Preparation and Characterization of Core−Shell Particles Containing Perfluoroalkyl Acrylate in the Shell

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ABSTRACT: We describe the preparation and characterization of core−shell latex particles, consisting of a polystyrene core, covered with a perfluoroalkyl acrylate shell. The core−shell particles were prepared by a two-stage emulsion polymerization under kinetically controlled conditions and were characterized by transmission electron microscopy, differential scanning calorimetry, and X-ray diffraction analysis. The surface properties of the latex films produced from the core−shell particles were investigated by the contact angle method. Compared with random copolymers or latex blends of styrene and perfluoroalkyl acrylate, the core−shell particles were the most effective to reduce the surface energy of the latex films. The effect of acetone as a cosolvent on the polymerization process was also considered.

Introduction

Core−shell particles are structured composite particles consisting of at least two different polymers: one in principle forms the core and the other the shell of the particles. These particles are useful in a broad range of applications since they often exhibit improved physical and chemical properties over their single-component counterparts. The core−shell particles have been used to produce materials possessing two kinds of properties: one being endowed by the core and the other by the shell. For example, the core−shell particles differing in their glass transition temperatures can be used to modify the mechanical properties of thermoplastic[1,2] or to manufacture polymeric nanocomposite materials with a periodic structure.[3−5] The properties of the core−shell particles largely depend on the morphological feature of the particles, which is governed by various polymerization parameters and conditions.[6] These particles are usually synthesized by a two-stage emulsion polymerization. At the first stage, the core latex particles are obtained. For the second stage polymerization, two different addition modes of monomers producing the shell have been considered. One is the continuous addition process (dropwise method),[7−10] and the other is batch process (swelling method).[11,12]

The unique property of the core−shell particles prepared in this study is that they have very low surface energy resulted from the perfluoroalkyl group ($-(CF_2)_n$-CF_3) contained in the shell, which is a prerequisite for excellent water and oil repellency. It has been known that perfluoroalkyl acrylate (or methacrylate) homopolymers with long side chains have extremely low surface energy, ranging from 10 to 11 mN/m.[13] These values of surface energy are much lower than that of poly(tetrafluoroethylene) (PTFE, 18 mN/m), which is a typical fluoropolymer.[14] The extraordinary surface properties of perfluorinated polymers are believed to arise from the segregation of CF_3 groups to the surface.[15−19] Nowadays, although varieties of polymers are available in the market, the fluorinated compounds remain the most common active ingredients for water and oil repellent purposes. Furthermore, low surface energy coatings play an essential role in microelectronics, antifogging, and antifouling applications and even have promising medical applications.[20] As far as water and oil repellency is concerned, the efficiency increases as the weight fraction of the fluorinated components in the polymer increases. However, the relatively high market prices of the fluorinated monomers limit their use, unless the amount of fluorinated compounds can be minimized while maintaining reasonable water and oil repellency. One possible strategy to resolve this dilemma is to design the particles consisting of a nonfluorinated core and a fluorinated shell. By doing so, it is anticipated that excellent water and oil repellency can be preserved while the amount of fluorinated compounds required in the polymer is reduced considerably.

In this study, the core−shell particles were prepared by a two-stage emulsion polymerization. The polystyrene (PS) core was polymerized by conventional batch emulsion polymerization (first stage), and the fluorinated shell was introduced to the particle by semicontinuous addition of monomers (second stage) in the same reactor under kinetically controlled conditions. It has been proven that this method is useful to obtain narrowly distributed latexes with well-defined particle morphology.[21,22] In the present study, heptadecafluorodecyl acrylate (FA) of the form $CH_2{=}CHCOO(CH_2)_2$-$(CF_2)_7CF_3$ was used as a fluorinated monomer. In general, the longer perfluoroalkyl side chain exhibits the lower surface energy due to the different crystalline state depending on the side chain length. Approximately, seven CF_2 units provide the optimal length for the perfluoroalkyl units for room temperature application because a terminal perfluoroalkyl chain is sufficiently long to shield the nonfluorinated segment beneath the fluorinated segment.[23] On the other hand, CH_2 spacer groups do not have a large effect on the surface energy, but the longer CH_2 spacer groups render the side chain packing more stable and the polymer becomes more soluble.[24]

Core−shell particles were characterized by various methods such as transmission electron microscopy, differential scanning calorimetry, and X-ray diffraction

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Table 1. Polystyrene and Poly(perfluoroalkyl acrylate) Homopolymer and Randomly Copolymerized Poly(styrene-*co*-perfluoroalkyl acrylate) Latex Parameters and Starting Components

latex	water (g)	FA (g)	styrene (g)	TTAB (g)	DT (g)	V50 (g)	particle size[a] (nm)	final conv[b] (%)
Homopolymers								
PS	40		6	0.15	0.1	0.05	71	97.1
PFA	50	7.5		0.25		0.05	142	98.3
Random Copolymers								
SFA05	40	0.3	5.7	0.15	0.08	0.05	81	98.0
SFA10	40	0.6	5.4	0.15	0.08	0.05	79	97.2
SFA20	40	1.2	5.4	0.15	0.08	0.05	89	97.6
SFA30	40	1.8	4.2	0.15	0.08	0.05	105	99.1
SFA40	40	2.4	3.6	0.15	0.08	0.05	105	95.8

[a] Measured by light scattering method. [b] Measured gravimetrically.

