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Latex Blends of Fluorinated and Fluorine-Free Acrylates: Emulsion Polymerization and Tapping Mode Atomic Force Microscopy of Film Formation

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ABSTRACT: Latex based upon fluorinated acrylates such as perfluorooctylethyl methacrylate (FMA) and perfluorooctylethyl acrylate (FA) and fluorine-free acrylates such as *n*-butyl methacrylate (BMA) was prepared by means of emulsion polymerization in the presence of octadecyltrimethylammonium bromide (C_{18}TAB) and 2,2′-azobis(2-amidinopropane) dihydrochloride (V50) as water-soluble azo initiator. Reaction calorimetric studies revealed that acetone addition, preferably 15−25 wt %, was the key to achieve high monomer conversion and to produce stable latex with average particle sizes varying between 50 and 300 nm. Monomer conversion was increased, and latex particle size was reduced when 2 wt % *n*-butyl acrylate (BA) was added together with fluorine-containing monomers. The reaction enthalpy of FMA was determined to be 62 kJ/mol with respect to 75 kJ/mol for the more reactive FA. Stable poly(perfluorooctylethyl methacrylate)/poly(*n*-butyl methacrylate) (PFMA/PBMA) latex blends were formed. According to tapping mode atomic force microscopy, PBMA formed a dense film at 65 °C containing PFMA nanoparticles dispersed in the PBMA matrix. Annealing at 100 °C caused accumulation of PFMA at the surface and formation of a gradient film containing a surface layer with high fluorine content. Such latex blends are of interest in water-, oil-, and soil-repellent coatings.

Introduction

Fluorine-containing acrylates are applied in emulsion polymerization to produce latex which affords fluorinated surface coatings during film formation. Such fluorine-containing coatings render textile, paper, and leather surfaces water, oil, and soil repellent due to their substantially reduced surface wettability.[1] Despite the obvious industrial interest, there exist only a few investigations of the basic correlations between emulsion polymerization, latex composition, and film formation of fluorinated acrylic latex,[2−4] although such correlations are well established for fluorine-free emulsion polymers.[5,6] Moreover, modern AFM microscopy, which has proven to be a very useful tool for monitoring film formation,[7−9] has not been applied to study morphology development of fluorine-containing acrylic latex. Today the development of latex blends is attracting attention in developments aiming at reducing the content of volatile organic compounds, which are frequently required to promote film formation.[10] Moreover, latex blends of highly immiscible polymers offer attractive opportunities of controlling morphology development during film formation. In fact, pioneering advances by researchers at Du Pont during the 1960s revealed that coatings derived from latex blends consisting of fluorinated and fluorine-free acrylates gave superior performance with respect to those derived from corresponding random copolymers.[11−13] Since then numerous patents by other companies have appeared, while little attention has been paid in the open literature to the study of morphology development. Therefore, an objective of our research was to use reaction calorimetry and light scattering to examine the emulsion polymerization of both fluorine-containing and fluorine-free acrylates using the same fluorine-free cationic surfactant in order

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to achieve formation of latex particles with average diameters well below 200 nm. In the presence of the same surfactant it is possible to produce latex blends containing variable contents of fluorinated and fluorine-free acrylic polymers. Consequently, another objective of this research was to use tapping mode atomic force microscopy (TMAFM) in order to study morphology development during film formation of poly(perfluorooctylethyl methacrylate)/poly(*n*-butyl methacrylate) (PFMA/PBMA) latex blends as a function of the film-forming temperature, taking into account the different glass temperatures of the blend components. Special emphasis was placed upon achieving gradient film formation with surface accumulation of PFMA upon annealing above the film-forming temperature of PBMA. Such gradient films can exhibit improved water, oil, and soil repellence at significantly lower total fluorine content.

Experimental Part

Materials. Perfluorooctylethyl acrylate AC800, AC812 and perfluorooctylethyl methacrylate MA800, MA812 were obtained from Hoechst AG and used without further purification. FMA8/10 (MA812) and FA8/10 (AC812) contain 2.7 wt % C_6F_{13}, 53.9 wt % C_8F_{17}, 24.2 wt % $C_{10}F_{21}$, and 8.7 wt % $C_{12}F_{25}$; FMA8 (MA800) and FA8 (AC800) contain 0.7 wt % C_6F_{13}, 95.5 wt % C_8F_{17}, and 0.4 wt % $C_{10}F_{21}$. Acetone (purity >99%) was supplied by Roth, butyl methacrylate (>98%) by Aldrich, and octadecyltrimethylammonium bromide (>97%) by Aldrich. The bis(2-amidinopropane) dihydrochloride azo initiator (V-50) was obtained from Wako. Dionized water was obtained by distillation.

