

## Creating Stable Hydrophobic Surfaces by Poly(butyl methacrylate) End-Capped with 2-perfluorooctylethyl Methacrylate Units

Juping Yang, Huagang Ni, Xiaofang Wang, Wei Zhang, Xinping Wang (✉)

Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Education Ministry, Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China  
E-mail: wxinping@yahoo.com; Fax: +86-571-8684-3600

Received: 18 November 2006 / Revised version: 3 February 2007 / Accepted: 5 February 2007  
Published online: 3 March 2007 – © Springer-Verlag 2007

### Summary

It is a challenge to fabricate fluorine-containing polymer surface with low-energy properties and superior long-lasting barrier properties as well as lower fluorine content. In this paper, poly(butyl methacrylate) end-capped with 2-perfluorooctylethyl methacrylate units (PBMA-ec-FMA), having the so-called push-me/pull-you structures, have been synthesized by ATRP and their surface properties were investigated. This structure was in favor of the longer  $-(CF_2)_7CF_3$  moieties self-assembling on the polymer surface during film formation, which resulted in better chain alignment and packing of the longer  $-(CF_2)_7CF_3$  moieties. Therefore, the contact angles of water and paraffin oil on the surface of the end-capped PBMA were  $118^\circ$  and  $84^\circ$ , respectively, approaching that of poly(2-perfluorooctylethyl methacrylate) homopolymer, even though the content of FMA was 0.34 mol% (the average polymerization degree of PFMA units is 1). However, more than 9 mol% was necessary for the relative random copolymer (PBMA-*r*-PFMA) to reach these values of the contact angle. Regardless of the wetting properties, the end-capped PBMA by fluorinated methacrylate has better resistance to surface reconstruction than PBMA-*r*-PFMA random copolymer even though FMA content in PBMA-ec-FMA is much lower than that in random copolymer. Therefore, it may be a facile method to create stable hydrophobic surfaces with lower price.

### Keywords

Surface free energy; Perfluoroalkyl side chain; Surface structure; Self-assembly; Hydrophobic surface; Surface reconstruction

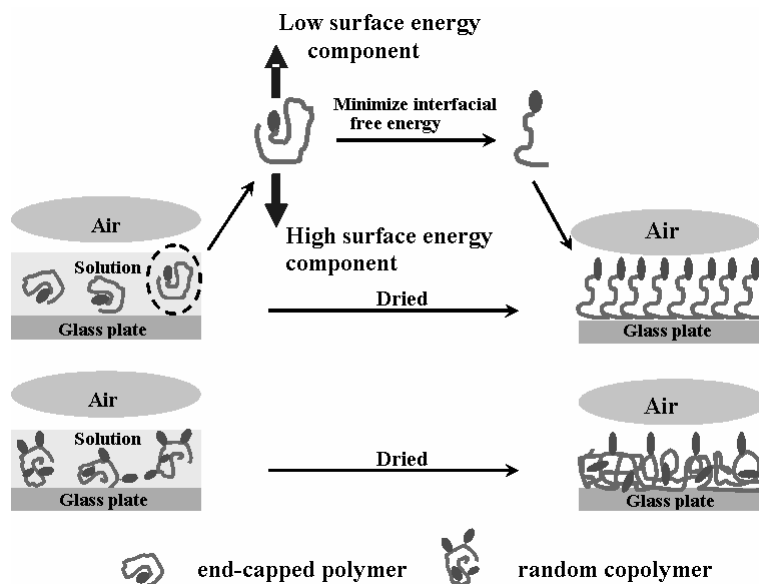
### Introduction

A hydrophobic surface has showed a great deal of specific properties such as water- and oil-repellencies, low coefficient of friction, biocompatibility, and durability. Fluoropolymers have long been known as an important class of materials with low surface energy [1-3]. But the price of the fluorinated monomers is relatively high,

which limits the application of fluorinated polymer. Up to now, the commercial products of fluoro-acrylate are mostly the random copolymers. The fluorinated units are distributed randomly on the polymer backbone. So the effect of fluorine on the surface energy is constrained. In order to achieve desirable surface property, one approach is to increase the fluorine content of the fluorinated copolymer.