Table 2. Recipe, Polymerization Conditions, and Principal Characteristics of the Polystyrene−Poly(perfluoroalkyl acrylate) Core−Shell Latex Particles

	AC-F10	AC-F20	AC-F30	AC-F40	AC-F50	F30	F50
First Stage (Batch)							
water (g)	45	30	30	30	30	30	20
styrene (g)	6.75	4.5	4.5	4.5	4.5	4.5	3
TTAB (g)[a]	0.22	0.15	0.15	0.15	0.15	0.15	0.1
1-dodecanethiol (g)[b]	0.113	0.075	0.075	0.075	0.075	0.075	0.05
V50 (g)[c]	0.075	0.05	0.05	0.05	0.05	0.05	0.03
polymerization time (min)	30	30	30	30	30	30	30
conversion of styrene (%)[d]	82	89	88	83	90	85	84
core particle size (nm)[e]	68.2	64.5	69.8	65.3	66.9	68.8	64.1
Second Stage (Semicontinuous)							
water (g)	5	7.3	12.7	20	30	14.6	23
FA (g)[f]	0.75	1.1	1.9	3	4.5	1.9	3
TTAB (g)[g]	0.05	0.07	0.13	0.2	0.3	0.13	0.2
acetone (g)	0.75	1.1	1.9	3	4.5		
feeding time (min)	75	105	190	305	440	190	300
final conversion of FA (%)[h]	98.2	99.1	98.4	97.3	97.0	97.6	98.0
core−shell particle size (nm)							
measured[i]	72.0	71.3	81.6	83.4	90.5	80.6	85.5
calculated[j]	71.7	72.5	83.0	82.4	91.6	81.8	87.5
styrene:FA ratio (wt:wt)	9:1	8:2	7:3	6:4	5:5	7:3	5:5

[a] Tetradecyltrimethylammonium bromide (TTAB). 3.3 wt % based on monomer. [b] 1.7 wt % based on monomer. [c] 2,2′-azobis(2-amidinopropane) dihydrochloride. 1.1 wt % based on monomer. [d] Measured at the end of the first stage polymerization. [e] Measured by light scattering method at the end of the first stage polymerization. [f] Heptadecafluorodecyl acrylate (FA). 11.4 wt % in FA pre-emulsion. [g] 6.7 wt % based on FA monomer. [h] Measured by gas chromatography. [i] Measured by light scattering method. [j] Calculated by eq 1 (see text).

analysis. The surface energy of latex films made from core−shell particles was investigated by contact angle measurement and compared with that of latex films from random copolymers and latex blends of styrene and FA.

Experimental Section

Materials. Styrene (St, 99%) was purchased from Aldrich, and the inhibitors were removed prior to polymerization by passing the monomer through an inhibitor removal column (Aldrich). Heptadecafluorodecyl acrylate (FA, 95+%) was obtained from Clariant and used without further purification. Tetradecyltrimethylammonium bromide (TTAB, 99%, Sigma), 1-dodecanethiol (DT, 98%, Acros), acetone (99%, Junsei Chemical), and 2,2′-azobis(2-amidinopropane) dihydrochloride (V50, Wako) were used as received. Deionized water was used throughout the experiments.

Emulsion Polymerization of Homopolymers and Random Copolymers. The homogeneous latex particles and random copolymers of St and FA were prepared by batch emulsion polymerization in a 100 mL glass reactor at 65 °C using V50 as an initiator and TTAB as a cationic surfactant (Table 1). Typically, the reactor was charged with an emulsified mixture containing 6 g of monomers, 40 g of deionized water, and 0.15 g (0.45 mmol) of TTAB purged with nitrogen gas and then heated to 65 °C. At that point, the cationic initiator V50 (0.05 g, 0.18 mmol) dissolved with a small amount of water (1 g) was added. Polymerization was allowed to proceed for 6 h at least. The final conversions were determined gravimetrically.

Preparation of Core−Shell Latex Particles. The core−shell particles were prepared by using a two-stage emulsion polymerization technique. For the synthesis of the PS core, 30 g of water and 0.15 g (0.45 mmol) of TTAB were added to the reactor. After purging nitrogen gas for 20 min, this solution was heated with stirring to reach 65 °C. 4 g (38 mmol) of St and 0.08 g (0.40 mmol) of DT as a chain transfer agent were added to the solution and emulsified for 20 min with stirring. The V50 initiator (0.05 g, 0.18 mmol) dissolved in water (1 g) was then added. The conversion of St in this reaction was determined gravimetrically in an independent experiment. The addition of the second stage monomer FA was started after 80−90% conversion of St for core−shell particle preparation. FA was pre-emulsified with TTAB and, if necessary, acetone as a cosolvent in water by using ultrasonic emulsifier. The recipe for FA pre-emulsions is summarized in Table 2. The FA pre-emulsion was added continuously with a rate of 0.01 g FA/min via a precision syringe pump. In all experimental runs for the preparation of core−shell particles, the weight fraction of FA monomer in the pre-emulsions was identical. The thickness of the shell was controlled by the amount of the FA pre-emulsion added in the second stage polymerization. To ensure complete consumption of FA, the reaction was prolonged for another 2 h after the addition of FA pre-emulsion was finished. To determine fractional conversion of FA, a small amount of reaction mixture was withdrawn from the reactor at regular time intervals. The conversion of FA was determined by gas chromatography. All the experimental parameters and the principal characteristics of core−shell latex particles are listed in Table 2.