Emulsion Polymerization, Reaction Calorimetry, and Latex Characterization. Batch emulsion polymerization was performed using the Mettler RC1 heat flow reaction calorimeter equipped with a 2 L glass reactor (AP01), internal thermocouple (PT100), internal calibration heat source of 5 W, and anchor-type stirrer. Typically, polymerizations were performed under nitrogen at 60 °C. For example, 500 g of deionized water, 163 g of acetone, 200 g of FMA8/10 (MA812, Hoechst AG), and 6.5 g of C_{18}TAB were charged into the reactor at room temperature after carefully removing oxygen by freeze thaw/vacuum cycles of the monomer and prolonged sparging with nitrogen in the reactor. It should be noted that fluorine-containing acrylics dissolve considerable amounts of oxygen which must be removed to avoid inhibition. Then temperature was increased to 40 °C to allow dissolution of the C_{18}TAB surfactant and to conduct internal calibration. Afterward the internal heat capacity was determined by heating to 57 °C at 2 K min^{-1}. This calibration is repeated by heating to 60 °C at 0.2 K min^{-1} heating rate. The polymerization was started by adding 5 g of the solid initiator (Wako V-50). After completing polymerization, typically after 5 h, calibration was repeated to determine heat capacity of the emulsion. Then temperature was lowered to room temperature. For comparison, conversion was also measured by means of gravimetric analysis of polymer formation. The PFMA blend sample was prepared accordingly using FMA8/10 using 500 g of water, 162.5 g of acetone (18.6 wt %), 200 g of FMA8/10, 6.5 g of C_{18}TAB, and 5 g of V50 to afford a latex with 101 nm particle size and polydispersity of 0.04; solids with contents of 20 and 11 wt % coagulate. The fluorine-free PBMA blend component latex was prepared using a seed latex process: To a 10 mL seed latex (prepared using 150 mL of water, 60 g of BMA, 3 g of C_{18}TAB, 0.4 g of V50, monomer feed during 290 min) at 63 °C and 300 rpm were added 180 mL of water and 0.3 g of V50. Then 34 g of BMA was fed into the reactor for 1760 min at 52 °C and 250 rpm. The average particle size was 169 nm, 10 wt % solids, 67 wt % total conversion, i.e., 22 wt % conversion with respect to coagulate and 45 wt % conversion with respect to latex formation.

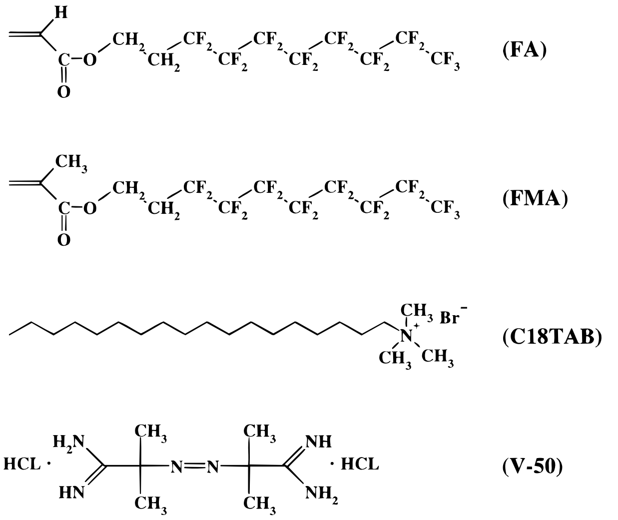

Figure 1. Components of emulsion polymerization based upon fluorine-containing monomers: perfluorooctylethyl acrylate (FA), perfluorooctylethyl methacrylate (FMA), octadecyltrimethylammonium bromide (C_{18}TAB), and 2,2′-azobis(2-amidopropane)dihydrochloride (V-50).

The solids content of the emulsions was determined gravimetrically by means of lyophilization of samples and removal of excess monomer at temperatures above 130 °C. Moisture content of the polymer was measured by means of a Sartorius MA 300 moisture analyzer using 1 g samples that were dried at 130 °C. Latex particles sizes were determined by means of light scattering using the Zetasizer 3 of Malvern using a He−Ne laser (632.8 nm, 5 mW), a photomultiplier, and an angle of 90°. The fluorine content was analyzed via elemental analysis following oxidation and potentiometric titration with fluoride selective electrodes.[14] This AODI system was supplied by IKA, Staufen/Germany. Titration was performed on a titrator from Metrohm.

Characterization of Polymer Properties and Film Formation. Glass transition temperatures were determined on a Perkin-Elmer series 7 during second heating using 20 K min^{-1} heating and −10 K min^{-1} cooling cycle. TMAFM experiments were performed at ambient conditions using a Nanoscope III from Digital Instruments. The height and the phase images were obtained simultaneously while operating the instrument in the tapping mode. Commercial Si cantilevers with force constants of 13−70 N/m were used. The data were taken at the fundamental resonance frequency of the cantilevers which was around 300 kHz. For TMAFM measurements 30 μL of the corresponding dispersions and blends were deposited on a cover glass. The samples were then dried at room temperature for 3 days before further treatment and investigation. The blends were annealed at different temperatures as specified below. Typically the TMAFM measurements were performed on the drying edge of the droplet.

