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ORIGINAL PAPER

Surface properties and chain structure of fluorinated acrylate copolymers prepared by emulsion polymerization

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Abstract The fluorinated copolymer poly (MMA–co–FMA), composed of methyl methacrylate (MMA) and 2-perfluorooctylethyl methacrylate (FMA), was prepared by emulsion polymerization using a pre-emulsified monomer addition process. The results showed that the contact angle of water on its solvent-borne film increased dramatically and reached 118° when the FMA content in the copolymer was only 0.65 mol%, approaching that of poly(2-perfluorooctylethyl methacrylate) homopolymer. Unlike the copolymer prepared by solution polymerization, X-ray photoelectron spectroscopy (XPS), and sum frequency generation (SFG) vibrational spectroscopy analysis results indicated that the fluorinated moieties in this polymer were very easily segregated at the surface of the film. The interfacial structure and properties of this polymer in solution were investigated using SFG, surface tension, and dynamic laser light scattering (DLS). It was found that emulsion polymerization produced a chain structure of the fluorinated copolymer similar to that of FMA capped PMMA, thereby providing a possible way to produce fluorinated end-capped polymers using a popular polymerization method.

Keywords Surface property · Fluorinated polymer · Emulsion polymerization · SFG · Microstructure

Introduction

Hydrophobic surfaces have a number of useful applications, such as in water and oil-repellent coatings, and for nonadhesive coatings which can repel soil, ice, and other unwanted contaminants. Fluorinated polymers are attractive functional

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materials, since the incorporation of fluorine is well known to be effective in producing a low energy surface [1–6]. Recently, it was found that the lowest surface energies of fluorinated polymers could be obtained by not only covering a surface with as many perfluoroalkyl groups as possible, but also by increasing the orientation of the perfluoroalkyl groups on the outermost layer of the polymer surface [7]. It is now widely accepted that the distribution of fluorinated segments greatly affects the surface activity. The segregation of fluorinated moieties in random copolymers will be constrained, due to the random distribution of fluorinated units in the polymer backbone.

An alternative approach is to change the chain molecular structure. Several studies have focused on the surface properties of block copolymers with fluorine-containing comonomers [8–14]. However, their fluorinated monomer content as reported was still relatively high and even reached 15 mol% [8, 13, 15–17]. Since block copolymers with a long fluorinated blocks are in favor of forming micelles with a core consisting of perfluorinated blocks [13, 15, 17], higher concentrations of non-fluorinated components can be localized at the surface due to micelle exposure during film formation [15]. Conversely, these copolymers exhibited a relatively high surface free energy. We proposed that fluorinated block copolymers with low fluorine content may favor segregation of fluorinated blocks on the surface of copolymers, which was confirmed by our previous study [18, 19]. Poly(methyl methacrylate) end-capped with several 2-perfluorooctylethyl methacrylate units (PMMA–ec–FMA) has been synthesized by ATRP. Hydrophobic surfaces having contact angles of water and paraffin oil of 120° and 84°, respectively, were prepared using the end-capped PMMA with only a few FMA units. However, it was found necessary to have more than 13.63 mol% FMA for PMMA–r–PFMA random copolymers to obtain similar values.

Hence, controlling the distribution of fluorinated segments is of importance as the first bench-mark for designing and constructing highly functionalized fluorinated polymer surfaces. Although ATRP represents one of the most versatile synthetic tools for preparing new polymer materials with well-controlled molecular weights and well-defined structures, one remaining challenge of ATRP is the difficulty to effectively separate the homogeneous catalysts from their products [21, 22]. It is both interesting and beneficial for industrial applications to find a simple way to produce end-capped PMMA with only a few FMA units. Emulsion polymerization is one possible method for producing blocky fluorinated copolymers [23–25]. Ha et al. prepared a series of latex particles by emulsion polymerization of the fluorinated monomers, heptadecafluorodecyl acrylate, and 2,2,-trifluoroethyl methacrylate [23]. The results showed that the batch emulsion polymerization produced latex particles with multi-block structure. Crevoisier et al. [24] compared the side-chain fluorinated copolymers prepared by both solution and emulsion polymerizations. It was found that a larger ratio of homotriads to heterotriads was associated with the presence of an increased block-like structure along the polymer chains in the case of emulsion process. However, the fluorinated monomer content was high. In our previous study [25], the fluorinated acrylate copolymer, poly (butyl methacrylate–co–dodecafluorheptyl methylacrylate), was prepared by emulsion polymerization using a pre-emulsified monomer addition process. The contact angle of water on the solvent-borne film increased dramatically and reached an equilibrium value (103°) when the fluorinated monomer content in the copolymer was only 0.97 mol%. Simultaneously, XPS results showed that the F/C ratio on the copolymer surface with only 0.97 mol% fluorinated monomer also reached equilibrium value. It is accordingly our goal to prepare a fluorinated acrylate copolymer by emulsion polymerization, in which the chains possess the end-capped polyacrylate with only a few FMA units.

In this study, the copolymers composed of methyl methacrylate and 2-perfluorooctylethyl methacrylate were prepared by emulsion polymerization, and surface properties and structures for both on their solvent-borne film and at the solution/air interface were investigated. It was found that the copolymers prepared by emulsion polymerization have chain architecture similar to that of end-capped polymethacrylate with FMA units.