Characterization of Latex Particles. The particle size was determined by using a photocorrelation spectroscopy (PCS) technique (Zetaplus, Brookhaven) and confirmed by transmission electron microscopy (EM 912 Omega, Carl Zeiss). Dried samples of latexes were obtained from precipitation in ethanol. The filtered latexes were washed several times with water and ethanol to remove emulsifier and then dried in a vacuum oven at elevated temperature. The thermal behavior of dried latex samples was observed by differential scanning calorimetry (DSC, DuPont 9900) with the scanning rate of 10 °C/min after quenching at 150 °C. The X-ray scattering intensity of dried sample was measured at room temperature using Ni-filtered Cu Kα radiation from an X-ray generator (40 kV, 50 mA, D/MAX IIIB, Rigaku).

Film Formation and Surface Energy Calculations. Latex films were prepared by spreading a diluted latex (~1% solids) directly on a cleaned glass plate and allowed to dry at room temperature. The dried films were annealed for 24 h at 130 °C. Contact angles were measured by an optical goniometer (Rame-hart, 100 series) at room temperature. Wetting liquids used for contact angle measurements were water and diiodomethane, as suggested by Owens and Wendt.[25] Total surface free energies (γ) and their polar (γ^p) and dispersion (γ^d) components were calculated by Fowkes' equation.[26] The contact angles of *n*-dodecane were also measured as the index of oleophobicity of latex films.

Results and Discussion

Synthesis of Core−Shell Latex Particles. The core−shell particles were prepared by a two-stage semicontinuous emulsion polymerization in the same reactor under kinetically controlled conditions as described earlier. In other words, after reaching 80−90% conversion of St monomer forming the core, the second stage polymerization was proceeded in order to prepare the shell by adding FA pre-emulsion into the reactor without further addition of initiator. According to the preliminary study on the emulsion polymerization of St with the same condition described in Table 2, 90% of St monomer was polymerized during the first 30 min in the first stage polymerization. At that moment, the diameter of PS core latex particles ranged from 65 to 70 nm, and the number-averaged molecular weight determined by gel permeation chromatography (Waters, R-401 ALC/GPC) using tetrahydrofuran as a solvent was about 25 000. The molecular weight was calibrated with PS standards. Unfortunately, the molecular weight of core−shell particles could not be measured because the particles were insoluble in solvent.

Figure 1 shows a typical TEM image of the core−shell latex particles obtained in experiment AC-F40. The size of resulting particles and the thickness of the shell (~10 nm) measured by light scattering, which listed in Table 2, are fairly coincident with the TEM images. To increase the phase contrast between the core and the shell, the latex samples were diluted in 2 wt % aqueous solution of phosphotungstic acid for negative staining and placed on a Cu grid. After evaporating water, the sample was then exposed to the RuO$_4$ vapor in order to stain PS phase positively. The PFA-rich phase seems to be inactive to both staining procedures. After staining samples, the structure of particles can be investigated more accurately. As shown in Figure 1, the particles have core−shell morphology consisting of the PS core and the PFA-rich shell as desired. In addition, we have confirmed the core−shell structure with a fluorinated shell by considering the surface properties of the particles as we shall see later.

Figure 2 compares the particle size distributions for PS core and the subsequent core−shell particles of AC-F40 measured from TEM photographs. In this case, the average particle size measured by light scattering was 65.3 and 83.4 nm for the core and core−shell particles, respectively, whereas TEM photographs gave 61.7 and 77.5 nm for the core and core−shell particles. At least 500 particles were counted to estimate particle size distribution. Both results give the shell thickness of 8−9

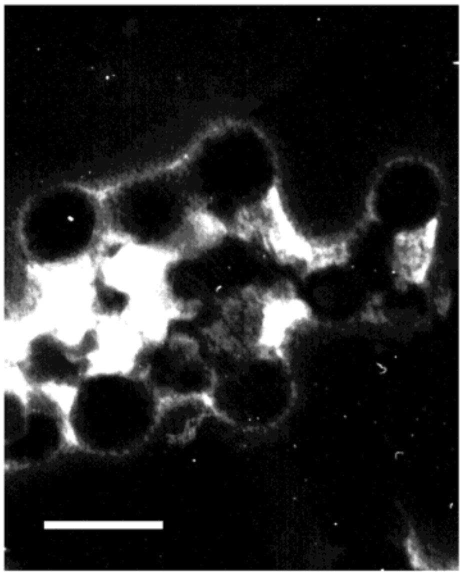

Figure 1. TEM photograph of the core−shell particles of AC-F40 (Table 2). The shell content is 40 wt %. The core−shell particles are stained negatively by phosphotungstic acid and positively by RuO$_4$. Polystyrene core appears as dark phase, whereas poly(perfluoroalkyl acrylate) shell exhibits lighter circular appearance. The thickness of the shell was measured to be 10 nm approximately. Scale bar = 121 nm.