Results and Discussion

Emulsion Polymerization. Similar to procedures previously reported by Raynolds and co-workers,[11] emulsion batch polymerization was performed in the presence of cationic surfactants such as octadecyltetramethylammonium bromide (C_{18}TAB), 2,2′-azobis(2-amidinopropane) dihydrochloride (V50) as water-soluble initiator, and perfluorooctylethyl acrylate (FA) and perfluorooctylethyl methacrylate (FMA) as fluorine-containing monomers. In the case of FA8 and FMA8, the perfluoroalkyl group consisted of 95 wt % perfluorooctyl, whereas FA8/10 and MFA8/10 comprised a mixture of perfluoroalkyl groups with 54 wt % perfluorooctyl and 24 wt % of the higher molecular weight perfluorodecyl groups. The components are displayed in Figure 1, and the emulsion polymerization runs are listed in Table 1. Initial experiments gave rather poor

Table 1. Emulsion Polymerization

sample	monomer	acetone [wt %]	butyl acrylate [wt %]	C_{18}TAB [wt %]	particle diameter [nm]	poly-dispersity	solids theor [wt %]	solids exp [wt %]	C_{exp} [%]	C_{latex} [%]	C_{coag} [%]
PFMA2-4[a]	FMA8/10	10	0	0.9	77	0.17	28	15	56	47	9
PFMA2-6[a]	FMA8/10	16	0	0.9	75	0.14	27	20	81	64	17
PFMA2-10[a]	FMA8/10	20	0	0.8	117	0.21	26	23	100	80	20
PFMA2-3[a]	FMA8/10	10	0.5	0.9	55	0.26	29	18	86	53	33
PFMA2-7[a]	FMA8/10	16	0.5	0.9	53	0.24	27	23	95	68	27
PFMA2-9[a]	FMA8/10	20	0.5	0.8	102	0.17	26	25	97	89	8
PFMA2-K3[b]	FMA8/10	19	0	0.8	101	0.04	24	20	82	71	11
PFMA2-K2[b]	FMA8/10	19	0.5	0.8	65	0.09	25	21	88	75	13
PFMA3-8[a]	FMA8	16	0	0.9	76	0.28	27	27	96	94	2
PFMA3-12[a]	FMA8	25	0	0.8	276	0.08	24	23	97	89	8
PFMA3-14[a]	FMA8	41	0	0.6			19	1	64	4	60
PFMA3-11[a]	FMA8	25	0.5	0.8	208	0.10	24	23	95	93	2
PFMA3-13[a]	FMA8	40	0.5	0.6			19	1	95	2	93
PFMA3-K5[b]	FMA8	12	0	0.9	69	0.12	26	24	82	81	1
PFMA3-K7[b]	FMA8	19	0	0.8	87	0.08	24	22	83	81	2
PFMA3-K9[b]	FMA8	26	0	0.8	190	0.07	22	21	92	91	1
PFMA3-K4[b]	FMA8	12	0.5	0.9	47	0.14	26	25	89	88	1
PFMA3-K6[b]	FMA8	19	0.5	0.8	59	0.07	25	24	91	90	1
PFMA3-K8[b]	FMA8	26	0.5	0.8	176	0.04	22	22	90	89	1
PFA4-4[a]	FA8/10	10	0	0.9	83	0.17	28	21	67	61	6
PFA4-8[a]	FA8/10	16	0	0.9	79	0.17	27	24	84	81	3
PFA4-10[a]	FA8/10	20	0	0.8	149	0.22	26	24	91	87	4
PFA4-12[a]	FA8/10	26	0	0.07	634	0.13	23	7	93	24	69
PFA4-13[a]	FA8/10	26	0	0.4	187	0.16	24	22	95	88	7
PFA4-14[a]	FA8/10	26	0	0.7	155	0.17	24	23	97	95	2

[a] Batch polymerization: H_2O, 90 g; acetone content, see table; monomer content, 40 g; butyl acrylate content, see table; octadecyltrimethylammonium bromide (C_{18}TAB), 1.3 g; 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50), 1.0 g. [b] Batch polymerization in Mettler reaction calorimeter RC1: H_2O, 500 g; acetone content, see table; monomer content, 200 g; butyl acrylate content, see table; C_{18}TAB, 6.5 g; V-50, 5.0 g.

monomer conversion accompanied by substantial losses of the fluorine-containing acrylate monomer due to severe coagulation during polymerization and during storage. Therefore, reaction parameters such as stirring speed, initiator, and surfactant concentration, as well as acetone and butyl methacrylate (BMA), were varied systematically to achieve high solids latex with average particle sizes of <100 nm, high storage stability, and no coagulation problems.

