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Solvent effect on the film formation and the stability of the surface properties of poly(methyl methacrylate) end-capped with fluorinated units

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Abstract

The surface structure and stability (the resistance to surface reconstruction) of end-capped poly(methyl methacrylate) films were greatly affected by the solvents used for film preparation. Films of end-capped PMMA with about four 2-perfluorooctylethyl methacrylate units cast with benzotrifluoride solution exhibited excellent stability and resistance to polar environments compared with those cast with cyclohexanone and toluene solutions. The observed difference in stability between these fluorinated surfaces is attributed to their surface microstructures formed during the film formation processes, which are closely related to the associative behavior of the end-capped PMMA in the solution. A relatively perfect close-packed and well-ordered structure of the perfluoroalkyl side chains at the surface of the PMMA_{857}-ec-$\text{FMA}_{3.3}$ film was formed when the film was cast with benzotrifluoride solution, in which only unimers existed. This study indicates that such a solvent effect may be used to promote the formation of a well-ordered packing structure of the fluorinated moieties at the film surface. The ordering of the packing structure is to a certain extent more important than the content of the fluorinated moieties at the surface for improving the surface stability.

Keywords: Hydrophobic surface; Perfluoroalkyl side chain; Surface structure; End-capped poly(methyl methacrylate); Solvent effect

1. Introduction

Fluorinated polymers are well-known low surface free energy materials, which have been widely applied in the modification of surfaces such as coatings and nonwetting biological applications to confer hydro- and oleophobicity upon them [1,2]. However, fluorinated polymers undergo rapid rearrangement when the polymer surface contacts water, in order to minimize the interfacial free energy; thus the high contact angle observed on dry surfaces quickly decreases in wet conditions [3–6]. This decrease in contact angle is undesirable for their long-term use in polar environments [7,8]. It is accordingly challenging to fabricate stable and low surface energy surfaces of fluorinated polymers.

It was reported that the packing density of fluorocarbon segments not only determines their surface free energy, but ultimately influences the stability of the surface and its resistance to surface reconstruction [3,6,9,10]. The undesired surface reconstruction effects can likely be minimized by increasing the packing density of the self-assembled fluorocarbon chain monolayers [6]. It is well known that low surface free energy fluorinated moieties always preferentially occupy the air-polymer interface via the process of surface segregation, which is affected by solvent when the film is prepared using a polymer solution [11,12]. In order to use very small amounts of fluorinated species to obtain optimally low wettability, poly(butyl methacrylate) and poly(methyl methacrylate) end-capped with 2-perfluorooctylethyl methacrylate (FMA) units were synthesized, and their surface properties were investigated [13,14]. We found that only a few 2-perfluorooctylethyl methacrylate units at the PMMA or PBMA chain ends are required to greatly im-

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prove their hydro- and oleophobicity, with water and paraffin oil contact angles of 120° and 84°, respectively.

The preparation of fluorinated polymer surfaces with perfectly ordered packing of perfluorinated species by controlling the solvent properties presents a new possibility in the area of fluorinated polymer surfaces. In this study, the solvent effects in film formation on the surface structure and the stability of the surface properties of end-capped poly(methyl methacrylate) with 0.38 mol% 2-perfluorooctylethyl methacrylate films are investigated.

2. Materials and methods

2.1. Sample preparation

Methyl methacrylate (MMA) and 2-perfluorooctylethyl methacrylate ($CH_2{=}C(CH_3)–COOCH_2CH_2(CF_2)_7CF_3$, Aldrich) (FMA) were washed with 5 wt% NaOH solution and deionized water, dried through CaH_2, and then vacuum-distilled before polymerization. CuBr, ethyl 2-bromopropionate and N,N,N',N',N''-pentamethyl-diethylenetriamine (PMDETA) were purchased from Aldrich and used as received. Cyclohexanone was distilled twice under reduced pressure in the presence of CaH_2. Other reagent grade chemicals were purchased from Shanghai Reagent Co. and used without further purification.

The end-capped poly(methyl methacrylate) with 0.38 mol% 2-perfluorooctylethyl methacrylate ($PMMA_{857}$-ec-$FMA_{3.3}$) was synthesized using atom transfer radical polymerization (ATRP) as described in a previous publication [14]. Upon completion of the ATRP experiment, the polymerization mixture was diluted with THF and precipitated in methanol after passing through an alumina column. The product was dried under vacuum at room temperature. The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) were 87,500 and 1.34, respectively.

The films were prepared by casting 4 wt% polymer solutions on clean glass slides, dried in air for 24 h and then at 40 °C under vacuum for 48 h. Cyclohexanone, toluene and benzotrifluoride were used as solvents.

Fused silica substrate (1 in. diameter, 1/8 in. thick) was purchased from ESCO Products Inc., China. A polymer film was prepared by solution cast directly on the silica substrate, dried in air for 24 h and then at 40 °C under vacuum for 48 h for sum frequency generation (SFG) vibrational spectroscopy measurement.

2.2. Measurements

The molecular weight and polydispersity of the polymers were determined using gel permeation chromatography (GPC) (Waters 1500) with THF as eluent, at a flow rate of 0.5 ml/min. Polystyrene standards were used to generate a calibration curve. X-ray photoelectron spectroscopy (XPS, PHI5000C ESCA System) was employed to characterize the films with a Mg$K\alpha$ X-ray source (1253.6 eV). The X-ray gun was operated at a power of 250 W and the voltage was maintained at 140 kV. Spectra were acquired at three different takeoff angles $\theta = 45°$, 60°, and 90°. Here, the takeoff angle is defined as the angle between the film plane and the entrance lens of the detector optics. All spectra were calibrated by the C_{1s} peak of the C–C bond at 284.6 eV.

X-ray diffraction profiles were obtained using a Rigaku Denki RINT 2000 diffractometer with symmetric reflection geometry. Samples were irradiated by Ni-filtered Cu$K\alpha$ radiation, generated at 40 kV, with 20 mA current. Nanoscale morphological surface properties were measured using AFM NTEGRA (NT-MDT, Russia). The topography and phase images were obtained in the intermittent contact mode with Si-cantilevers, spring constant $k = 5.5$ N/m (NSG01, NT-MDT, Russia). The measurements were performed in air at room temperature at a humidity of 45–50%. The surface roughness was evaluated by the root mean square (RMS) value from the AFM image of the film.