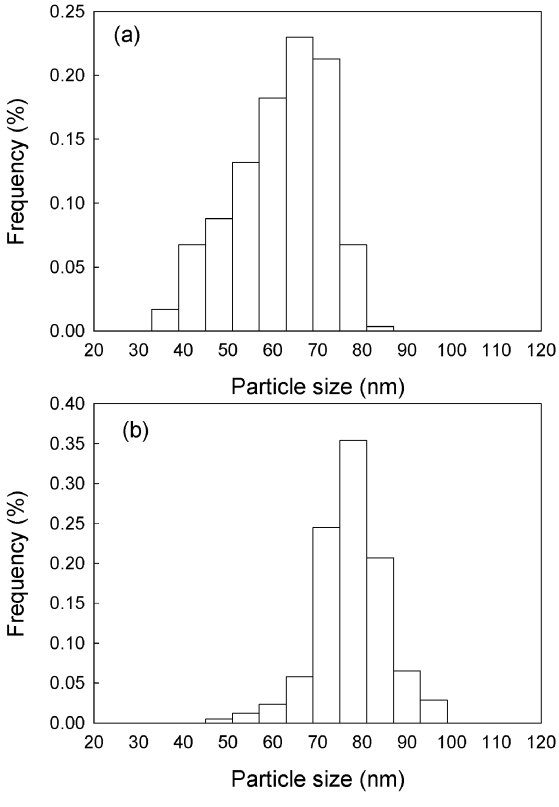

Figure 2. Size distribution curves for (a) core particles and (b) core−shell particles of AC-F40 measured from TEM photographs. The average particle sizes were 61.7 and 77.5 nm for the core and the core−shell particles, respectively.

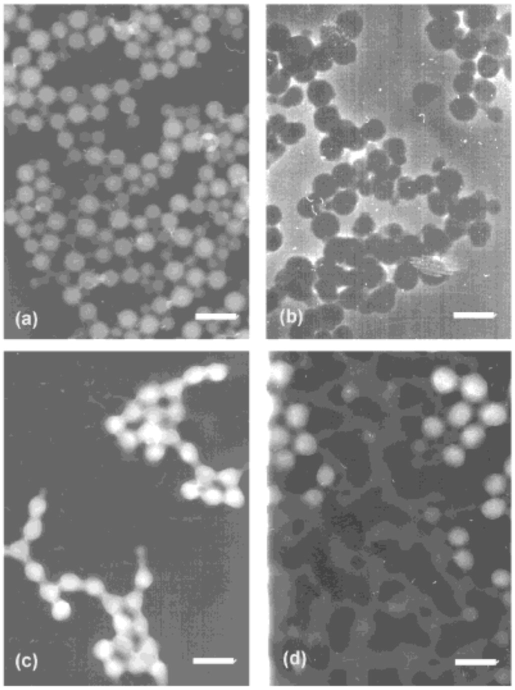

Figure 3. TEM photographs of latex particles synthesized (a, b) using the recipe given in AC-F40 (Table 2) and (c, d) using methyl methacrylate instead of styrene in the first stage polymerization with the same condition in AC-F40: (a) polystyrene core particles after first stage polymerization, (b) polystyrene−poly(perfluoroalkyl acrylate) core−shell particles after second stage polymerization, (c) poly(methyl methacrylate) core particles after first stage polymerization, and (d) poly(methyl methacrylate) particles and poly(perfluoroalkyl acrylate) particles after second stage polymerization. Polystyrene and poly(methyl methacrylate) particles are stained by RuO_4 in (b) and (d), and thus, polystyrene core appears as dark phase in (b) and poly(methyl methacrylate) particles as gray phase in (d). The formation of secondary poly(perfluoroalkyl acrylate) particles of about 200 nm is obvious. Scale bars stand for 121 nm in (a), (b), and (c), whereas 242 nm in (d).

nm, which is consistent with the TEM image of core−shell particles in Figure 1. The particle size distributions before and after second stage polymerization show that there is no sign of secondary particle nucleation, and thus, it can be assumed that composite particles of St and FA were produced without doubt.

The secondary particle nucleation, if occurs, also can be examined by electron microscopy. As observed in Figure 3a,b, the core and the core−shell particles of AC-F40 retain their size-monodispersity during the shell formation. We have observed recently that the kinetically controlled two-stage emulsion polymerization did not always produce desired particles with core−shell morphology. For example, when methyl methacrylate (MMA) was used instead of St in order to form the core with the same conditions of AC-F40 reported in Table 2, it was not possible to obtain PMMA−PFA core−shell particles.[27] The resulting structure of latexes was blends of small PMMA particles and large PFA particles according to TEM analysis, although the reason has not been fully understood yet. It is obvious that PFA homopolymer particles of more than 200 nm in diameter were produced during the second stage polymerization by comparing with Figure 3c,d.

Although two-stage emulsion polymerization is a well-known and effective technique for preparing latex particles with defined structures, the synthesis of core−shell particles usually does not lead to an ideal core−shell morphology with a complete phase separation between the core and the shell. Various alternative structures, for instance, raspberry-, confetti-, champignon-, or sandwich-like, have been described in the literature as intermediates of the phase separation process.[28] This is due to an interplay of thermodynamic as well as kinetic parameters during the polymerization process such as relative hydrophilicity of the monomers, type and concentration of emulsifier used, particle cross-linking, and so on. Another important factor affecting the particle morphology is the mode of monomer addition at the second stage polymerization. For example, PMMA−PS latex particles with PS domains concentrated at the particle interface were obtained only by continuous monomer feeding during the second stage polymerization.[29] Hence, semicontinuous monomer addition is one of the widest methods to obtain desired composite particle morphology in cases where thermodynamically nonequilibrium morphologies are desired. However, in the case of kinetically controlled two-stage emulsion polymerization, the conversion of the core also plays an important role to determine the internal morphology of the composite particles. Recently, Cunnungham et al.[30] reported that the particle morphology could be controlled by varying the conversion of the core at which the second monomer addition began. In that study, when St was added in semicontinuous mode as the second monomer, particle morphologies were changed from core−shell to finely dispersed St domains in the PMMA core particles by varying the conversion inside the prepolymerized PMMA particles at the start of St feeding. In contrast, when the core was copolymer of more hydrophobic butyl methacrylate and styrene instead of relatively hydrophilic methyl methacrylate, core−shell morphology with a composition gradient was produced. Thus, the compatibility and relative hydrophilicity of monomers are still a crucial factor to determine the particle morphology even in the case of semicontinuous addition of second monomer.