In Table 1 experimental and theoretical solids content as well as the total monomer conversion (C_{exp}) and monomer conversion corresponding to formation of dispersions (C_{latex}) and undesirable coagulation (C_{coag}) are given. Monomer conversion was calculated from heat flow curves and also measured gravimetrically via the solids content. Particle sizes of the latex was determined by means of light scattering. According to initial screening experiments, a stirring speed of 300 rpm and polymerization at 60 °C for the duration of a minimum of 5 h in the presence of 0.6−1 wt % V50 initiator gave the best performance although this variation was not sufficient to afford stable emulsions. A stable latex of the desired average particle size varying between 50 and 300 nm was obtained only when acetone or small amounts of butyl acrylate were added together with the fluorine-containing acrylate monomers. The acetone content was varied between 0 and 41 wt % with respect to the total amount of components including water. For both classes of fluorine-containing acrylates with narrow and broad molar mass distribution of the perfluoroalkyl groups, an optimum range of 15−25 wt % acetone was found to give high conversions, approaching 100%, without coagulation and with excellent storage stability of latex particles with average sizes well below 100 nm. However, at high acetone content exceeding 25 wt %, conversions were reduced and much larger particles were formed. In fact, at 40 wt % acetone content, PFMA8 gave exclusively coagulate as evidenced by precipitation of fiberlike polymers during polymerization. With pure FMA8 it was possible to achieve higher conversions with respect to those of FMA8/10. It appears that the presence of long perfluoroalkyl groups is detrimental to latex stability and promotes coagulation. For example, under optimized polymerization conditions FMA8 with high perfluorooctyl content gave only 1.6 wt % coagulation, whereas FMA8/10 containing both perfluorooctyl and perfluorodecyl groups gave 21 wt % coagulate.

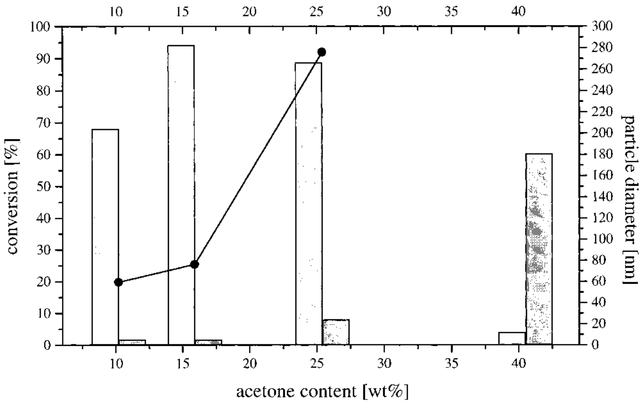

Figure 2. Influence of acetone addition on average latex particle size and on monomer conversion with respect to polymer formed as latex and as coagulate (experimental conditions: 90 g of water, acetone content varying between 0 and 41 wt %, 1.3 g of C_{18}TAB, 1.0 g of V50, 300 rpm, 65 °C, 4 h). The light and dark gray bars indicate the conversion in dispersion and coagulation, respectively (left ordinate). The filled circles indicate the particle size (right ordinate).

The occurrence of an optimum acetone content around 15 wt % is illustrated in Figure 2 for FMA8 emulsion polymerization producing stable latex of 50−70 nm average diameter without coagulate byproduct. More-

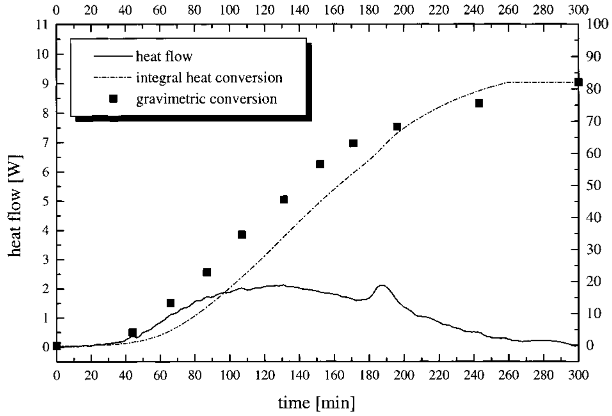

Figure 3. Conversion measured via heat flow and gravimetric analysis of solids as a function of time (run PFMA3-K4, Table 1) for 12 wt % acetone content.

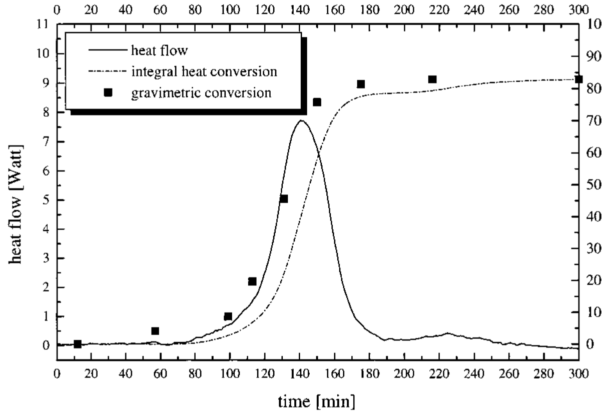

Figure 4. Conversion measured via heat flow and gravimetric analysis of solids as a function of time (run PFMA3-K6, Table 1) for 19 wt % acetone content.