Experimental

Materials

Methyl methacrylate (MMA) was washed by 5 wt% sodium hydroxide solution to remove inhibitor, and was then distilled under reduced pressure. 2-Perfluorooctylethyl methacrylate ($CH_2{=}C(CH_3){-}COOCH_2CH_2(CF_2)_7CF_3$; FMA, Aldrich Chemical Co.) had a purity above 97% and was accordingly used without further purification. The water-soluble initiator (potassium persulfate, $K_2S_2O_8$) and emulsifiers including sodium dodecyl sulfate (SDS) and dodecyl polyoxy ethylene (OP-10) were used without further purification. Deionized water was obtained by ion exchange. Other chemicals were of reagent grade and used without further purification.

Copolymer synthesis and sample preparation

Emulsion polymerization was carried out in a 100-ml reactor using a typical pre-emulsified monomer addition process [26]. A typical recipe is: MMA (15 g); $K_2S_2O_8$ (0.12 g); SDS (0.067 g), OP-10 (0.134 g); and deionized water (46.7 g). The mole ratio of FMA to MMA was changeable and the solid content of the final latex remained about 24 wt%. The synthesis of the poly(MMA–co–FMA) latex was performed as follows: part of the total water, emulsifiers, initiator, and all monomers were emulsified for 30 min by stirring and then dispersed by 40 kHZ ultrasonically for 15 min. The resulting monomer emulsion was then charged successively for 2 h into the reactor containing the remaining water, emulsifiers, and initiator at 80 °C. After completion of monomer introduction, the reaction was maintained for another 3 h. For the preparation of the solvent-borne film, the resulting latex particles were first precipitated in 5 wt% $CaCl_2$ solution. The resulting precipitates were washed with water several times after filtration. The precipitates were then dried under vacuum at 40 °C. The products were purified by two reprecipitation cycles using THF and methanol. The characteristics of these copolymers are listed in Table 1.

Table 1 Characteristics of the poly (MMA–co–FMA) copolymers used in this study

Sample	Mn × 10^{4c}	Mw/Mn[c]	W_F[d] (wt%)	FMA (mol%)[e]
E-1[a]	4.95	1.65	0	0
E-2[a]	4.33	1.77	1.99	0.65
E-3[a]	3.93	1.82	4.75	1.51
E-4[a]	4.52	1.99	10.62	3.83
E-5[a]	5.94	1.79	13.95	5.32
E-6[a]	4.63	2.01	17.72	7.13
$PMMA_{144}$-ec-$FMA_{2.3}$	1.92	1.27	4.78	1.57
S-1[b]	4.41	1.57	14.37	5.52

[a] Prepared by emulsion polymerization

[b] Prepared by solution polymerization

[c] Determined by GPC

[d] W_F represents fluorine content obtained from fluorine elemental analysis

[e] Calculated from fluorine element analysis results

The preparation of end-capped poly (methyl methacrylate) with 1.57 mol% FMA ($PMMA_{144}$–ec–$FMA_{2.3}$) by atom transfer radical polymerization (ATRP) and the preparation of the random copolymers of PMMA–r–PFMA by radical solution polymerization were described in a previous publication [18, 19]. The dried products were dissolved in cyclohexanone to make a 4 wt% solution. The films were prepared by casting the polymer solution onto clean glass slides and drying in air at 25 °C for 24 h and then under vacuum at 40 °C for 48 h.

Characterization

The molecular weight and molecular weight distribution (MWD) of the polymers were determined by gel permeation chromatography (GPC) using a Waters 515 GPC apparatus with THF as eluent at a flow rate of 0.5 ml/min. The GPC chromatograms were calibrated against standard polystyrene samples. The FTIR spectra of the copolymers were measured on a Nicolet Avatar 370 Fourier Transform Infrared (FTIR) spectrometer. X-ray photoelectron spectroscopy (XPS) was employed to characterize the surface composition of the copolymer films. The XPS experiments were carried out on a PHI5000C ESCA System with an Mg Kα X-ray source (1253.6 eV). The X-ray gun was operated at a power of 250 W and the high voltage was kept at 140 kV with a detection angle of 54°. The chamber pressure during analysis was about 1×10^{-8} Torr. All spectra were calibrated by the C1s peak of the C–C bond at 284.6 eV.

^1H NMR spectra were recorded on a Bruker Avance AV-400 NMR instrument in $CDCl_3$ solvent with tetramethylsilane (TMS) as internal standard. For triad investigation, polymers were analyzed by ^{13}C NMR in $CDCl_3$ solution at room temperature using a Bruker Advance AV-400 spectrometers, operating at a frequency of 100.6 MHz. Measurement were made on a 10% w/v solution of polymer. The chemical shift scale was calibrated on the basis of the solvent peak (77 ppm).

The intensities of each resonance for the pure PMMA were compared with the expected values to assure that the spectra were suitable for quantitative work [27].

Hydrodynamic diameters of the copolymers in solution were measured by dynamic light scattering using a Nicomp 380 NanoParticle Size Distribution Analyser (Particle Sizing Systems Ltd., USA). The polymer solutions were prepared at a concentration of 0.01 g/ml, and were filtered through a 0.45 μm PTFE membrane.