Water and paraffin oil contact angles on the films were measured by the Sessile drop method using DSA-10 drop shape analysis (Krüss Co., Germany) at 25 °C. The volume of the liquid drops used was 3 µl. Variations in surface properties of polymer films during exposure to water were measured using a previously published method [14]. Each sample was coated on a glass slide and immersed in water at various temperatures for a certain time. Each time the sample was removed from water, it was immediately cooled in room temperature water for 3 min to slow the surface reconstruction during the measurements, and then dried quickly with a stream of nitrogen prior to the contact angle measurement. In order to ensure that the results were sufficiently credible, the experimental errors in measuring the θ values were evaluated to be less than ±1°.

Sum frequency generation (SFG) vibrational spectra were obtained by a custom-designed EKSPLA SFG spectrometer, which has been described in detail by various researchers [15–17]. 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 1000 and 4300 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 $AgGaS_2$ crystals, which were pumped by the second harmonic and the fundamental output of the laser. Both beams had a pulse width of ∼30 ps, a repetition rate of 50 Hz, and a typical beam diameter of ∼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 ∼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 collected.

Hydrodynamic diameters of $PMMA_{857}$-ec-$FMA_{3.3}$ in each solution were measured by dynamic light scattering with a 90Plus NanoParticle Size Distribution Analyser (Brookhaven Instruments Ltd., UK). The polymer solutions were prepared at a concentration of 0.01 g/ml, and were filtered through a 0.45 µm PTFE membrane.

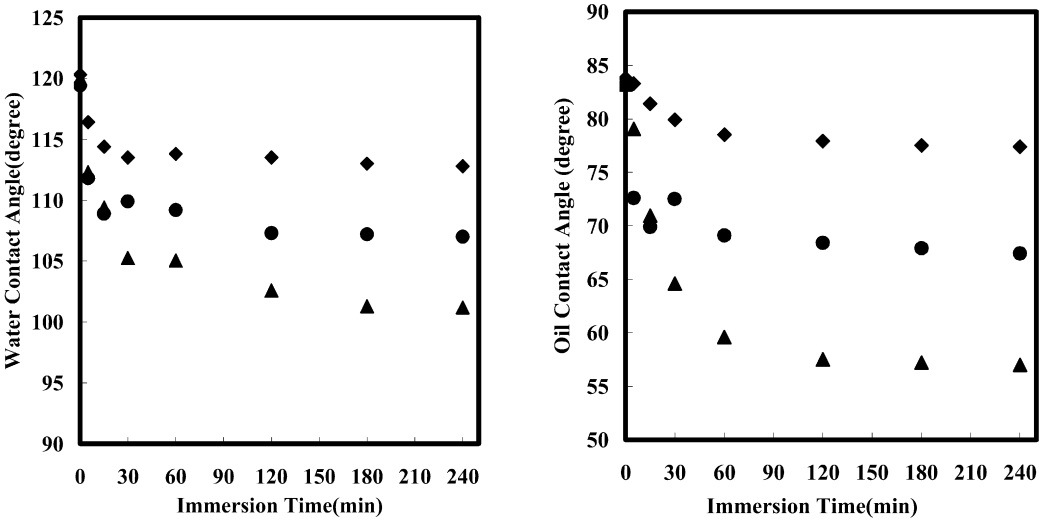


Fig. 1. Time-dependent water and oil contact angles of end-capped PMMA with 0.38 mol% FMA cast from benzotrifluoride (◆), cyclohexanone (●) (published in Ref. [14]) and toluene (▲) solutions immersed in water at 50 °C.

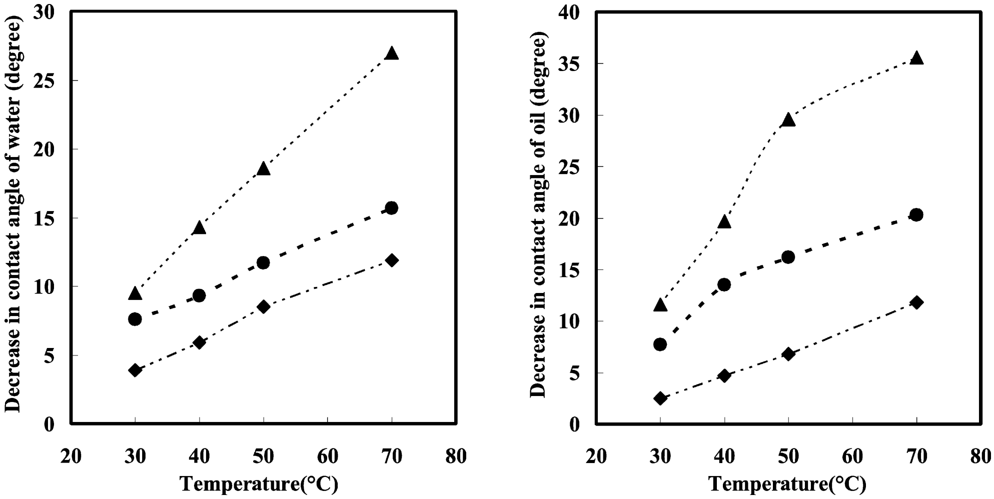


Fig. 2. Effect of water temperature on the decrease in water and oil contact angles of end-capped PMMA with 0.38 mol% FMA cast from benzotrifluoride (◆), cyclohexanone (●) (published in Ref. [14]) and toluene (▲) solutions after exposure in water for 3 h.

3. Results and discussion

3.1. Effect of film-forming solvents on surface properties of PMMA$_{857}$-ec-FMA$_{3.3}$ films

The surface stabilities of the films were compared by immersing them in water at 50 °C. Fig. 1 shows that regardless of solvent, the contact angles of water and paraffin oil on the surface of the PMMA$_{857}$-ec-FMA$_{3.3}$ films were about 120° and 84°, respectively, which were the same as those of poly(2-perfluorooctylethyl methacrylate) homopolymer (120°) [11,18]. However, a great difference in the surface stability was found when the films were prepared using different solvents. The water contact angle of the PMMA$_{857}$-ec-FMA$_{3.3}$ film cast from benzotrifluoride solution only dropped to around 114° and became stable at 113° after exposure in water for 4 h. Its oil contact angle decreased from 84° to 77°. These values represent only a 6.8% and 8.3% decrease in water and oil contact angles, respectively. The water and oil contact angles of the film cast from toluene solution rapidly decreased by about 20° and 29°, respectively, with the same treatment. It is evident that the PMMA$_{857}$-ec-FMA$_{3.3}$ film prepared by casting benzotrifluoride solution exhibits the best stability and resistance to the polar environments. Similar results were obtained after water immersion at various temperatures, as shown in Fig. 2.