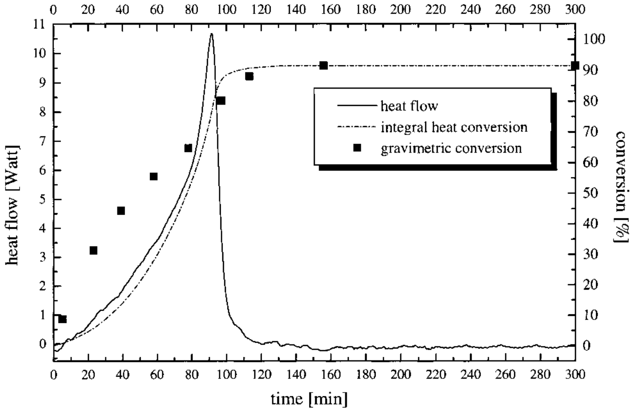

Figure 5. Conversion measured via heat flow and gravimetric analysis of solids as a function of time (run PFMA3-K8, Table 1) for 26 wt % acetone content.

over, only 2 wt % butyl acrylate addition appears to be enough to lower average particle size and to improve monomer conversion and storage stability without affecting polydispersity of the latex. For example, at 11 wt % acetone content, the addition of 2 wt % BA increased FMA8/10 conversion from 57 to 75 wt %, whereas the average particle diameter was lowered from 101 to 65 nm. Melting temperature of PFMA8/10 was only lowered by 2 °C. The more reactive FA polymerization was much less affected by BA addition.

The increase of monomer conversion in the presence of acetone and BA was also verified by reaction calorimetry. In Figures 3−5 the heat flow of emulsion polymerization runs of FMA8 in the presence of various amounts of acetone is plotted against time. The corresponding properties of PFMA are listed in Table 1. When the acetone content increased from 12 to 26 wt % the total FMA8 monomer conversion increased from 82 to 92%, whereas the particle size was increased from 69 to 190 nm. Coagulate formation accounted for less than 1.5% FMA8 conversion! At 12 wt % acetone content, maximum polymerization rate was observed after 130 min and the polymerization lasted 4 h. At 26 wt % acetone no induction period was observed, and the polymerization rate maximum occurred already after 90 min with complete conversion after 2 h! Conversions measured by reaction calorimetry are in accordance with those determined by means of gravimetric analysis of solids. Reaction calorimetry can be used to determine the reaction enthalpy. For FMA8 the polymerization reaction enthalpy was determined to be 62 kJ/mol, whereas the more reactive FA8 exhibited 75 kJ/mol. These enthalpies agree very well with polymerization enthalpies of other acrylate monomers reported in the literature,[14] e.g., 77 kJ/mol for butyl acrylate, 78 kJ/mol for ethyl acrylate, and 60 kJ/mol for butyl methacrylate, thus indicating that the perfluoroalkyethyl substitution has very little influence on reactivity.

For FMA8 the optimum acetone content with respect to formation of latex was found to be 19−25 wt %. For FA8/10 the concentration of the cationic emulsifier C_{18}-TAB was varied between 0.07 and 0.7 wt % (runs PFA4-12-a,b in Table 1). Increasing C_{18}TAB content reduced average particle size from 630 to 155 nm and gave much higher total monomer conversion and much less coagulate formation.

The above experiments clearly indicate that the solubility of the monomers or monomer/solvent mixtures plays an important role in emulsion polymerization. While FMA and FA are highly water insoluble, cause prolonged induction periods, and do not form stable emulsions, acetone mixtures with FMA and FA give much higher conversions, no induction period, and smaller particle sizes. However, at very high acetone content exceeding 40 wt % the polymer precipitates because the emulsifier does not stabilize particles that are swollen with acetone and readily agglomerate. Moreover, there may be a change in mechanism due to the presence of a homogeneous medium above 40 wt % acetone content. This is in accord with observations that at around 15 wt % acetone very uniform particles with small particle sizes, typical for emulsion polymerization, are formed, thus indicating that no particle nucleation takes place during polymerization. Above 20 wt % acetone much larger particles are obtained which are typical for dispersion polymerization. For further evaluation of mechanisms, more information concerning the location of the polymerization in micelles or polymer particles would be required.

