, with 1.2 wt % emulsifier (weight percentage of the emulsifier with respect to the monomer mixture), stable latexes with a particle diameter of about 152 nm can be obtained. The size of the final particles can be reduced to 114 nm by the amount of

TABLE I
Identification of the Chemical Structures
of the FA–LMA–MMA Copolymers

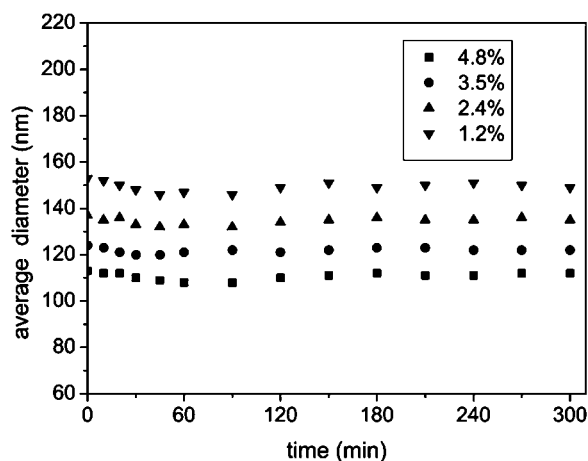| FA/LMA/MMA feed ratio (wt %)	FA/LMA/MMA ratio in the copolymer latex	
	Miniemulsion	Emulsion
8 : 46 : 46	7.2 : 42.7 : 50.1	5.2 : 45.3 : 49.5
25 : 37.5 : 37.5	23.3 : 36.4 : 40.3	8.3 : 43.6 : 48.1
40 : 30 : 30	37.3 : 29.2 : 33.5	12.2 : 42.6 : 45.2
60 : 20 : 20	56.8 : 19.4 : 23.8	16.8 : 40.3 : 42.9

Figure 3 Average particle size as a function of the reaction time. The emulsifier concentrations were 1.2, 2.4, 3.5, and 4.8%.

the surfactant being increased from about 1.2 to 4.8%. The surface area of the droplets increases with a decrease in the average particle size, and more emulsifier is needed to cover the surface of the droplets. In fact, the value of the average droplet size obtained from the dynamic light scattering method (volume mean size) is bigger than the value from transmission electron microscopy (TEM; surface mean size). Monomer droplet nucleation and propagation and polymerization in monomer droplets are dominant mechanisms in miniemulsion polymerization.[17] Thus, in contrast to emulsion polymerization, more stable droplets are required in miniemulsion polymerization to prevent coalescence and other instable events. Here, we introduced the reactive FA monomer as the cosurfactant to improve the stability of the monomer droplets in miniemulsion polymerization. From Figure 3, we can conclude that the introduction of reactive monomer FA is able to enhance the stability of miniemulsion systems containing fluorinated acrylates.

Figure 4 shows typical TEM images of latex particles obtained by miniemulsion and conventional emulsion polymerizations. The prepared miniemulsion particles consisting of acrylate and FA show a broad size distribution and are heterogeneous in morphology; this is supported by TEM of the final polymer dispersions. As can be seen in Figure 4, the size distribution of the miniemulsion is much broader than that of the emulsion. Because nucleation takes place in monomer droplets and the free-radical capture efficiency of the droplets is lower than that of
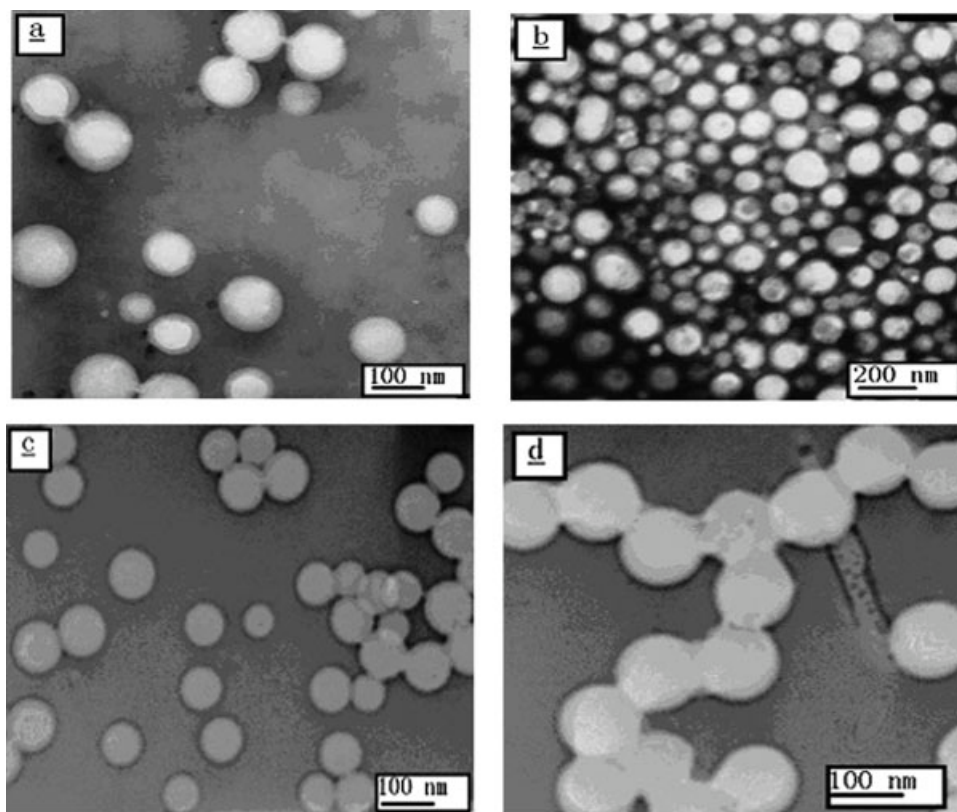