The surface properties of polymeric materials are governed by physico-chemical nature of a few atomic layers at the outermost surface [4]. If the surface region can be precisely controlled, the surface properties would be perfectly regulated without changing any bulk properties. These were confirmed by end-functional polymers, fluorocarbon-terminated polystyrene (PS-F). Lots of techniques, such as neutron reflection (NR), nuclear reaction analysis (NRA), X-ray photoelectron spectroscopy (XPS), static secondary ion spectroscopy (SSIMS) and contact angle analysis, were employed to document that the low energy fluorocarbon end-groups in PS-F adsorbed preferentially at the surface [5-10]. To consider the goal of creating a low-energy release surface through the incorporation of low-surface-tension functional groups into a polymer chain, the optimal polymer architecture was suggested that both high- and low-energy functional groups can both be placed on the polymer chain [11]. The so-called push-me/pull-you structure was shown in Scheme 1. This structure was in favor of low-surface-tension moieties self-assembling on the polymer surface during film formation, which resulted in better chain alignment and packing of the low-surface-tension moieties. The surface component, orientation packing and end groups will affect the surface behavior of the polymer films [12, 13]. It was found that when the surface is uniformly covered with a trifluoromethyl ( $\text{CF}_3$ ) array, a very low energy surface can be achieved [14]. These polymers critical surface tension ( $\gamma_c$ ) will be much lower than that of the polyterafluoroethylene.

Given sufficient mobility, the macromolecules at the surface of a polymer tend to reorient or restructure in order to raise the surface concentration of polar or nonpolar



Scheme 1

moieties depending on the polarity of the surrounding phase [15]. This phenomenon is attributed to the thermodynamic driving force to minimize the interfacial free energy. Therefore, fluorinated polymers are usually quite susceptible to rapid rearrangement when the polymer surface is contacted with water, and high contact angles observed on dry surfaces can quickly decrease at wet state. This is contradictory with a long-term use in polar environment [16,17]. For examples, the antifouling performance of fluorocarbon-based polymers was inferior to that of silicone polymers which was attributed to the reconstruction of surface molecule under water [18]. At the same time, it was found that the surface reconstruction could be minimized or completely avoided by manipulating  $-\text{CF}_3$  to form very closely packed arrays [19].

Up to now, a few researches focus on surface properties of copolymers with fluorine-containing comonomers and their copolymers were reported to show very low surface free energy [14, 20-25]. However, usually molecular weight of acrylate block was low and fluorinated monomers content was a little high. In this paper, poly(butyl methacrylate) end-capped with 2-perfluorooctylethyl methacrylate units (PBMA-ec-FMA), having characteristics of the push-me/pull-you structure, were prepared by ATRP technique and their surface properties were investigated. The results indicated that it may be a facile method to create long-lived hydrophobic surfaces with lower price.

## Experimental Part

### *Materials*

Both butyl methacrylate (BMA) and 2-perfluorooctylethyl methacrylate ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2-(\text{CF}_2)_7\text{CF}_3$ , Aldrich) (FMA) were washed with 5% NaOH and deionized water, dried through  $\text{CaH}_2$ , and then vacuum-distilled before polymerization. CuBr (Aldrich), ethyl 2-bromopropionate (Aldrich) and  $\alpha, \alpha'$ -bispyridine (bpy) (Aldrich) were used as received. Toluene was freshly distilled from sodium/benzophenone after refluxing several days. Other chemicals were of reagent grade and used without further purification purchased from Shanghai Reagent Co.

### *Synthesis of fluorinated polymers*

Poly(butyl methacrylate) end-capped with 2-perfluorooctylethyl methacrylate units (PBMA-ec-FMA) were synthesized by atom transfer radical polymerization (ATRP) using the bromine terminated PBMA (PBMA-Br) as macroinitiators according to reported method [14]. Preparation of the macroinitiator PBMA-Br has been carried out in a 500 ml flask under following conditions: ethyl 2-bromopropionate 0.2276ml, CuBr 0.2524g, bpy 0.5469g, BMA 70 ml and toluene 159ml. The system was degassed three times by freezing and thawing and then heating to  $100^\circ\text{C}$  under nitrogen for 24 h. Upon completion of the experiment the polymerization mixture was diluted with THF and precipitated into methanol after passing through an alumina column. The products were dried under vacuum at room temperature.

A typical preparation of PBMA-ec-FMA was described as follow. 10g of macroinitiator (PBMA-Br) was dissolved in 30 ml of toluene, 0.046g of CuBr, 0.1g of bpy and 0.51g of FMA were added. After three freeze-thaw cycles, the mixtures was heated to  $100^\circ\text{C}$  for 24 h. The end-capped poly(butyl methacrylate) solutions were dissolved in THF and precipitated into methanol after passing through an alumina column. The products were dried under vacuum at room temperature.