In the case of FMA, BA addition gives slightly higher conversions in latex formation. Since BA is slightly water-soluble, it appears possible that BA promotes homogeneous nucleation of latex particles where oligo-BA functions as nucleating agents. In fact, this nucleating effect could account for the reduced average particle sizes and the larger amount of particles associated with higher conversion. The average particle size can be controlled via BA addition and especially via C_{18}TAB content. Stable emulsions of particles with 50−100 nm

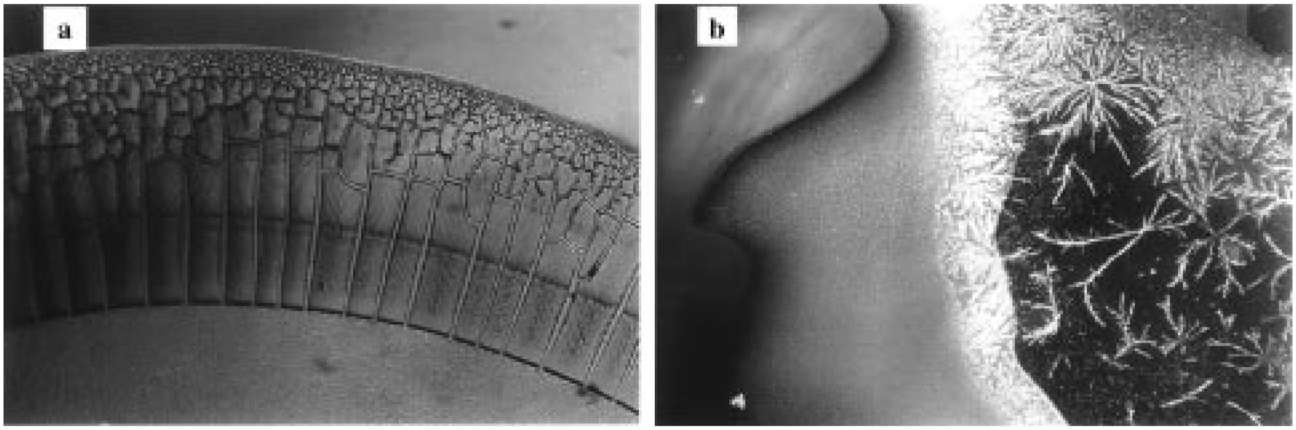

Figure 6. Light microscopy images of PFMA/PBMA (a) and PFMA/PEHA (b) blends. Both blends have a 1:1 composition and were dried at room temperatures. Demixing is observed only for the PFMA/PEHA case.

average PFMA particle size and fairly narrow particle size distributions are available without encountering coagulation problems. Moreover, it is possible to use the same procedures to polymerize fluorine-free acrylates such as butyl methacrylate. Therefore, this synthetic approach allows to prepare cationic particle dispersions of fluorinated and fluorine-free acrylates which are very useful as versatile model systems to investigate latex blend formation and to produce novel multiphase polymers.

Film Formation and Morphology Development. For latex blend formation fluorine-containing PFMA dispersions with 101 nm average particle size based upon FMA8/10 (PFMA2K3, Table 1) were blended together with PBMA latex with 169 nm average diameter. According to differential thermal analysis, PFMA exhibits a glass transition at 57 °C and a melting temperature of 91.4 °C, which are in good agreement with values reported previously by Shimizu[15] and Volkov[16] for PFMA prepared by solution processes. The PBMA samples were amorphous with a glass temperature of 30 °C. The acetone was removed by evaporation at reduced pressure prior to blend formation. In contrast to poly(ethylhexyl acrylate) (PEHA) dispersions, PBMA did not show demixing of the latex blends upon storage at room temperature, as evidenced by the typical texture of a drying edge of a droplet during film formation displayed in Figure 6 for PFMA/PBMA and PFMA/PEHA blends dried at room temperature. Latex demixing was also observed for fluorine-free latex derived from butyl acrylate, lauryl acrylate, and ethylhexyl acrylate. This may be due to their low glass temperatures and the possibility to form films below room temperature. PBMA requires film-forming temperatures above room temperature.

According to TMAFM measurements, the PBMA latex formed a dense film upon annealing at 65 °C, whereas the PFMA latex required temperatures well above 100 °C to cause film formation by coalescence of the latex particles. At 80 °C only slight deformation of PFMA latex particles are observed in accord with the well-established mechanisms of latex film formation. The TMAFM phase image sequence displayed in Figures 7−10 shows how annealing can affect morphology developments in PFMA/PBMA blends. For heterogeneous samples, TMAFM phase imaging[17] provides compositional maps because of its sensitivity to variations in local material properties. In TMAFM phase imaging the difference between the phase angle of vibration of the free oscillating tip and the phase of the tip as it interacts with the sample surface describes the characteristics of the tip−sample force interactions. Monitoring these phase changes allows one to obtain the above-mentioned compositional maps. It should be noted, however, that the assignment of the cause of the phase contrast to specific properties differences of the sample components can be difficult.[18−21] Nevertheless, the ability of TMAFM phase imaging to local mechanical and adhesive differences and the high sensitivity of the phase contrast to sample composition has been demonstrated.[22−25]