The contact angles on the film surfaces were measured by the Sessile drop method [10, 28] using a KRÜSS (Hamburg, Germany) DSA 10 goniometer. The contact angles reported in this study are the average of the values obtained from at least eight different points on the film surface. The experimental error for contact angle measurement is within the range of ±1°.

Sum frequency generation (SFG) vibrational spectroscopy

Sum frequency generation (SFG) vibrational spectra were obtained using a custom-designed EKSPLA SFG spectrometer, which has been described in detail by various researchers [20]. Briefly, the visible input beam at 0.532 μm was generated by frequency doubling a part of the fundamental output from an EKSPLA Nd:YAG laser. The IR beam, tunable between 1,000 and 4,300 cm^{-1} (with a line width <6 cm^{-1}) was obtained from an optical parametric generation/amplification/difference frequency generation (OPG/OPA/DFG) system based on LBO and AgGaS2 crystals, which were pumped by the second harmonic and the fundamental output of the laser. Both beams had a pulse width of about 30 ps, a repetition rate of 50 Hz, and a typical beam diameter of about 0.5 mm at the sample surface or interface. The incident angles of the visible beam and the IR beam were 60° and 55°, and their energies at the sample surface were about 230 and 130 μJ, respectively. In this study, SFG spectra with polarization combination ssp (s-polarized sum frequency output, s-polarized visible input, and p-polarized infrared input) were obtained.

Results and discussion

Characterization of fluorinated copolymers prepared by emulsion polymerization

Figure 1 shows the FTIR spectra of poly (MMA–co–FMA) prepared by emulsion polymerization and that of pure PMMA. When the FTIR spectra of the copolymers and PMMA were compared, two new absorption bands appeared at 660 and 708 cm^{-1} in the spectra of the former, and their intensities increased with increasing FMA content. These peaks were assigned to the rocking and wagging vibrations of CF2 groups [8]. In addition, the absorbance around 1,200–1,270 cm^{-1} for C–F stretching vibration bands overlapped with the C–O stretching vibration bands around 1,270–990 cm^{-1} [29, 30]. The ^{1}H NMR spectra of PMMA–co–PFMA and pure PMMA are presented in Fig. 2. Two new peaks at 4.25 and 2.45 ppm were observed in the spectrum of poly(MMA–co–FMA), which were assigned to the

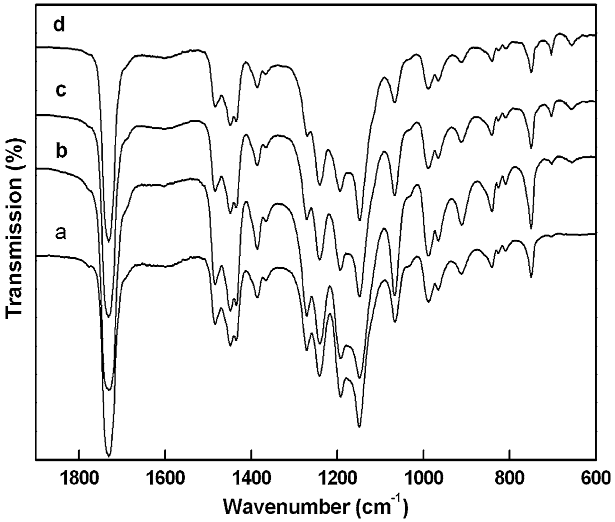


Fig. 1 FTIR spectra of pure PMMA (**a**), E-2 (**b**), E-4 (**c**), and E-6 (**d**)

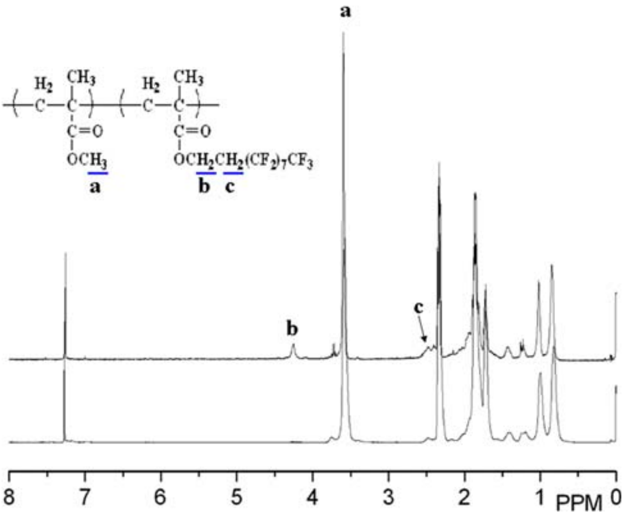


Fig. 2 ^{1}H NMR spectra of poly (MMA–co–FMA) (**a**) with 7.13 mol% FMA prepared by emulsion polymerization and pure PMMA (**b**)

protons of $–OC\underline{H}_2CH_2–(CF_2)_7CF_3$ and $-OCH_2C\underline{H}_2–(CF_2)_7CF_3$ in the FMA unit, respectively [14]. Moreover, it was found that the prepared poly(MMA-co-FMA) was soluble in tetrahydrofuran (THF). This suggests that the polymer used in this study was a copolymer, since the FMA homopolymer could not be dissolved in THF. These results also indicate that the FMA has copolymerized with MMA. The low FMA content and the intrinsic association of the FMA units made it difficult to use ^{1}H NMR to characterize the fluorinated units [31–33]. Thus, fluorine elemental analysis was employed to measure the fluorinated monomer content. Table 1 shows the characteristics of the copolymers utilized in the present study.