Despite that FA is sparingly soluble in water and highly hydrophobic monomer, we have seen that it is possible to obtain the core−shell latex particles with a fluorinated shell by continuous addition of FA monomer. According to solid-state NMR study performed by Landfester et al.,[31] when the more hydrophobic monomer is employed as the second monomer, the complete core−shell structure cannot be built, but the second monomer forms microdomains in the outer region of the core with an effective phase separation of the components, e.g., a confetti-like structure with little interface. In our case, St consisting of the core is also highly hydrophobic monomer, and thus, it is not easy to predict the exact internal structure of core−shell particles by simply considering hydrophobicity of St and FA. One thing to be noteworthy is that, according to our procedure to prepare core−shell particles, random copolymer of St and FA might be produced initially in the second stage polymerization as we shall see shortly. This might increase the phase compatibility between PS core and PFA shell. The characterization of the internal structure of the particles is under pursuit in our research group.

In Figure 4, the conversion of FA monomer is represented as a function of time for the experiment AC-F50 in the second stage polymerization. It was confirmed that St monomer remaining in the first stage was polymerized completely within 1 h after starting second stage polymerization by gas chromatography analysis.

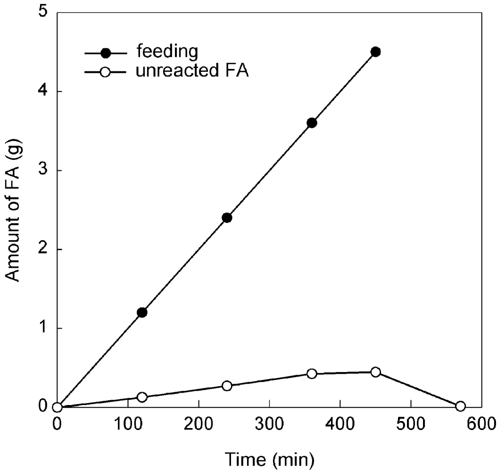

Figure 4. Fractional conversion of perfluoroalkyl acrylate (FA) monomer as a function of time in the second stage polymerization of experiment AC-F50. Second stage reactants were fed into the reactor for 440 min, and the reaction was proceeded for another 2 h at 65 °C.

As a result, before homopolymerization of FA, copolymerization of St and FA had occurred in the initial period of the second stage polymerization. According to the synthesis method employed, approximately 10% of St should be participated in the second stage polymerization. As the reaction proceeded, a small amount of FA monomer was accumulated in the reactor. This reflects that the feeding rate of FA pre-emulsion was slightly faster than the rate of FA consumption. The accumulated FA monomer was polymerized completely within an additional 2 h after finishing FA pre-emulsion addition.

In Figure 5, the size evolution of core−shell particles determined by light scattering method is shown as a function of reaction time in the second stage. In all experimental runs, a monotonic increase of particle sizes with the addition of FA pre-emulsion was observed. As listed in Table 2, the thickness of the shell was proportional to the amount of the FA monomer added. It increased up to 10 nm in the case of AC-F50. It can be found that the rate of particle growth is identical in all experimental runs as shown in Figure 5 despite the slight fluctuation of core particle sizes. By assuming that the shell has the density of bulk PFA, the diameter of the core−shell particle, D_2, can be calculated theoretically using the following relationship:

$$D_2 = D_1(1 + M_2\rho_2/M_1\rho_1)^{1/3} \qquad (1)$$

where D_1, M_1, and ρ_1 stand for the diameter, the mass fraction, and the density of PS core, respectively, and M_2 and ρ_2 represent the mass fraction and the density of PFA shell. The density of bulk PFA homopolymer was found to be 1.62 g/cm^3 by pycnometry. By the same method, the density of bulk PS homopolymer was measured to be 1.04 g/cm^3, which agrees well with the literature value of 1.05 g/cm^3.[32] As can be found in Table 2, the measured and calculated particle size show a slight discrepancy in quantitative point of view. It may be attributed to the fact that the density and weight fraction of the shell are not certain due to the presence of unreacted St monomer in the first stage polymerization. In addition, it is not sure that the density of latex particles is equal to that of bulk polymer.