3.2. Effect of film-forming solvents on surface structure of PMMA$_{857}$-ec-FMA$_{3.3}$

It is known that, in addition to the surface chemical composition, surface roughness also plays a very important role in determining the wettability of a film [19,20]. Tapping mode AFM with topographical detection has been successfully used to demonstrate nanoscale surface roughness of films [21]. The three-dimensional AFM images of the end-capped PMMA films cast from the various solutions are shown in Fig. 3. These

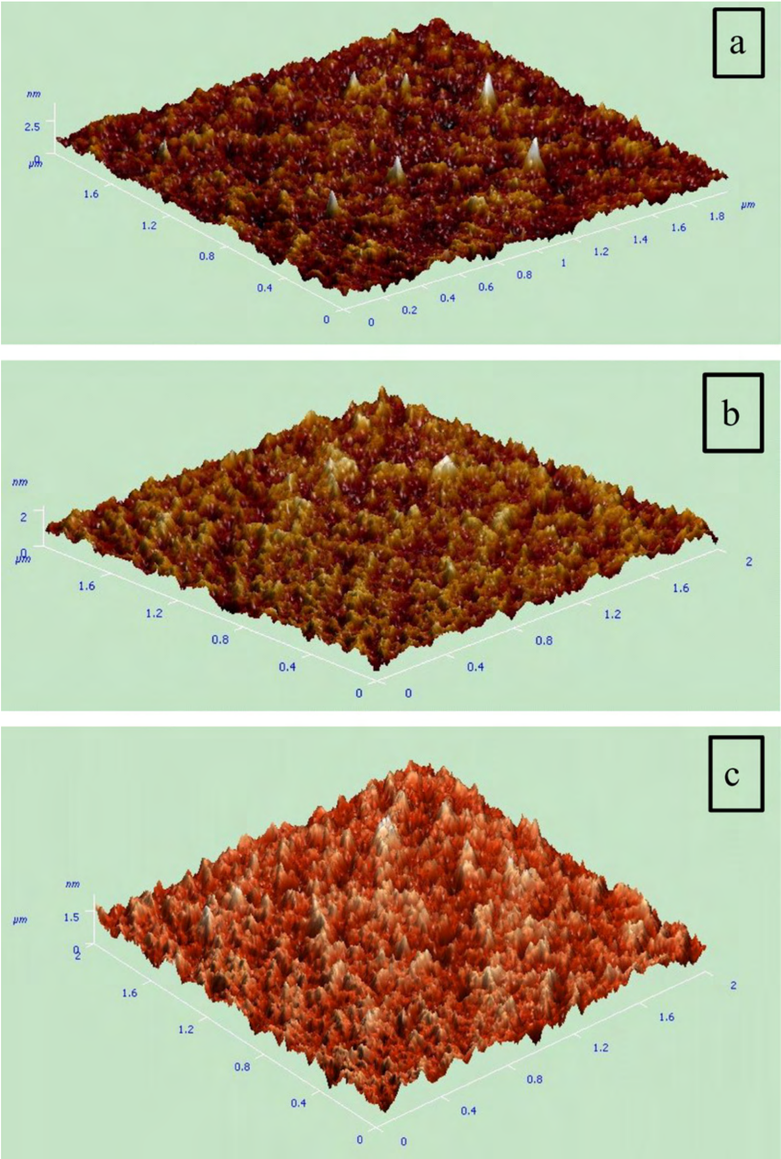


Fig. 3. AFM images of the $PMMA_{857}$-ec-$FMA_{3.3}$ film surfaces cast from toluene (a), cyclohexanone (b) and benzotrifluoride (c) solutions.

films possessed a very smooth and flat surface, with the RMS values of all the three films below 4.0 nm. This indicates that the effect of physical roughness on the contact angle can be considered negligible [20]. In other words, this suggests that the difference observed in surface properties of the films cast from various solutions in this study is governed primarily by the surface chemical composition rather than by surface roughness.

The surface enrichment of the fluorinated species in the films was investigated by XPS. The analysis depth, d, is controlled by the mean free path [22] of the ejected photoelectron through the following simplified equation [23]:

$$d = 3\lambda \sin\theta,$$

where λ is the inelastic mean free path of the electron and θ is the takeoff angle. A nondestructive depth profile analysis can be obtained by changing the takeoff angle and the analysis depth will increase with increasing value of the takeoff angle. The atomic ratios of fluorine to carbon (F_{1s}/C_{1s}) near the surfaces of the polymers are shown in Table 1. It was observed that the F_{1s}/C_{1s} ratio of $PMMA_{857}$-ec-$FMA_{3.3}$ film cast by benzotrifluoride was 1.083 when the takeoff angle was 45°. However, the F_{1s}/C_{1s} ratios were only 0.610 and 0.367 near the end-capped PMMA surfaces cast by cyclohexanone and toluene, respectively. At the same time, the F_{1s}/C_{1s} ratio decreased with increasing film depth from the top surface of the films cast from benzotrifluoride or cyclohexanone solutions. However, a completely inverse trend was observed for the film surface cast by toluene solution.

Fig. 4 shows the XPS C_{1s} core level spectra of $PMMA_{857}$-ec-$FMA_{3.3}$ films cast from various solutions at 45°, 60° and 90° takeoff angles. 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. The peak assignments agree

Table 1
Surface composition of PMMA$_{857}$-ec-FMA$_{3.3}$ films cast from different solutions

Solvent	Takeoff angle (°)	Atomic ratio (F_{1s}/C_{1s})	Surface composition (%)				
			–CF_3	–CF_2–	–C=O	–COC=O	–CH_n
Benzotrifluoride	45	1.083	4.3	32.9	10.9	10.9	40.9
	60	0.974	3.9	27.9	12.2	12.3	43.6
	90	0.853	3.7	21.3	14.3	14.3	46.5
Cyclohexanone	45	0.610	2.1	16.9	13.8	13.6	53.5
	60	0.454	1.0	8.1	16.3	16.3	58.3
	90	0.393	0.5	5.8	16.9	16.9	60.0
Toluene	45	0.367	0.4	5.6	13.5	13.6	67.0
	60	0.456	1.0	8.2	12.7	12.8	65.3
	90	0.579	1.8	13.0	11.3	11.3	62.6
Toluene[a]	45	0.503	1.2	10.6	12.8	12.8	62.6
	60	0.373	0.4	6.8	14.5	14.5	63.9
	90	0.321	0.4	5.2	14.3	14.3	65.9
Cyclohexanone[a]	45	0.659	2.3	17.2	13.7	13.7	53.1
	60	0.554	1.4	11.1	14.7	14.7	58.1
	90	0.476	1.1	8.7	14.8	14.8	60.6
Benzotrifluoride[a]	45	1.074	4.2	33.0	10.9	10.9	40.9
	60	1.004	4.0	28.2	12.1	12.2	43.5
	90	0.753	2.8	19.3	14.3	14.3	49.3