Surface properties and structure of the copolymers prepared by emulsion polymerization

The surface wettability of the poly (MMA–co–FMA) copolymers prepared by emulsion polymerization with various PFMA content was studied. Figure 3 shows that the contact angles of water and paraffin oil were dependent on the content of FMA in the copolymers. The contact angles of water on the surface of poly (MMA–co–FMA) increased sharply as the FMA content increased, reaching a value of 118° at 0.65 mol% FMA, approaching that of poly(2-perfluorooctylethyl methacrylate) homopolymer (120°) [13, 34]. A similar trend was observed for the contact angles of paraffin oil on the surface of copolymers. The paraffin oil contact angles on the poly (MMA–co–FMA) increased from 22° and reached a maximum of 80° with 0.65 mol% FMA. This result was similar to that of poly(methyl methacrylate) end-capped with 2-perfluorooctylethyl methacrylate units [18, 19]. The fluorinated polymer with only one FMA unit (MMA_{144}–ec–$FMA_{0.7}$, 0.47 mol%) exhibited excellent water and oil repellence, with the contact angles of water and paraffin oil on the surface of the films being about 120° and 84°, respectively. This finding was very different from that of the random copolymer prepared by solution

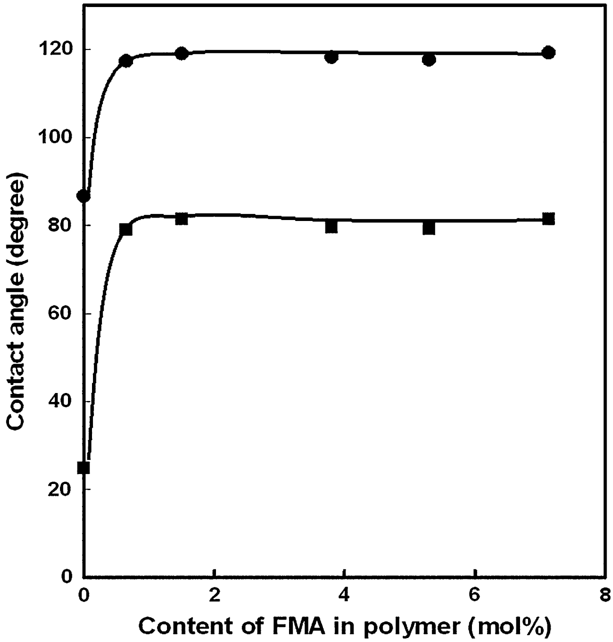


Fig. 3 Dependence of water (*filled circle*) and paraffin oil (*filled square*) contact angles on the content of FMA in copolymer prepared by emulsion polymerization

polymerization [18], which required as high as 13.63 mol% of FMA in the random copolymer to achieve a paraffin oil contact angle of 73°.

In order to investigate the water and oil repellency of the resulting fluorinated acrylate copolymer films in detail, the surface compositions of three polymer films with various FMA content were investigated by XPS measurements. The atomic ratios of fluorine to carbon (F/C) near the surfaces of these polymer films are given in Table 2. The F_{1s}/C_{1s} ratio of the copolymer surface dramatically increased to 0.67 when the FMA content was only 0.65 mol%, and then increased gradually to 0.75 as FMA content increased to 5.3 mol%. Figure 4 shows the XPS C1s core level spectra of fluorinated copolymers with various FMA content prepared by emulsion polymerization. The spectra were resolved into five Gaussian curve-fitted peaks: $-CF_3$ around 294.0 eV, $-CF_2-$ around 291.5 eV, $-C=O$ around 288.5 eV, $-C-O-C=O$ around 286.5 eV, and hydrocarbon ($-CH_n$: $n = 0$–3) around 284.6 eV, from high to low binding energy. These peak assignments agreed well with the reported values [13–15, 35, 36]. The surface composition is well known to have a large influence on the contact angles and the surface free energy. Table 2 summarizes the composition of the functional groups on the surface of the copolymer films with various FMA content. The concentration of $-CF_3$ and $-CF_2-$ groups on the copolymer surface were found to increase sharply with only a small amount of FMA, whereas the concentration of $-CF_3$ and $-CF_2-$ groups on the surface of the random copolymer prepared by solution polymerization increased gradually with only a larger increase of FMA [18]. For example, the poly(MMA–co–FMA) with 0.65 mol% FMA prepared by emulsion polymerization had 2.2% of $-CF_3$ and 16.9% of $-CF_2-$ on its surface, which increased gradually to 3.4 and 21.6% for the copolymer with 5.3 mol% FMA. The results above clearly suggest that the fluorinated moieties in the poly(MMA–co–FMA) prepared by emulsion polymerization aggregated easily near the film surface.