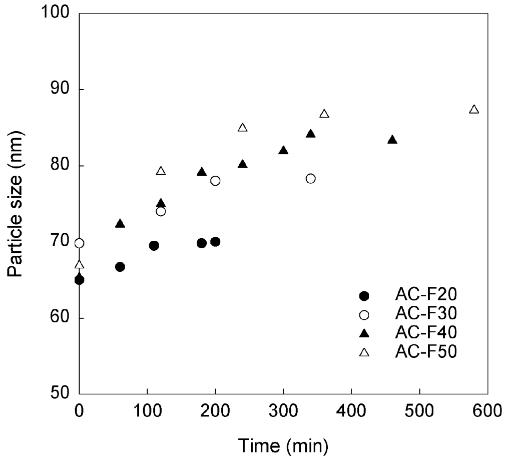

Figure 5. Particle size evolution of the core−shell particles as a function of time in the second stage polymerization.

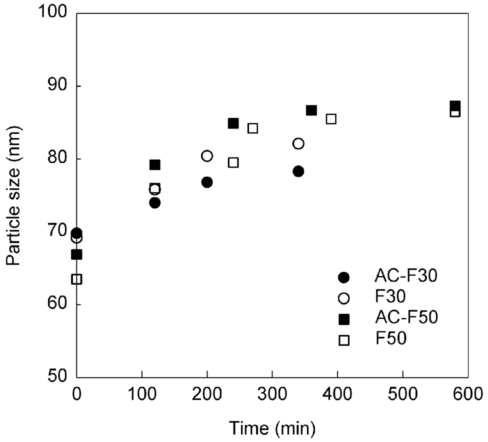

Figure 6. Effect of acetone as a cosolvent on the particle size evolution of core−shell particles as a function of time in the second stage polymerization.

The effect of acetone as a cosolvent on the polymerization process is depicted in Figure 6. Recently, Linemann et al.[33] reported that the addition of acetone enhanced the monomer conversion and produced more stable latex in the emulsion polymerization of perfluoroalkyl acrylates, and there was an optimum acetone content above which the monomer conversion was reduced and large amount of coagulate formed. It was insisted that, in the presence of acetone, the emulsification of fluorinated acrylates became relatively easy, and thus, there was no induction period and high monomer conversion and stabilization of latex could be accomplished. However, as can be seen in Figure 6, in our study, there was no noticeable effect of acetone as a cosolvent in the preparation of core−shell particles. It was also impossible to find out any considerable difference in particle morphology by TEM analysis.

Thermal Analysis. The thermal behavior of two homopolymer latexes of St and FA is shown in Figure 7a. PS homopolymer exhibits glass transition at 100 °C, which concords with literature data.[31] On the other hand, PFA homopolymer shows single first-order transition at 75 °C without noticeable glass transition. It is well-known that the perfluoroalkyl acrylate homopolymers are semicrystalline due to the long side chains if the number of CF_2 units in perfluoroalkyl side chain is larger than 7, and the crystallinity and melting temperature increase with increasing the number of CF_2 units.[17] More specifically, the endothermic peak at 75 °C is due to the mesomorphic−isotropic phase transition. According to Volkov et al.,[34] the structure of PFA

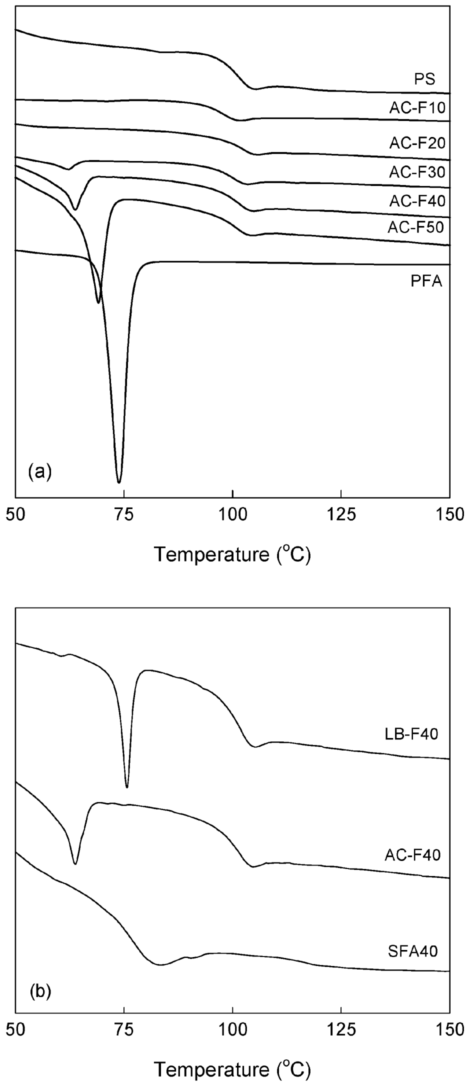

Figure 7. DSC thermograms of (a) polystyrene, poly(perfluoroalkyl acrylate) homopolymers and the core–shell particles (AC-F10 to AC-F50) and (b) latex particles containing 40% of perfluoroalkyl acrylate (FA) monomer by weight with different structures, core–shell particle (AC-F40), random copolymer (SFA40), and latex blend (LB-F40) of polystyrene and poly(perfluoroalkyl acrylate).

below 75 °C seems to be ordered smectic liquid crystalline which can be classified as smectic B (S_B) type. The structure of the S_B mesophase is characterized by the arrangement of the side chains in layers where the axes of the side chains are perpendicular to the plane of the layers with ordering of the side chains in layers. In fact, PFA is a typical of comb-shaped polymers so that closely spaced side chains within the same backbone create the conditions for their interaction, which is very similar to what takes place for a group of small molecules of similar structure.