[a] The films were heated at 120 °C under vacuum for 24 h.

well with previously reported values [11,24–26]. Table 1 summarizes the composition of the functional groups at various probe depths of PMMA$_{857}$-ec-FMA$_{3.3}$ films cast from different solutions. The concentration of –CF_3 and –CF_2– groups near the surface of the films prepared by benzotrifluoride or cyclohexanone solutions decrease gradually with increasing analysis depth, whereas those near the surface prepared by toluene solution increase gradually with increasing takeoff angle. At the same time, the PMMA$_{857}$-ec-FMA$_{3.3}$ film cast with benzotrifluoride solution had 4.3% of –CF_3 and 32.9% of –CF_2– on its surface at a 45° takeoff angle, which was far higher than those for the films cast by cyclohexanone or toluene solutions. A high segregation of perfluoroalkyl side chains (–CF_3 and –CF_2–) at the surface was revealed from the spectrum of PMMA$_{857}$-ec-FMA$_{3.3}$ film cast with benzotrifluoride solution, whereas the concentrations of the other three components based on methacrylate backbones were higher for the films with cyclohexanone and toluene solutions. The results above clearly suggest that the fluorinated moieties in the end-capped PMMA aggregated more easily at or near the surface when the film was cast with benzotrifluoride solution.

Fig. 5 shows the X-ray diffraction profiles of PMMA$_{857}$-ec-FMA$_{3.3}$ films from various solutions. The films cast by benzotrifluoride and cyclohexanone solutions exhibited a crystalline diffraction peak at around $2\theta = {\sim}17°$ overlapped with an amorphous halo (from the curve-resolved spectra with dotted line shown in Fig. 5), together with the additional weak peaks in the small-angle region ($2\theta = 3°, 6°$). These peaks arise from the self-assembled structure of perfluoroalkyl side chains [3,11,24,27]. The diffraction peaks in the small-angle region around $2\theta = 3°$ and $6°$ amount to ca. 30 and 15 Å, respectively. These peaks could be assigned as the interferences from first- and second-order spacings, reflecting a double-layer packing and a single-layer packing structure of the side chains. The crystalline peak (located at $2\theta = 17.2°$) is equivalent to 5.2 Å according to Bragg's equation. This reflection corresponds to the interside-chain interference from the hexagonal packing of perfluoroalkyl side chains [11,24,28]. Compared with diblock copolymers with higher FMA content (15.2 mol%) [11], the diffraction peaks associated with the self-assembled perfluoroalkyl side chains were much weaker and broader, which can be attributed to the fact that a well-ordered packing of perfluoroalkyl side chains was not possible due to low FMA content. Nevertheless, it is obvious that the film cast with benzotrifluoride solution exhibits a stronger peak, which indicates better hexagonal packing of perfluoroalkyl side chains compared with the film cast with cyclohexanone solution. Simultaneously, the XRD profile of the film cast with toluene solution is obviously different from those of the other films. The diffraction peak around $2\theta = 13°$ was observed without any weak peak in the small-angle region, which is very similar to that observed in the diffraction profile of the pure PMMA film. This peak was attributed to an amorphous halo of PMMA. According to the result above, an ordered and close-packed structure, such as the double-layered and hexagonal packing of the perfluoroalkyl side chains, was formed when cyclohexanone and benzotrifluoride were used as solvent, whereas this structure was not observed for the film obtained from casting with toluene solution.

In order to understand the origin of the surface properties of MMA$_{857}$-ec-FMA$_{3.3}$ films affected by solvent, the conformation of perfluoroalkyl side chains at the surface was investigated by surface-sensitive vibrational sum frequency generation spectroscopy (SFG). SFG has emerged as a powerful tool for the study of the molecular structure of the polymer surfaces [16,29–36]. SFG can uniquely probe the molecular spectroscopy and

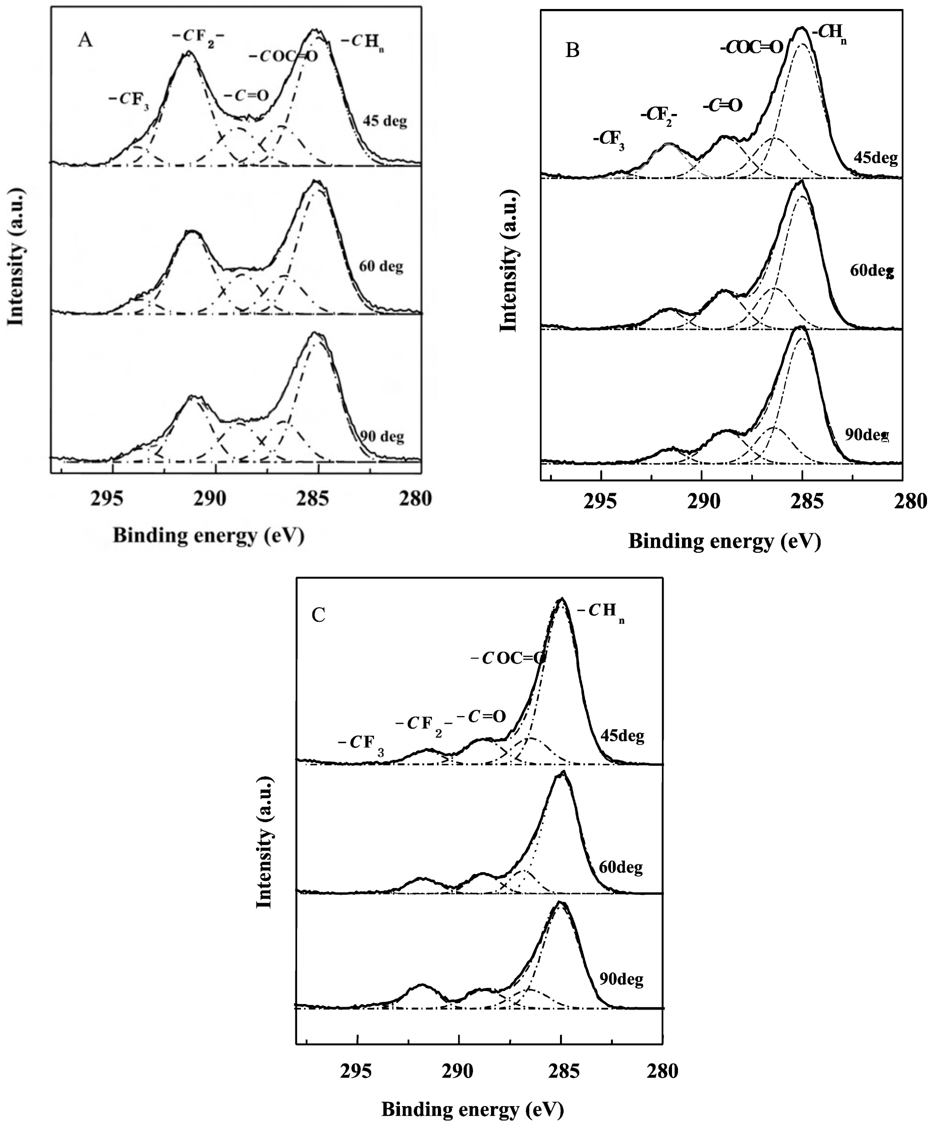


Fig. 4. XPS C_{1s} core level spectra of fluorinated copolymer film cast by solutions with benzotrifluoride (A), cyclohexanone (B) and toluene (C) as solvents at 45°, 60° and 90°.