In order to understand the origin of the surface properties of poly (MMA–co–FMA) films prepared by emulsion polymerization, the conformation of the perfluoroalkyl side chains at the surface was investigated by surface-sensitive vibrational sum frequency generation spectroscopy (SFG). Surface-sensitive vibrational sum frequency generation spectroscopy (SFG) has emerged as a powerful tool for the study of the molecular structure of the polymer surfaces [37–41], which could uniquely probe the molecular spectroscopy and molecular group orientation at surfaces [41–46].

Figure 5 shows SFG ssp polarization combination spectra in the 2,800–3,000 cm^{-1} region of pure PMMA, the FMA capped poly(methyl methacrylate),

Table 2 Surface composition of PMMA–co–PFMA films with various FMA content

Sample	FMA (mol %)	F_{1s}/C_{1s}	Composition (%)				
			CF_3	CF_2	–C=O	–C–O–C=O	CH_n ($n = 0$–3)
E-2	0.65	0.67	2.2	16.9	14.6	14.6	51.8
E-3	1.5	0.72	2.9	20.2	16.3	16.3	44.4
E-5	5.3	0.75	3.4	21.6	15.4	15.4	44.3

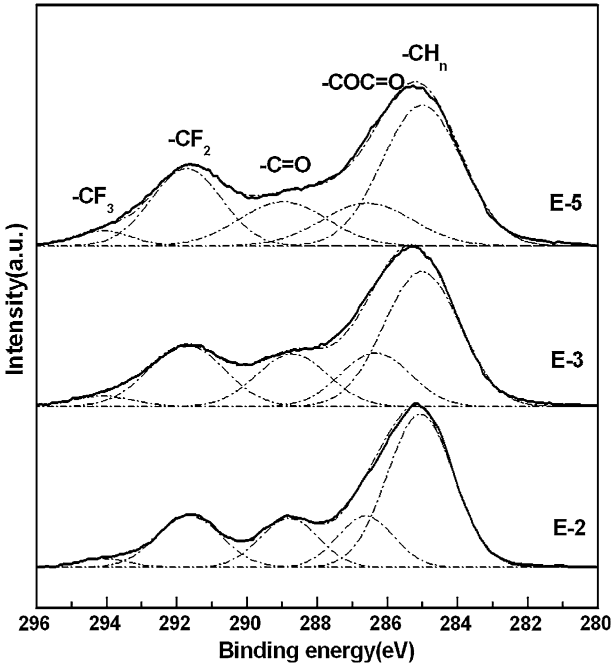


Fig. 4 XPS C_{1s} core level spectra of fluorinated copolymers with various FMA content prepared by emulsion polymerization

and poly (MMA–co–FMA) prepared by solution and by emulsion polymerization. There have been extensive studies on the assignment of the C–H stretching vibration in SFG-VS [41–46]. No SFG signals for C–F stretching modes were observed in the high frequency range of 2,700–3,100 cm^{-1} [46]. As observed in the literature on the ssp SFG spectra of pure PMMA, there are three bands at 2830, 2910, and 2950 cm^{-1}. However, a new peak was observed at 2,875 cm^{-1} in the SFG spectra of poly (MMA–co–FMA) prepared by emulsion polymerization, and its intensity increased slightly with increasing FMA content (Fig. 5b), while simultaneously, the peaks at 2,830 and 2,910 cm^{-1} disappeared. In addition, it was obvious, as shown in Fig. 5a that the spectrum of the copolymer prepared by solution polymerization was similar to that of pure PMMA, while the spectra of both the end-capped polymer and the copolymer prepared by emulsion polymerization films were very similar. The bands at 2,830 and 2,910 cm^{-1} are assigned to the harmonic or combination vibrations of the bending of –OCH_3 groups, respectively, which are enhanced by Fermi resonance [47]. The peak at 2,875 cm^{-1} was assigned to the symmetric stretching vibration of the methylene groups [CH_2(s)] connected to the perfluoroalkyl group [C_8F_{17}] [20]. According to the SFG results, the perfluoroalkyl groups in the copolymer prepared by emulsion polymerization segregated well to the film surface, and the PMMA segments were covered, similar to the FMA capped PMMA. When the poly (MMA–co–FMA) was prepared by solution polymerization, PMMA segments in the copolymer were exposed on the polymer surface.

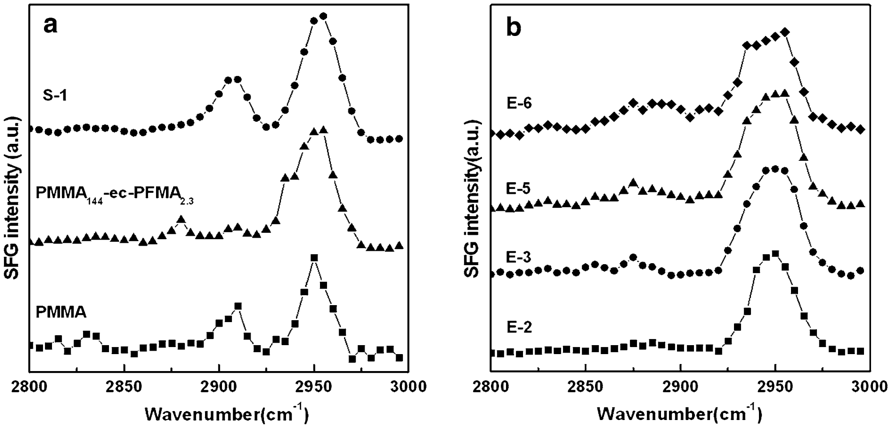


Fig. 5 SFG spectra (ssp) of pure PMMA, FMA capped PMMA, and poly (MMA–co–FMA) copolymer films

This result also correlates well with the results obtained from contact angle and XPS measurements.