Figure 7a also includes thermograms of the core–shell particles prepared in this study. Except AC-F10, one glass transition temperature and one first-order transition are clearly observed, which indicates the existence of two separated polymeric microdomains within the same sample. The glass transition appears at the same temperature (ca. 100 °C) in all core–shell particles and corresponds to the T_g of the PS core. Only glass transition was observed without noticeable first-order transition for AC-F10. Since St was not consumed completely by polymerization when the addition of FA pre-emulsion was started, the random copolymer of St and FA was produced actually during the initial period of the second stage polymerization. In the case of AC-F10, a small amount of St monomer was still remained even at the end of FA pre-emulsion feeding. Thus, the structure of AC-F10 may be interpreted as the composite particle consisting of a PS core covered by random copolymer of St and FA rather than well-defined core–shell morphology. As increasing the shell portion of the particles, the longer reaction time was required because the FA pre-emulsions were added at the same flow rate. In these cases, homopolymerization of FA occurred following copolymerization of St and FA during the second stage polymerization after complete consumption of St. Consequently, the resulting particles possessed two distinctive polymer phases, in actual, PS core and PFA shell and possibly an intermediate phase of copolymer. In the case of AC-F20, very weak first-order transition appears at a little below 75 °C. This means that phase separation between PS and PFA becomes noticeable. Further addition of FA monomers results in more considerable phase separation between the core and the shell so that an obvious first-order transition originated from the PFA-rich phase appears as well as a glass transition from PS core. The transition temperature increases with the amount of FA monomer in the particle and approaches closely to that of PFA homopolymer. It can be assumed that the structure of the shell changes from random copolymer of St and FA to PFA homopolymer depending on the amount of FA monomer.

Thermal behavior of random copolymer or latex blend is quite different from that of core–shell particles containing the same amount of FA as depicted in Figure 7b. All of the latex samples appear in this figure have 40% of FA by weight. In the case of random copolymer, only the glass transition can be observed at 80 °C, which is much lower than T_g of PS without any crystalline behavior. On the other hand, the glass transition originated from PS particles and the first-order transition from PFA particles are completely reproduced in latex blend. This means PS and PFA phases are incompatible and phase-separated without any microscale mixing between them. This behavior was observed always without regard to the composition of latex blends of PS and PFA.

X-ray Diffraction Study. The diffraction spectra performed on homopolymers and core–shell particles at room temperature are shown in Figure 8. At room temperature, PFA homopolymer exhibits a strong diffraction peak at $2\theta = 18°$ with several additional strong diffraction peaks in the small-angle region due to the perfluoroalkyl group layering. The diffraction peak at $2\theta = 18°$ corresponds to the intermolecular spacing of the cylindrical perfluorocarbon molecules arranged in a hexagonally packed layer.[17,34] On the other hand, there is no apparent diffraction peak in the case of amorphous PS. For the core–shell particles, the diffraction peak at $2\theta = 18°$ and others in the small-angle region become more obvious as increasing the amount of FA in the particles, while the smectic layer spacing does not change. The X-ray diffraction result of the PFA–PS latex blend is also included in Figure 8. This sample has both the characteristics of two homopolymers as expected. There was no noticeable diffraction peak in the case of random copolymer. These results agree well with those obtained from the DSC study.

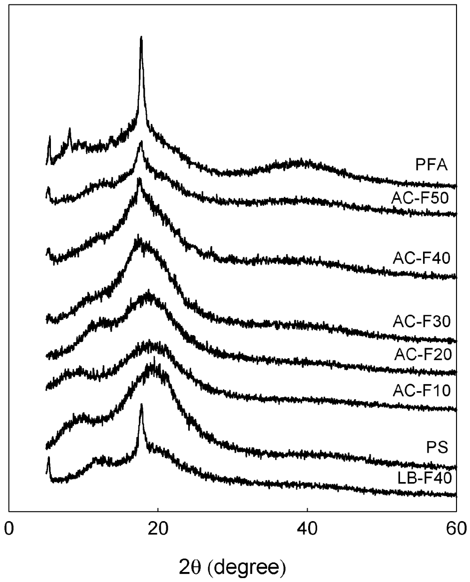

Figure 8. X-ray diffraction results of polystyrene, poly(perfluoroalkyl acrylate) homopolymers, core–shell particles (AC-F10 to AC-F50), and latex blend (LB-F40). The latex blend consisted of 40 wt % of poly(perfluoroalkyl acrylate) and 60 wt % of polystyrene latex particles.

Table 3. Contact Angles for Water, Diiodomethane (DIM), and *n*-Dodecane on Latex Films and Surface Energies Calculated by Fowkes' Equation[26] from Contact Angle Measurements

	contact angle (deg)			surface free energy (mN/m)[a]		
	water	DIM	*n*-dodecane	γ^d	γ^p	γ
PFA	119.6	97.1	72.2	0.33	9.43	9.76
AC-F10	114.3	93.8	67.3	0.79	10.41	11.20
AC-F20	120.4	98.9	71.8	0.34	8.74	9.09
AC-F30	118.1	95.6	72.3	0.40	9.96	10.36
AC-F40	119.8	96.1	72.6	0.26	9.89	10.15
AC-F50	120.0	96.9	71.7	0.28	9.56	9.83
F30	118.7	97.0	71.8	0.42	9.40	9.82
F50	119.2	96.4	73.0	0.33	9.70	10.03
SFA05	106.3	65	30.1	0.13	25.61	25.74
SFA10	108.4	70.8	41.6	0.15	22.41	22.56
SFA20	114.8	79.4	55.5	0.03	18.02	18.05
SFA30	120.0	95.8	63.3	0.23	10.04	10.27
SFA40	119.8	96.9	66.4	0.30	9.54	9.83
LB-F20[b]	101.3	60.3	49.7	0.40	28.05	28.45
LB-F30[b]	113.0	90.4	50.8	0.73	11.88	12.61
LB-F40[b]	116.1	93.7	61.4	0.52	10.63	11.15