Figure 4 TEM photographs of copolymer latexes by miniemulsion polymerization with FA/LMA/MMA ratios of (a) 2.5 : 3.75 : 3.75 and (b) 4 : 2 : 2 (emulsifier concentration = 2.4%; temperature = 70°C) and TEM photographs of copolymer latexes by conventional emulsion polymerization with emulsifier concentrations of (c) 2.4 and (d) 3.5% (FA/LMA/MMA = 2.5 : 3.75 : 3.75).
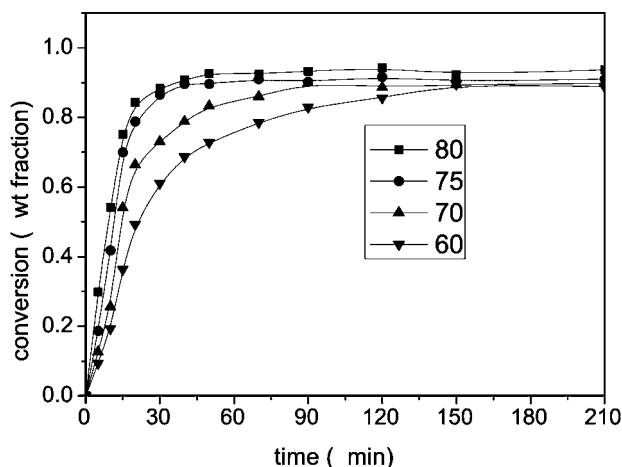
Figure 5 Monomer conversion as a function of the reaction time (FA/LMA/MMA = 4 : 3 : 3; temperature = 80, 75, 70, or 60°C).

micelles or even polymer particles, the nucleation period in miniemulsion polymerization is longer than that in emulsion polymerization. However, in conventional emulsion polymerization, most of the particles are transformed from micelles containing monomers in the same period of time. In addition, these particles have similar growth periods that lead to rather homogeneous particle sizes. Because of the severe coagulation in the emulsion polymerization of acrylate and FAs, the samples used for TEM characterization (Fig. 4) need to be filtered to form homogeneous emulsions before observation. Figure 4 shows that the particles of the miniemulsion consisting of acrylate and FA have a variety of internal structures, such as a core–shell morphology or multiblob structures, and the reaction parameters greatly influence the morphology of the resulting copolymer miniemulsion. These results stem from the difference in the performance between FAs and acrylates, especially their poor thermodynamic consistency.

Effects of the kinetic parameters on the polymerization

The effects of the temperature on the monomer conversion in miniemulsion polymerization are shown Figure 5. It suggests that the reaction will reach a final rate of conversion after polymerization in 30 min at a temperature above 75°C. In miniemulsion polymerization, almost all monomer droplets are initiated to propagate at the same time, and every droplet is just like a individually independent nanoreactor. Therefore, the rate of polymerization is faster than that of conventional emulsion polymerization. If the reaction temperature is higher, the polymerization stability of a miniemulsion may be damaged by the heat of the reaction, which is not eliminated in time. By varying

the temperature and maintaining other kinetic parameters, we can obtain the monomer conversion curve as a function of the reaction time at various temperatures (Fig. 5). The final rate of conversion is reached at the polymerization time of 120 min in the temperature range of 60–80°C. With an increase in the reaction temperature, the rate of polymerization is accelerated, and the final conversion is increased as well. As can be seen in Figure 5, the effect of the temperature on miniemulsion polymerization is slight. This is because the mass transport of monomers through the water phase is largely limited in miniemulsion polymerization. Droplet nucleation of the minidroplets is the predominant initiation mechanism, so the effect of the monomer diffusion and transport phenomenon on polymerization in a miniemulsion system is minimized.