Study on the structure of the copolymers by various techniques

Why was the surface structure and properties of the copolymer prepared by emulsion polymerization similar to that of the FMA capped polymer, completely different from that of one prepared by solution polymerization? A molecular-level self-consistent field theory was employed to study physical and thermodynamic properties of partially fluorinated poly(methyl methacrylate) chains in the vicinity of the polymer vapor interface [48]. The result indicated that both the surface tension and surface structure are very sensitive to the degree of its blockiness. The molecular sequence of the copolymer is one of the most important factors in lowering the surface free energy. Choi and co-workers investigated the surface properties of random and graft copolymers with perfluoroalkyl side chains and found that the graft copolymer surface had lower surface free energy than the random copolymer [49]. Therefore, chain architecture of the copolymer prepared by emulsion copolymer may be similar to that of the FMA-capped polymer.

In order to determine the statistics of the chains of the copolymers, ^{13}C NMR spectrum was employed. In the spectrum of the copolymers, the resonances of carbonyl, methine and α-methyl carbons provide information about how the monomer units are arranged along the copolymer chain. Particular interest may be drawn to the resonance of α-methyl carbons, many new signals will appear covering a range of about 6 ppm in chemical shifts (15–21 ppm) in which containing rich information about monomer unit sequence distributions [27, 50]. A new peak around at 18.2 ppm appeared in PMMA–b–PFMA block copolymer with 6.7 mol% FMA, which may be assigned to FMA–FMA–FMA triads. However, this peak cannot be observed in ^{13}C NMR spectrum of the copolymers presented in Table 1. The reason was attributed to low FMA content. For example, the amount of FMA units in copolymer was estimated about five for poly (MMA–co–FMA) with 1.5 mol% FMA according to fluorine content and the molecular weight, it is hard to determine the chain structure of the copolymer by ^{13}C NMR spectra. Therefore, the other relative techniques have to be employed to study the chain structure of these polymers.

Figure 6 shows the distributions of the hydrodynamic diameters of the poly (MMA–co–FMA) prepared by emulsion polymerization in cyclohexanone solutions. Three kinds of aggregates, below 20 nm, about 150 nm and about 400 nm, were found in poly(MMA–co–FMA) solution when FMA content was 0.65 mol%, in which the distributions of the large diameter aggregates are very wide. With increasing of FMA content in copolymers, only two kinds of aggregates, about 20 and 300 nm, existed in copolymers solution. At the same time, the size of the large diameter aggregates decreased and its distributions became narrow. The FMA capped polymer PMMA$_{144}$–ec–FMA$_{2.3}$ in cyclohexanone exhibits the micelle with an average diameter of 120 nm and very narrow distribution [19]. However, there are no obvious aggregates in the cyclohexanone solution of S-1 random copolymer

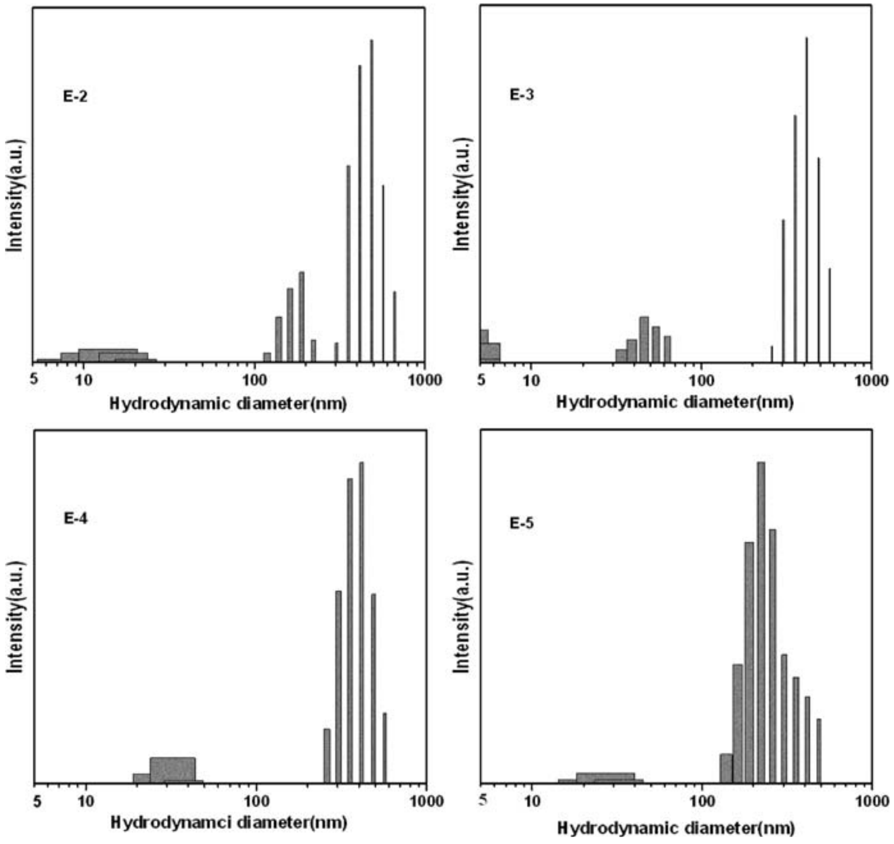


Fig. 6 Distributions of hydrodynamic diameters for poly (MMA–co–FMA) prepared by emulsion polymerization in cyclohexanone