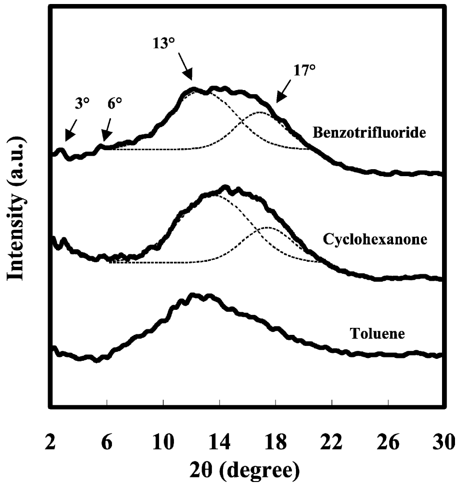


Fig. 5. X-ray diffraction profiles of $PMMA_{857}$-ec-$FMA_{3.3}$ films cast from benzotrifluoride, cyclohexanone (published in Ref. [14]) and toluene solutions.

molecular group orientation at surfaces which other surface-sensitive techniques cannot detect [17,37–46]. As revealed by SFG spectroscopy, the surface of polystyrene is covered with phenyl groups standing perpendicular to the surface or with a slight tilt, and the backbones of polymers are rarely observed [29]. Knowledge of the local conformation of the side chains at the surface is extremely important for understanding the surface properties of polymers.

Fig. 6 shows SFG spectra in the 2800–3000 cm^{-1} region, which corresponds to the C–H stretching vibrations, with an ssp polarization combination of pure PMMA and $PMMA_{857}$-ec-$FMA_{3.3}$ films cast from different solutions in the ambient condition. p and s denote the polarized light perpendicular and parallel to the surface, respectively. The first s, second s, and last p denote the polarizations of SFG, visible, and infrared light, respectively. There have been extensive studies on the assignment of the C–H stretching vibration in SFG-VS [17,42,43,47]. As observed in the literature on the ssp SFG spectra of pure

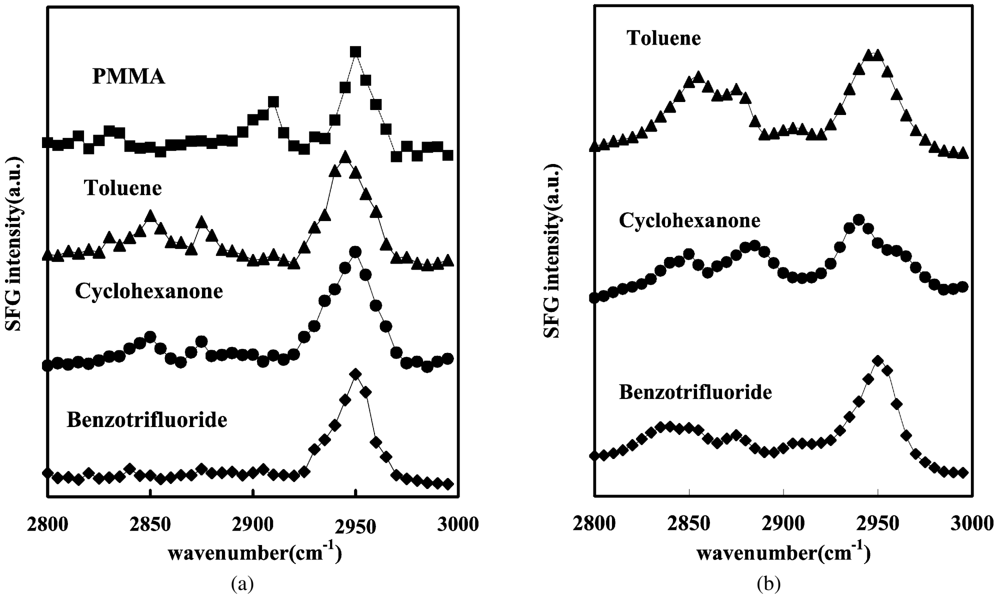


Fig. 6. SFG spectra (ssp) of PMMA$_{857}$-ec-FMA$_{3.3}$ films (a) cast by benzotrifluoride (◆), cyclohexanone (●) and toluene (▲) solutions and (■) pure PMMA film cast by cyclohexanone solution. (b) SFG spectra (ssp) of the corresponding films heated at 120 °C under vacuum for 24 h.

PMMA, there are three bands at 2830, 2910 and 2950 cm^{-1}. The strong band at 2950 cm^{-1} is assigned to the symmetric stretching vibration of the ester methyl groups [16,36,48]. The other bands at 2830 and 2910 cm^{-1} are assigned to the harmonic or combination vibrations of the bending of –OCH$_3$ groups, respectively, which are enhanced by Fermi resonances [48]. However, the ssp SFG spectra of PMMA$_{857}$-ec-FMA$_{3.3}$ films cast with different solutions in this study were quite different from those of the homo PMMA. As shown in Fig. 6, there are three main peaks at 2850, 2875 and ~2950 cm^{-1} in the SFG spectra of PMMA$_{857}$-ec-FMA$_{3.3}$. The intensities of the peaks at 2850 and 2875 cm^{-1} decreased with the following order of the solvents used: toluene, cyclohexanone, and benzotrifluoride. These two peaks essentially disappeared when benzotrifluoride was used as the film-forming solvent.