The kinetics of copolymerization as a function of the AIBN concentration in the miniemulsion system are illustrated in Figure 6. The conversion percentage increases with an increase in the initiator concentration in these systems. Moreover, similar kinetic curves of copolymerization can be observed. These can be explained by the generation of more free radicals per reaction locus per second. If the amount of the initiator is much lower (0.6%), the final conversion of the monomer is not very high, and a long induction period can be observed. Figure 6 also indicates that the maximum conversion (70–95%) is obtained within 2–3 h. There are two ways for monomers in small droplets to capture free radicals: the decomposition of the initiator dissolved in the monomer droplets and the adsorption of free radicals in the disperse phase. The initiation efficiency depends on the exit rate of the two newly born free radicals with respect to their termination rate. In a particle or droplet, once two free radicals
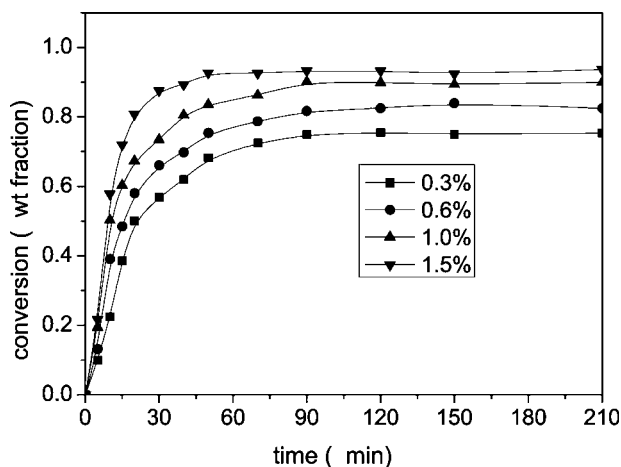

Figure 6 Monomer conversion as a function of the reaction time (FA/LMA/MMA = 4 : 3 : 3; temperature = 70°C; [AIBN] = 0.3, 0.6, 1.0, or 1.5%).
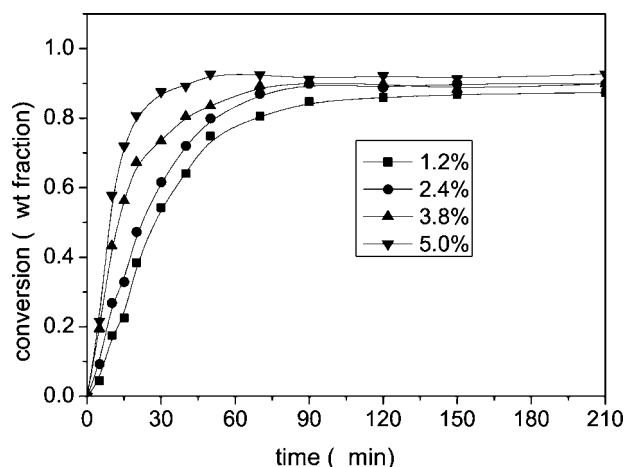
Figure 7 Monomer conversion as a function of the reaction time (FA/LMA/MMA = 4 : 3 : 3; temperature = 70°C; emulsifier concentration = 1.2, 2.4, 3.8, or 5.0%).

are generated, they will immediately terminate with each other. One of them will exit and leave the other to propagate. The possibility of biradical termination in miniemulsion polymerization is much higher than that in conventional emulsion systems. As a result, the initial efficiency of oil-soluble AIBN in a miniemulsion is relatively low. Furthermore, the conversion percentage and rate of polymerization increase with an increase in the initiator concentration.

It is known that, to improve the stabilization of an emulsion containing fluorinated monomers, fluorocarbon emulsifiers should be used.[13] However, the relatively high market prices and environmental concerns of fluorinated emulsifiers limit their use. In the case of excellent surfactant packing, long-chain hydrophobic surfactants can also be employed. In this study, the utilization of a composite emulsifier system containing a quaternary ammonium salt and nonylphenol polyethoxylate also provides suitable stability for the preparation and polymerization of miniemulsions containing FA.