prepared by solution polymerization. This result indicates that these copolymers formed micelles more readily than those copolymers prepared by solution polymerization, but this micelle formation is less facile than that which occurred with FMA-capped PMMA.

The surface activity of poly (MMA–co–FMA) copolymers prepared by emulsion polymerization in solution was determined by the Wilhelmy plate method. Figure 7 depicts the surface tension for the copolymers as a function of polymer concentration and FMA content. The surface tension of poly (MMA–co–FMA) copolymer with 0.65 mol% FMA dramatically decreased to 20.5 mN/m with increasing polymer concentration. A similar trend was found for the copolymers with various FMA content. The critical micelle concentration (CMC) of the copolymer decreased from 9.64×10^{-3} to 1.96×10^{-3} g/ml with increase of FMA content from 0.65 to 5.3 mol%. Compared to the end-capped PMMA [19], the CMC of the copolymer prepared by emulsion polymerization was one order higher. This means that this copolymer has less tendency to form micelles than the end-capped PMMA.

Figure 8 shows the SFG spectra at the solution/air interface of poly (MMA–co–FMA) copolymers with various FMA content in cyclohexanone. Two peaks from pure cyclehexanone were observed at 2,855 and 2,945 cm^{-1}, assigned as the symmetric stretch and Fermi resonance of $–CH_2–$ groups [51]. A new band appeared at 2,910 cm^{-1} for pure PMMA and poly (MMA–co–FMA) prepared by solution polymerization, while a new shoulder peak appeared at 2,930 cm^{-1} for the end-capped PMMA with FMA. The bands at 2,930 and 2,910 cm^{-1} were attributed to the asymmetric stretching vibration of the methylene groups [CH_2(s)] connected to

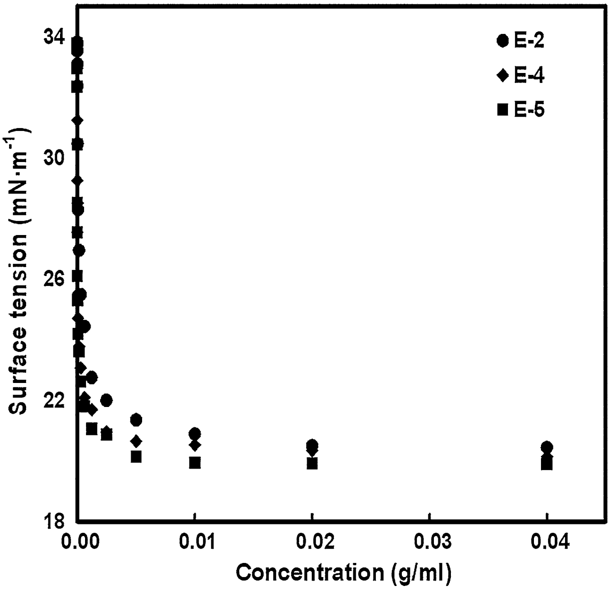


Fig. 7 Surface tension as a function of poly (MMA–co–FMA) concentration in cyclohexanone

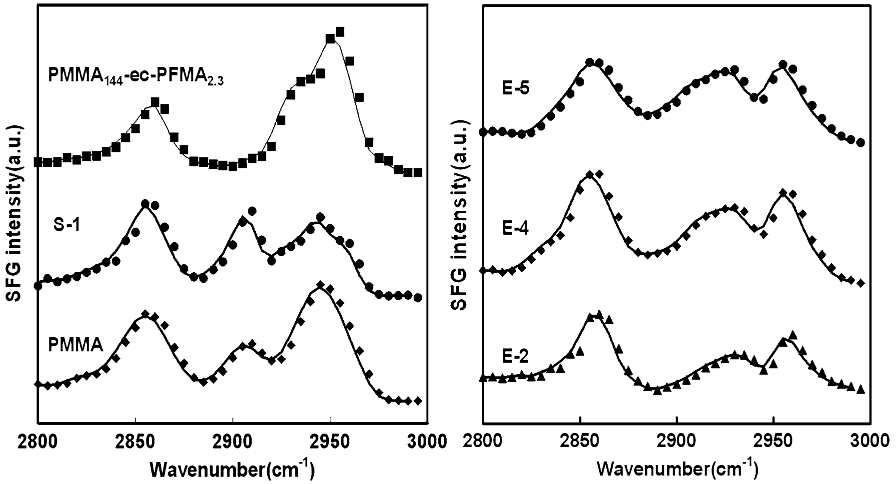
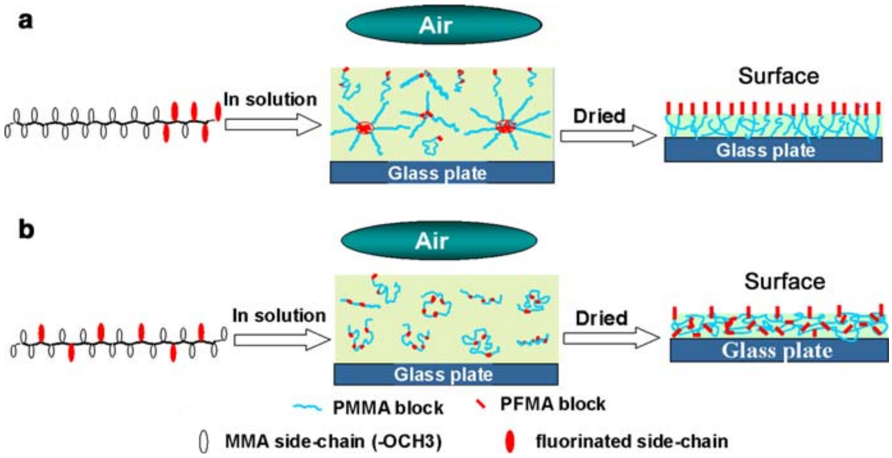