[a] The surface free energy (γ) is expressed as a total of polar (γ^p) and dispersion (γ^d) components. [b] Latex blends of polystyrene and poly(perfluoroalkyl acrylate) homopolymers. The weight fractions of poly(perfluoroalkyl acrylate) in latex particles are 20, 30, and 40 wt % for LB-F20, LB-F30 and LB-F40, respectively.

Surface Properties of Latex Films. Latexes containing fluorinated polymers can be used to prepare low-energy surfaces. To achieve a low surface free energy, the surface of materials needs to be covered with perfluoroalkyl groups through surface segregation and phase separation.[35] Surface segregation relies on a difference of surface energy between a fluorinated material and a matrix and is observed with soluble fluorinated materials. On the other hand, phase separation is driven by incompatibility of components in a mixture. Statistically, perfluoroalkyl groups would be present on the film surface in an amount equal to their weight fraction in the bulk, and thus, large weight fractions of perfluoroalkyl monomer in the latex particles would be required to achieve the greatest surface energy reduction. In the core–shell particles prepared in this study, the fluorinated component was concentrated at the shell, and the phase separation between the fluorinated component and the PS core was accomplished in the course of particle synthesis. As a consequence, the kinetical aspect of the segregation of CF_3 or phase separation during the film formation becomes less important. In addition, if the perfluorinated shell encloses the core completely, the surface properties of the core–shell particles would be identical to that of PFA homopolymer in principle. To confirm this idea, we measured the surface energy of latex films made from core–shell particles by the contact angle method.

The PFA homopolymer has a low surface energy of about 10 mN/m as listed in Table 3. Low-energy modification of polymer surface can be also accomplished by using the additive fluorinated graft copolymer[36,37] and block copolymer[38] or by employing fluorinated monomers.[39–43] It has been shown that a very small amount of fluorinated monomers is needed in order to create low-energy surface. For example, by adding only 1.5 wt % of fluorinated monomer, a water contact angle of 110° was observed in acrylic polymers modified by perfluoroalkyl methacrylate.[37] However, to impart excellent water and oil repellency to the surface, a further reduction of surface energy is required. In an industrial application for textile coating, more than 50 wt % of fluorinated monomer is used in the polymer to produce acceptable water and oil repellency with a water contact angle of 120°. As can be seen in Table 3, the core–shell morphology of the latex particles is very effective to reduce surface energy. The data for varying amounts of FA monomer in the core–shell particles do not show any obvious advantage upon increasing the weight percent of fluorinated monomer beyond 20 wt %. The contact angle measurement also shows that the surface properties of core–shell particles are identical to those of PFA homopolymer, which insists that the PS core be enclosed by PFA as desired. The latex film produced from AC-F10 shows slightly higher surface energy compared with that of the PFA homopolymer. As discussed previously, the core–shell morphology was not achieved in this case. However, even in this case, the surface energy reduction is considerable because the PS core was covered with a copolymer of St and FA, which contains large amounts of FA as much as 50 wt % theoretically. In contrast, more than 30 wt % of FA monomer was needed to reduce the surface energy of latex films of random copolymer to 10 mN/m as reported in Table 3. Moreover, latex blending was less effective in reducing the surface energy of films. If we take into account the oleophobicity of the latex films, which can be deduced from contact angle data of *n*-dodecane, the advantages of core–shell particles become more outstanding compared with random copolymers or latex blends.

Conclusions

It was shown that core–shell particles with a fluorinated shell could be synthesized successfully by a two-stage emulsion polymerization under kinetically controlled conditions. The particle morphology was examined by transmission electron microscopy, and it was found that the perfluoroalkyl acrylate phase encapsulated the polystyrene core. Because of the kinetically controlled reaction scheme, there existed unreacted St monomer in the earlier state of the second stage polymerization. Thus, random copolymerization of St and FA had occurred prior to homopolymerization of FA during the second stage polymerization. It resulted in gradual transition in surface composition from random copolymer of St and FA to FA homopolymer. The core−shell particles exhibited two thermal phenomena. One was a glass transition originating from the PS core, and the other was a mesomorphic−isotropic transition from a PFA shell. As increasing FA content in the particles, the latter became more pronounced, and the transition temperature increased while the former unchanged, which can be understood as the evidence of PFA shell growth. Thermal and crystalline properties of core−shell particles were quite different from those of random copolymers or latex blends of St and FA. There was no considerable effect of cosolvent on the preparation of core−shell particles. The contact angle measurement represented the reduction of surface energy due to the presence of FA in the latex films. It was found that the core−shell morphology was the most effective method to create hydrophobic and oleophobic surface with the reduced amount of fluorinated monomer compared with other particle structures such as random copolymer or latex blending.

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