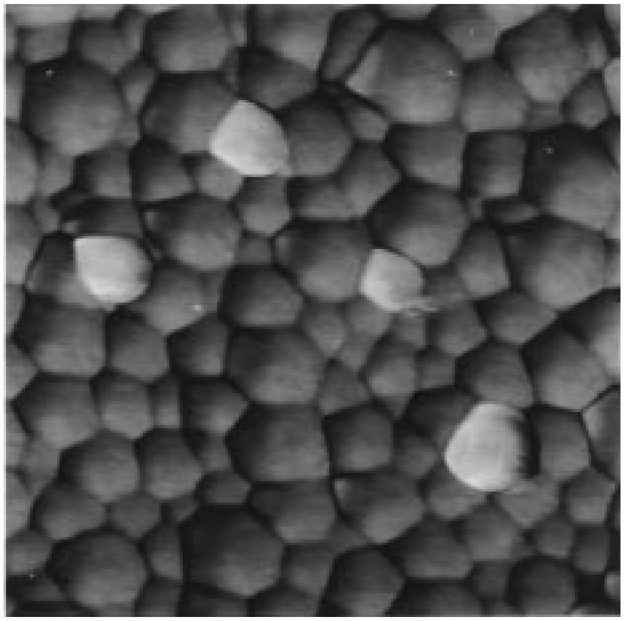

Figure 7. Phase image of PFMA8/10-PBMA blend of 1:100 composition ratio. The sample was dried at room temperature without further annealing. The contrast covers phase angle variations in the 30° range. The scan size was 1 μm.

Figure 7 shows a TMAFM phase image of a PFMA/PBMA blend that was dried at room temperature without further annealing. Individual particles can be distinguished since PBMA requires temperatures above room temperature for film forming. Some particles appear in brighter contrast in the phase image which can be assigned to PFMA particles. This assignment is based on the fact that the crystalline PFMA particles are more rigid then those of PBMA. In many cases for a particular choice of measurement parameters a brighter phase contrast is expected for stiffer materials as

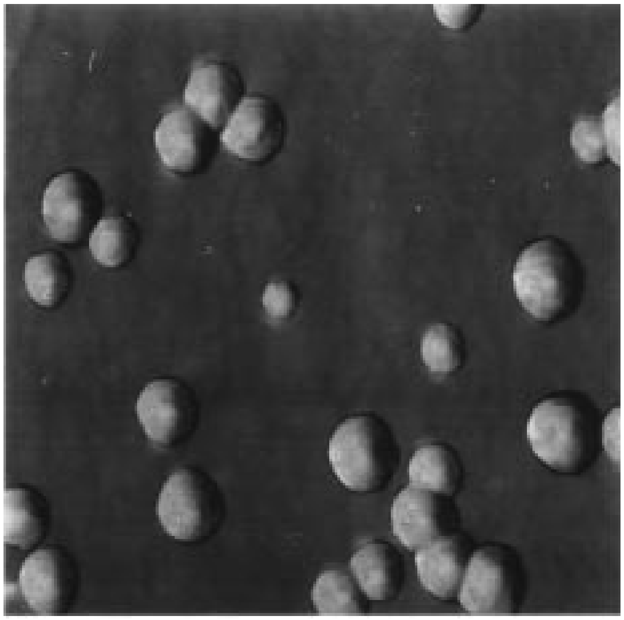

Figure 8. Phase image of PFMA8/10-PBMA blend of 1:5 composition ratio. The sample was annealed at 65 °C for 3 days. The contrast covers phase angle variations in the 10° range. The scan size was 1 μm.

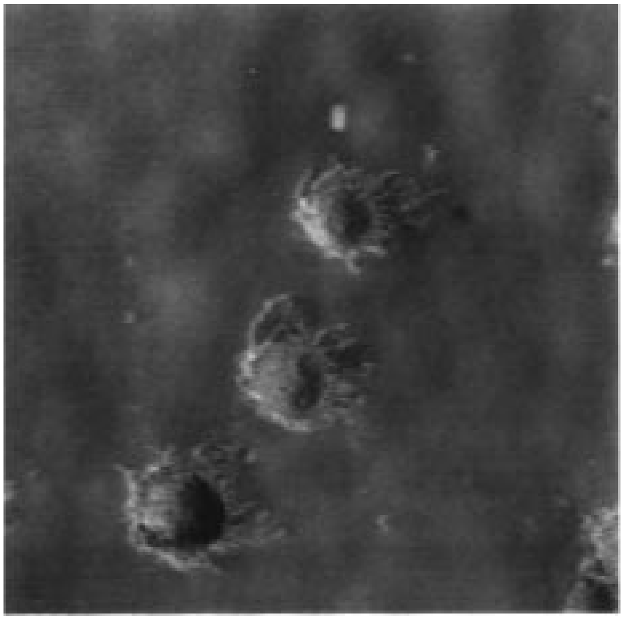

Figure 9. Phase image of PFMA8/10-PBMA blend of 1:100 composition ratio. The sample was annealed at 100 °C for 10 min. The contrast covers phase angle variations in the 10° range. The scan size was 1 μm.