Fig. 8 SFG spectra (ssp) of the copolymers in solution with cyclohexanone as solvent

the perfluoroalkyl group [C_8F_{17}] [19] and vibrations of –OCH_3 groups in PMMA [47, 51], respectively. The SFG spectra from the solution/air interface for poly (MMA–co–FMA) copolymers prepared by emulsion polymerization were different from the spectra of both the end-capped polymers and the copolymers prepared by solution polymerization. A broad peak was observed between 2,900 and 2,940 cm^{-1}, indicating that the interfacial structure of poly (MMA–co–FMA) prepared by emulsion polymerization exhibits the characteristics of both random chains and block chains. Therefore, according to the above results obtained by various techniques, it may be concluded that a block-like structure for the poly (MMA–co–FMA) copolymers was formed during emulsion polymerization, as depicted in Scheme 1a. Thus, only loosely packed and unstable micelles were formed in cyclohexanone solution, and the interfacial structure at the air/solution interface exhibited the characteristics of both random chains and block chains. At the same time, as this copolymer possesses a special push-me/pull-you architecture, the perfluoroalkyl side chains can easily segregate on the surface and form an ordered structure, as shown in Scheme 1a. However, the fluorinated moieties in copolymers prepared by solution polymerization were limited in their ability to effectively segregate on the surface, due to the random distribution of the fluorinated units in the molecular chain, as shown in Scheme 1b.

Although no reactivity ratio of MMA with FMA was available in the literature, the reactivity ratio of 1,1-dihydroperfluoroheptyl methacrylate (FHMA) and methyl methacrylate (MMA) was reported to be $r_{\mathrm{FHMA}} = 1.31$, $r_{\mathrm{MMA}} = 0.76$, respectively [52], while the reactivity ratio of perfluoroalkylethyl acrylate (FA) and methyl acrylate (MA) was reported to be $r_{\mathrm{FA}} = 1.2$, $r_{\mathrm{MA}} = 0.83$, respectively [53]. Therefore, it is reasonable to deduce $r_{\mathrm{FMA}} > 1$ and $r_{\mathrm{MMA}} < 1$ due to similar structure of fluorinated monomer. The monomer transport from the emulsion droplets to the growing particles is essential in conventional emulsion polymerization. During polymerization, the partitioning of the different monomers between



Scheme 1 Segregation of the fluorinated components in poly (MMA–co–FMA) copolymer prepared by (**a**) emulsion polymerization and (**b**) solution polymerization, during film formation

the organic and aqueous phase is a crucial factor to determine the composition of the copolymer chains formed due to the heterogeneous nature of the reaction. As a result, depending on the monomer polarity and reactivity as well as solubility in water, statistical copolymerization in emulsion polymerization is doubtful. Some other studies have shown that the copolymer structure becomes rather blocky by varying the type of polymerization [23, 24]. The reason why the blocky structure of fluorinated copolymer was formed by emulsion polymerization was still unclear. Further investigation on this aspect will be undertaken and reported in the future.

Conclusions

Hydrophobic surfaces having contact angles of water and paraffin oil of 118° and 80°, respectively were prepared using poly (MMA–co–FMA) copolymers with 0.65 mol% 2-perfluorooctylethyl methacrylate prepared by emulsion polymerization. However, more than 13.63 mol% FMA was necessary for random copolymers prepared by solution polymerization to reach similar values of the contact angles. Although there was no direct evidence regarding chain microstructure that could be obtained by ^{13}C NMR due to the low fluorinated monomer content, capped-like polymers appear to be produced by emulsion polymerization. This was confirmed by investigating both their solvent-borne film surface structure and solution properties using various techniques. This special push-me/pull-you architecture was in favor of fluorinated moieties self assembling to ordered and close-packed structures on the surface during film formation. Herein, we have shown a possible way to produce fluorinated end-capped polymers by a popular method, namely, emulsion polymerization.

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