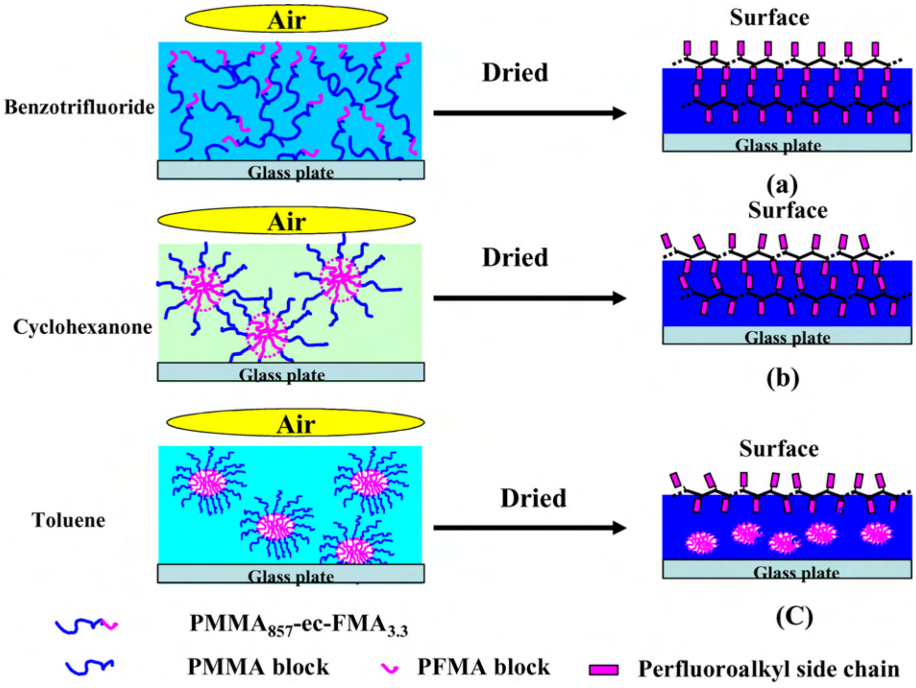
It was reported [43,49] that the methylene groups of the polymer backbone may exhibit vibrational modes for the symmetric stretch [CH$_2$(s)] at 2855 cm^{-1}. At the same time, the methylene groups of the ester ethyl side chain in poly(2-hydroxyethyl methacrylate) have vibrational modes for the symmetric stretch [HOCH$_2$(s)] at 2880 cm^{-1}. No SFG signals for C–F stretching modes was observed in the high frequency range (2700–3100 cm^{-1}) [50]. However, when taking into consideration the results obtained from other techniques discussed in this work, we surmise that these two peaks are related to the local conformation of the perfluoroalkyl group at the surface. Therefore, the peaks at 2875 and 2850 cm^{-1} in Fig. 6 may be assigned to the symmetric stretching vibration of the methylene groups [CH$_2$(s)] connected to the perfluoroalkyl group [C$_8$F$_{17}$] and that of the backbone methylene, respectively.

The effect of the film-forming solvents on the PMMA$_{857}$-ec-FMA$_{3.3}$ SFG spectra can be explained pictorially by the models presented in Scheme 1. An ordered and close-packed structure, such as the double-layered and the hexagonal packing of the perfluoroalkyl side chains, was formed on the PMMA$_{857}$-ec-FMA$_{3.3}$ film surface when benzotrifluoride was used as solvent. Therefore the methylene groups neither connected to the perfluoroalkyl groups nor on the backbone could be observed in the SFG spectra (Scheme 1a). However, these groups were exposed to the air when the perfluoroalkyl side chains on the polymer surface were disordered when toluene was used as solvent (Scheme 1c). Accordingly, relatively strong peaks at 2875 and 2850 cm^{-1} appeared in the SFG spectra. Thus, it is reasonable to conclude that the packing density and order of the fluorinated side groups are dependent on the film-forming solvent and are in the following order: benzotrifluoride > cyclohexanone > toluene. These results are also consistent with the results obtained from the angular-dependent XPS and XRD measurements. Therefore, the increasing resistance of the PMMA$_{857}$-ec-FMA$_{3.3}$ films cast with benzotrifluoride can be attributed to a structure with greater chain alignment and ordered packing of the longer –(CF$_2$)$_7$CF$_3$ moieties than those resulting when cyclohexanone or toluene are used as solvents.

Ming reported that high contact angles (water, 120°; hexadecane, 80°) and low wettability can be achieved by nanoscale phase-separated fluorinated surfaces using very small amounts of fluorinated species [51]. In the present study, it appears that the band at 2950 cm^{-1} in the SFG spectra of PMMA$_{857}$-ec-FMA$_{3.3}$ can be assigned to the symmetric stretching vibration of the ester methyl groups of poly(methyl methacrylate) in the fluorine-poor regions of the surface. Further investigation on this aspect will be undertaken and reported in the future.

3.3. Effect of annealing on surface properties and structure of PMMA$_{857}$-ec-FMA$_{3.3}$ films cast by different solvents

In considering PMMA$_{857}$-ec-FMA$_{3.3}$ in a PMMA matrix, the PMMA chain will be miscible with the matrix, while the PFMA chains will tend to segregate to the surface to minimize the surface free energy of the system. This segregation



Scheme 1. (a) Self-assembly of $PMMA_{857}$-ec-$FMA_{3.3}$ on the interface during film-formation when benzotrifluoride was used as solvent. (b) Self-assembly of $PMMA_{857}$-ec-$FMA_{3.3}$ on the interface during film-formation when cyclohexanone was used as solvent. (c) Segregation of the fluorinated components in $PMMA_{857}$-ec-$FMA_{3.3}$ during film formation when toluene was used as solvent.