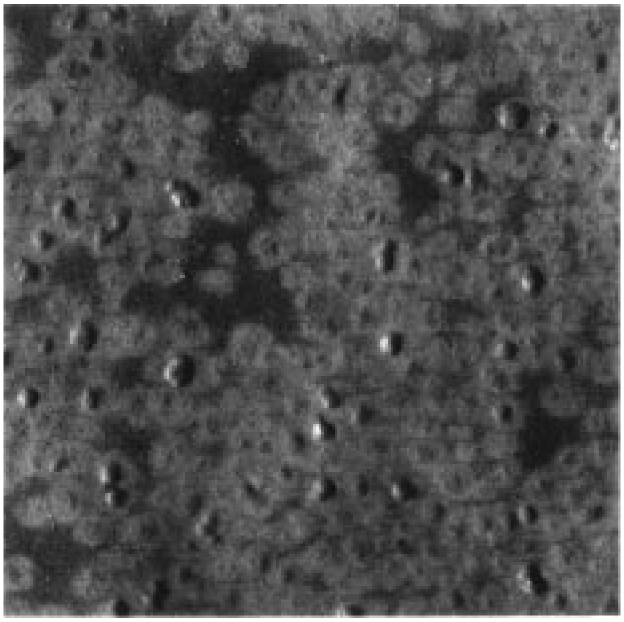

Figure 10. Phase image of PFMA8/10-PBMA blend of 1:100 composition ratio. The sample was annealed at 100 °C for 50 min. The contrast covers phase angle variations in the 10° range. The scan size was 5 μm.

described in the literature.[22-25] It should be noted that particles of brighter contrast were not detected in the phase images of the homopolymers. A further piece of evidence was found from phase images of PFMA/PBMA blends that were annealed above room temperature (Figures 8−10). Annealing at 65 °C for several hours led to complete film formation of PBMA; however, it did not alter the shape of PFMA particles because this temperature is well below the melting temperature of 91.4 °C. Figure 8 shows a phase image of PFMA/PBMA after annealing at 65 °C. It demonstrates that PBMA formed a dense film containing isolated embedded PFMA nanoparticles which are uniformly dispersed in the continuous PFMA matrix. In the phase image the more soft amorphous PBMA appears in dark contrast whereas the more rigid crystalline PFMA gives brighter contrast. Upon annealing at 100 °C for 15 min, the spherical PFMA particles show very rough surfaces and formation of a pronounced interfacial region. At prolonged annealing PFMA particles disintegrate (Figure 9), and the film surface is much rougher with brighter contrast. Since it is known that emulsifiers can migrate to the surface during annealing,[26] extraction with water was performed. Immersion in water for 3 days did not alter brightness and structure of TMAFM images. Most likely, PFMA films are formed as dense surface skin of a gradient film with higher fluorine content near the film surface as demonstrated in Figure 10. More than 20 wt % PFMA content is required to form a dense fluorinated skin! Accumulation of fluorine at the surface can be confirmed by means of ESCA and accounts for the improved water, oil, and soil repellence of such films. Applications of such latex blends in textile coatings with respect to the much less effective random copolymers of the same fluorine content will be reported elsewhere in more detail.[27]

Conclusions

Emulsion polymerization in the presence of 15−25 wt % acetone and cationic fluorine-free emulsifiers such as octadecylammonium bromide afford stable latex of fluorinated acrylates such as FMA and FA as well as fluorine-free acrylates such as BMA. Coagulation is also prevented by copolymerization of small amounts of butyl acrylate. The particle size is influenced by acetone and emulsifier content and can be varied between 50 and 300 nm. Due to the presence of the same emulsifier, fluorine-containing and fluorine-free latex can be blended together without encountering coagulation or premature phase separation of the latex. Morphology development during film formation is governed by the film-forming temperature and annealing conditions. Since the glass temperature of PBMA is much lower with respect to the melting temperature of PFMA or PFA, it is possible to form a dense PBMA film containing dispersed fluorine-containing nanoparticles embedded in the continuous PBMA matrix. Above the melting temperature of the fluorine-containing blend component, accumulation at the surface and film formation of the fluorine-containing polymer is achieved, thus producing gradient films with high fluorine skin. This enrichment of fluorine at the surface is the key to tailor dispersions that exhibit water, oil, and soil repellence at reduced total fluorine content. This finding could account for improved performance of such latex blends with respect to that of random copolymers containing the same monomer composition. Such stable nanoparticle blends represent attractive model systems to study interparticle interaction and multiphase polymer formation. TMAFM represents a very powerful tool that will help to achieve a better understanding of the role of nanostructure formation in coatings applications. Moreover, this basic insight in film formation of fluorine-containing acrylic latex blends will assist developments of new water, oil, and soil repellent environmentally friendly coatings with low fluorine content.

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