Figure 7 demonstrates the effects of the surfactant concentration on the miniemulsion polymerization of FA, MMA, and LMA at 70°C. If the concentration of the surfactants is increased, both the polymerization rate and conversion rate increase. This type of behavior is due to the fact that the stability and particle size of the emulsion are greatly affected by the amount of the emulsifier mixture. The sizes of the monomer droplets decrease with an increase in the surfactant concentration. Smaller droplets with higher surface coverage also have a higher equilibrium concentration of free surfactants. In miniemulsion polymerization, the concentration of the surfactants usually stays well below the critical micelle concentration. In other words, there are no free micelles present in miniemulsions. The concentration of the emulsifier does

not greatly influence the rate per particle but does affect the overall rate of polymerization. When the surfactant concentration is increased from below the critical micelle concentration to above, the overall rate slightly increases. However, the residual concentration of the surfactant in the water phase increases at a higher level and presumably leads to another mechanism of micelle nucleation.

CONCLUSIONS

Stable FA copolymer emulsions in the size range of 110–150 nm were obtained by miniemulsion polymerization. FA with a long fluorocarbon chain could be used as a reactive costabilizer and was capable of creating a stable miniemulsion. High conversions of FA and high reaction rates were obtained in miniemulsion polymerization because miniemulsion polymerization does not rely on hydrophobic monomer transport through the water phase, and the effect of monomer diffusion in the dispersion system on kinetics was minimized. In addition, the particle sizes of the latexes were almost constant in the process of polymerization, but the distribution of the particle size was broad. The particles consisting of acrylate and FA showed microphase-separation structures, such as core–shell morphology structures. The calculated copolymer compositions were in good agreement with the feed ratio in each case of samples synthesized by miniemulsion polymerization. However, the fluorine content of the copolymer in the experiments was lower than the theoretical value in conventional emulsion polymerization.

References

 1. Iyengar, D. R.; Perutz, S. M.; Dai, C. A.; Ober, C. K.; Kramer, E. J. Macromolecules 1996, 29, 1229.
 2. Yi, L.; Zhan, X.; Chen, F.; Huang, L.; Du, F. J Polym Sci Part A: Polym Chem 2005, 43, 4431.
 3. Park, I. J.; Lee, S. B.; Choi, C. K. Macromolecules 1998, 31, 7555.
 4. Chen, Y.; Cheng, S.; Wang, Y.; Zhang, C. J Appl Polym Sci 2005, 99, 107.
 5. Li, K.; Wu, P. P.; Han, Z. W. Polymer 2002, 43, 4079.
 6. Marita, M.; Ogisu, H.; Kubo, M. J Appl Polym Sci 1999, 73, 1741.
 7. Park, I. J.; Lee, S. B.; Choi, C. K.; Kim, K. J. J Colloid Interface Sci 1996, 181, 284.
 8. Thomas, R. R.; Anton, D. R.; Graham, W. F.; Darmon, M. J.; Sauer, B. B.; Stika, K. M.; Swartzfager, D. G. Macromolecules 1997, 30, 2883.
 9. Linemann, R. F.; Malner, T. E.; Brandsch, R.; Bar, G.; Ritter, W.; Mulhaupt, R. Macromolecules 1999, 32, 1715.
10. Huang, P. Y.; Chao, Y. C.; Liao, Y. T. J Appl Polym Sci 2004, 94, 1466.
11. Chen, Y.; Cheng, S.; Wang, Y.; Zhang, C. J Appl Polym Sci 2006, 99, 107.
12. Ha, J. W.; Park, I. J.; Lee, S. B. Macromolecules 2005, 38, 736.

13. Dreher, W. R.; Jarrett, W. L.; Urban, M. W. Macromolecules 2005, 38, 2205.
14. Landfester, K.; Rothe, R.; Antonietti, M. Macromolecules 2002, 35, 1658.
15. Ha, J. W.; Park, I. J.; Lee, S. B.; Kim, D. K. Macromolecules 2002, 35, 6811.
16. Huang, P. Y.; Chao, Y. C.; Liao, Y. T. J Appl Polym Sci 2004, 94, 1466.
17. Ugelstad, J.; El-Aasser, M. S.; Vanderhoff, J. W. Polym Lett 1973, 11, 503.
18. Mouran, D.; Reimers, J.; Schork, F. J. J Polym Sci Part A: Polym Chem 1996, 34, 1073.
19. Wu, X. Q.; Schork, F. J. J Appl Polym Sci 2001, 81, 1691.
20. Schork, F. J.; Luo, Y.; Smulders, W.; Russum, J. P.; Butte, A.; Fontenot, K. Adv Polym Sci 2005, 175, 129.
21. Chern, C. S.; Liou, Y. C. Polymer 1999, 40, 3763.
22. Kim, N.; Sudo, E. D.; Dimonie, V. L.; El-Aasser, M. S. Macromolecules 2004, 37, 2427.
23. Bechthold, N.; Landfester, K. Macromolecules 2000, 33, 4682.