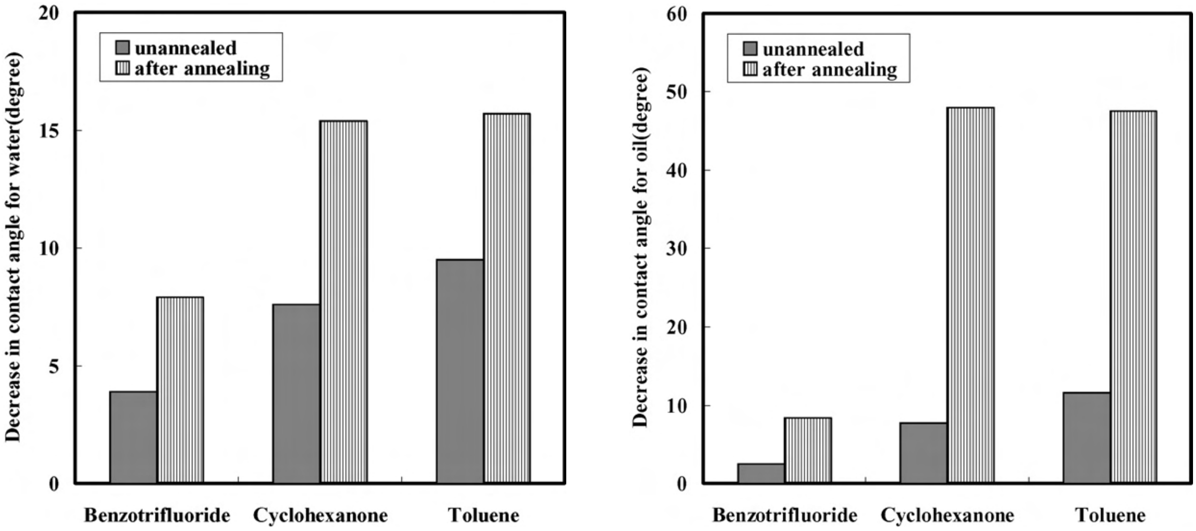


Fig. 7. Decrease in water and oil contact angle of the $PMMA_{857}$-ec-$FMA_{3.3}$ films cast from various solutions after exposure in water for 3 h at 30 °C. The films were annealed at 120 °C under vacuum for 24 h.

will be driven both by the unfavorable enthalpic interactions between the fluorinated units FMA and the PMMA chain and by the decrease in the surface energy produced by substituting the PMMA chain. The segregation of the fluorinated units is actually a process whereby the fluorinated chains move to the air–polymer surface. Since temperature can markedly affect polymer chain movement, heat treatment was employed to enhance the segregation of fluorinated units in the present study. After annealing under vacuum at 120 °C for 24 h, both the water and oil contact angles of the films cast with cyclohexanone and toluene solutions were unexpectedly found to decrease by about 5° while the contact angles of the film cast with benzotrifluoride solution were unchanged when compared with the nonannealed films. The surface stability of the $PMMA_{857}$-ec-$FMA_{3.3}$ films in the polar environment after annealing was compared and the results are presented in Fig. 7. The decrease in water and oil contact angles of the films increased greatly after annealing; that is to say, their surface stabilities or resistance to the polar environments decreased considerably.

The surface composition of the films after annealing was investigated with angle-dependent XPS measurements, and these results are summarized in Table 1. With a takeoff angle of 45°, the F_{1s}/C_{1s} ratios of films cast with cyclohexanone and toluene solutions after annealing were 0.659 and 0.503, respectively,

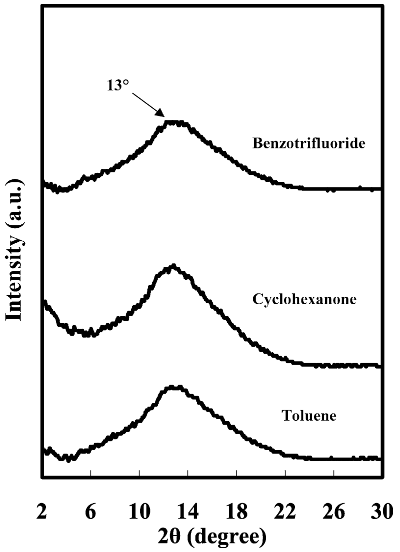


Fig. 8. X-ray diffraction profiles of PMMA$_{857}$-ec-FMA$_{3.3}$ films cast with benzotrifluoride, toluene and cyclohexanone solutions after annealing for 24 h at 120 °C under vacuum.

which were higher than the values of each corresponding film before annealing. This suggests that more fluorinated moieties segregate to the surface, driven by thermal effects. In contrast, the surface composition of the films cast with benzotrifluoride solution shows no obvious change after annealing. However, for the film cast with toluene solution, the F_{1s}/C_{1s} ratio shows a reverse tendency after annealing, decreasing with increasing depth of the probe.

In the X-ray diffraction profiles (Fig. 8) of the PMMA$_{857}$-ec-FMA$_{3.3}$ films cast with different solutions after annealing, only one peak at $2\theta = 13°$ was observed, while the peaks at $2\theta = 17.2°$, 3° and 6° disappeared. These XRD results indicate that although the F_{1s}/C_{1s} ratios near the surface of the PMMA$_{857}$-ec-FMA$_{3.3}$ films increased, the ordered packing of the perfluoroalkyl side chains was destroyed after the annealing. These observations were also confirmed by SFG spectra, as shown in Fig. 6b. The peaks at 2875 and 2850 cm^{-1} for the corresponding films became stronger and broader after heat treatment. Somorjai et al. reported that the existence of an ordering at the surface of polyethylene resulted in narrower widths of the peaks in its SFG spectrum [30]. It is therefore likely that the stronger and broader peaks observed at 2875 and 2850 cm^{-1} after annealing indicate the presence of more disordered structure of the perfluoroalkyl side chains at the PMMA$_{857}$-ec-FMA$_{3.3}$ film surface. Therefore, compared with the ordered packing of fluorinated moieties, the extent of their segregation seems to play a less important role in improving the surface stability of the films.

3.4. Study on the cause of solvent influence

Fig. 9 shows the distributions of the hydrodynamic diameters of the PMMA$_{857}$-ec-FMA$_{3.3}$ in benzotrifluoride, cyclohexanone and toluene solutions. The hydrodynamic diameters of the polymers in benzotrifluoride were about 13 nm, which may be regarded as unimers [12,24]. However, only large-diameter micelles were observed in other solutions. The polymer micelle size in toluene (about 275 nm) was smaller than that formed in cyclohexanone (about 480 nm), indicating a solvent dependence on micelle formation. Since the PFMA segments are insoluble and collapse [12,52,53] in a common solvent such as toluene or cyclohexanone, PMMA$_{857}$-ec-FMA$_{3.3}$ forms a micelle composed of the PMMA corona and the PFMA core, in which PMMA blocks construct a shell and expand like a corona over the core. At the same time, the solvents with lower polarity have weaker PMMA-solvent interactions, resulting in weaker repulsive interactions in the corona [52]. This is the reason why the polymer micelle size in the more polar cyclohexanone is larger than that in toluene.

According to our previous work [14], the PMMA$_{857}$-ec-FMA$_{3.3}$ end-capped polymer possesses a special push-me/pull-you architecture [4], in which the perfluorinated moieties can self-assemble to form an ordered and close-packed structure. In order to minimize the interfacial free energy, the low-energy functional groups in the polymer are pulled to the air–polymer interface and the high-energy functional groups are pulled to the glass–polymer interface. When the surface was formed by casting the polymer solutions, a selective accumulation of functional groups would take place. The polymer chains adopt the configurations or orientations which favor maximizing the surface exposure of either the polar or nonpolar moieties, according to the polarity of the environment. As the solvent evaporates, the macromolecules are then frozen into this structure. Since PMMA$_{857}$-ec-FMA$_{3.3}$ molecules exist as unimers in benzotrifluoride solution, the perfluoroalkyl side chains can segregate easily on the surface and self-assemble into an ordered structure, such as double-layer, single-layer, or hexagonal packing, as shown in Scheme 1a. When cyclohexanone was used as solvent, the resulting micelles were loosely packed and unstable due to their large size. The micelles will thus be destroyed with dissolution of micellar end-capped polymer during film-formation, which also results in formation of an ordered structure of the perfluorinated moieties, as shown in Scheme 1b. Therefore, the PMMA$_{857}$-ec-FMA$_{3.3}$ films cast with benzotrifluoride solution have higher ordered self-assembled structures of the perfluoroalkyl side chains as compared to the films prepared with cyclohexanone solution. When toluene was used as solvent, the resulting micelles were more compact and stable due to their relatively smaller size. The perfluoroalkyl side chains could not be easily disentangled and they could not completely segregate at the outermost surface and form a well-ordered packing structure. Similar to the polystyrene-*b*-poly(2-perfluorooctylethyl methacrylate) thin films reported by Green [54], the fluorinated moieties may be mainly organized into micelle-like aggregates with PFMA composing the core under the surface, as shown in Scheme 1c. This is the reason why the F_{1s}/C_{1s} ratio of the PMMA$_{857}$-ec-FMA$_{3.3}$ films cast with toluene solution became larger with the increase of the probe depth. When the film was heated at 120 °C under vacuum for 24 h, the micelle-like aggregates would be destroyed and the fluorinated units would actually segregate to the air–polymer surface interface. This is the most probable reason why the F/C ratio near PMMA$_{857}$-ec-FMA$_{3.3}$ surface cast with

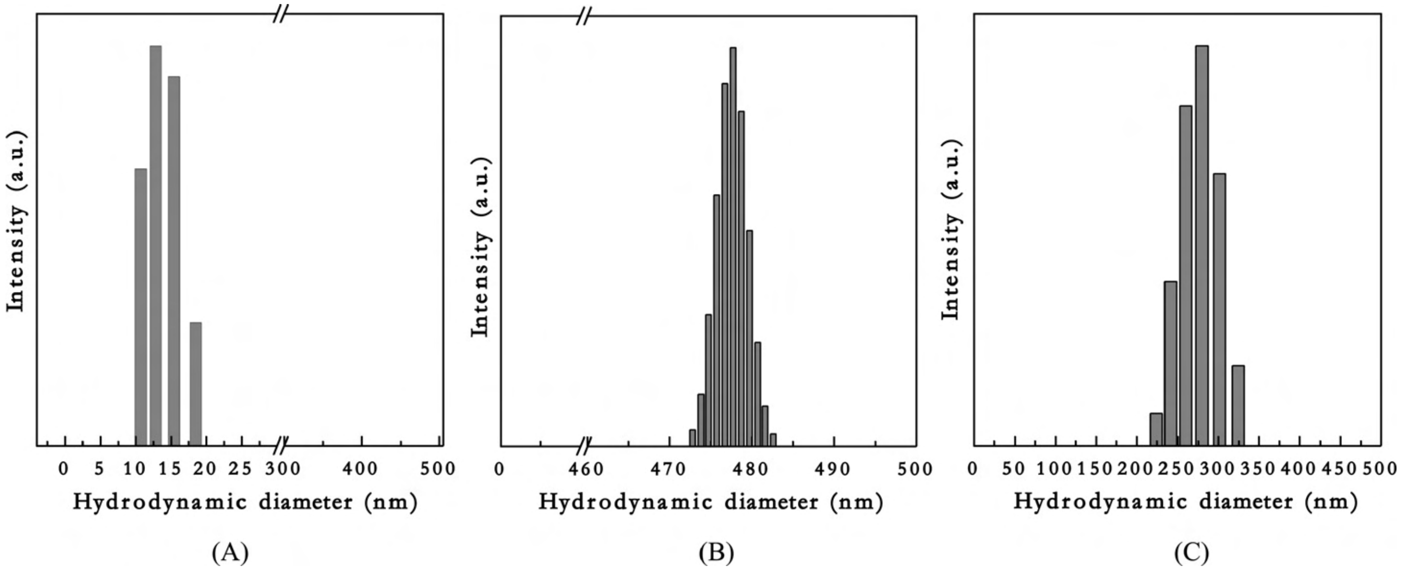


Fig. 9. Distributions of hydrodynamic diameter for $PMMA_{857}$-ec-$FMA_{3.3}$ in benzotrifluoride (A), cyclohexanone (B) and toluene (C).

toluene solution decreased with the probing depth after heat treatment. Therefore, the conformation of the aggregates in the various solutions has a significant effect on the segregation and self-assembly of the perfluoroalkyl side chains during film formation from the evaporation of solvents.

4. Summary

Poly(methyl methacrylate) end-capped with 0.38 mol% 2-perfluorooctylethyl methacrylate units ($PMMA_{857}$-ec-$FMA_{3.3}$) was synthesized by the ATRP technique. Solvent effects on the film formation, the $PMMA_{857}$-ec-$FMA_{3.3}$ surface properties and structure were investigated by dynamic light scattering, contact angle measurement, angle-dependent X-ray photoelectron spectroscopy (XPS), sum frequency generation (SFG) vibrational spectroscopy and X-ray diffraction (XRD). We found that the surface structure and stability (the resistance to surface reconstruction) of the films were greatly affected by the type of solvent. The end-capped PMMA film prepared using benzotrifluoride solution shows an excellent resistance to surface reconstruction compared with those prepared using toluene and cyclohexanone solutions. This can be attributed to the fact that a relatively perfect close-packed and ordered structure of perfluoroalkyl side chains on the surface of $PMMA_{857}$-ec-$FMA_{3.3}$ film is formed when the film is cast from benzotrifluoride solution, in which only unimers exist. For the toluene solution, however, the micelle structure is more stable; therefore, the perfluoroalkyl side chains cannot be easily disentangled and they cannot completely segregate at the outermost surface to form a well-ordered packing structure during film formation. The fluorinated moieties may be organized into micelle-like aggregates with PFMA composing the core underneath the surface, resulting in lower resistance of the film to surface reconstruction. Although the segregation of fluorinated moieties of the film was found to be enhanced by heat treatment, the surface stability greatly decreased. This study indicates that solvent effects on film formation are significant, and may be used to promote the formation of well-ordered packing structure of the fluorinated moieties at the film surface. A well-ordered packing structure appears to a certain extent to be more important than the content of the fluorinated moieties at the surface for improving the surface stability.

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