The relative random copolymers were prepared by free radical copolymerization at 70°C for 8 h in toluene using 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The product were purified by dissolving in THF, and then reprecipitated in methanol twice.

#### *Characterization*

The molecular weight and molecular weight distribution (MWD) of polymers were determined by gel permeation chromatography (GPC) using a Waters 1500 apparatus (THF as eluent at a flow rate of 0.5 ml/min). The GPC chromatogram was calibrated against standard polystyrene samples. <sup>1</sup>H NMR spectra were recorded on a Bruker Advance AMX-400 NMR instrument in CDCl<sub>3</sub> with tetramethylsilane (TMS) as internal standard. 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 film. The XPS were carried out on a PHI5000C ESCA System with an MgK $\alpha$  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 $\times$ 10<sup>-8</sup> Torr. All spectra were calibrated by the C<sub>1s</sub> peak of the C-C bond at 284.6 eV. Fluorine percent of the end-capped PBMA (PBMA-ec-FMA) was obtained through fluorine-element analysis of ignition method. Characteristics of macroinitiator, end-capped PBMA and random copolymers are given in Table 1 and 2.

#### *Measurement of contact angles and surface property variations of polymer films against water*

The polymer was dissolved in cyclohexanone to make the 4 wt % solution. The samples were prepared by casting polymer solution on clean glass slides and dried in air for 24 h and then under vacuum for at least 20 h.

Contact angles of water and paraffin oil on the films were measured by the sessile drop method using DSA-10 drop sharp analysis (Krüss Co., Germany) at 25°C. The volume of the liquid drops used was always 3 $\mu$ l. The contact angles of water and diiodomethane were used to make estimates of surface free energy for various samples according Owens and Wendt's theory [26].

Variations in surface property of polymer films against water were measured as follows. The sample coated on glass side was immersed in water at 60°C for a certain time. Each time the sample was removed from water, it was immediately cooled in the room-temperature water for 3 min to slow the surface reconstruction during the measurements, and then was dried quickly with a stream of nitrogen prior to contact angle analysis [27]. In order to ensure that the results were sufficiently credible, the experimental errors in measuring the  $\theta$  values were evaluated to be less than  $\pm 2^\circ$ .

## **Results and discussion**

#### *Characterization of PBMA-ec-FMA and random copolymer*

ATRP is a versatile method of synthesizing well-defined polymer. In order to prepare poly(butyl methacrylate) with one or two units of 2-perfluorooctylethyl methacrylate,  $\alpha,\alpha'$ -Bispyridine (bpy) was used as the ligand and toluene was used as solvent [28].

The end-capped PBMA with few polymerization degree of PFMA were prepared as shown in Table 1.

Since the amount of FMA was very low in end-capped polymer, the difference between the PBMA-Br macroinitiator and the resulting PBMA-ec-FMA was hard to be traced by GPC. At the same time, since fluorine content was so little that  $^1\text{H}$  NMR and IR method weren't suitable for characterization of the end-capped PBMA, fluorine-element analysis of ignition method was employed to measure fluorinated monomer content. The polymerization degree ( $y$ ) of PFMA in the end-capped PBMA was calculated according to the equation as follows [14]:

Table 1. Characteristics of PBMA-ec-FMA synthesized by ATRP.

Sample	PBMA-ec-FMA ( $M_n \times 10^{-4}$ )	MWD	$W_F$ (%) <sup>c)</sup>	FMA (mol%)	$BMA_xFMA_y$
PBMA-Br <sup>a)</sup>	3.12	1.26	0	0	$BMA_{220}$
Sample-ec-1 <sup>b)</sup>	3.14 <sup>e)</sup>	1.26	0.400 <sup>d)</sup>	0.19	$BMA_{220}FMA_{0.38}$
Sample-ec-2 <sup>b)</sup>	3.15 <sup>e)</sup>	1.27	0.510	0.23	$BMA_{220}FMA_{0.50}$
Sample-ec-3 <sup>b)</sup>	3.16 <sup>e)</sup>	1.31	0.755	0.34	$BMA_{220}FMA_{0.74}$
Sample-ec-4 <sup>b)</sup>	3.20 <sup>e)</sup>	1.29	1.620	0.73	$BMA_{220}FMA_{1.61}$

a) [CuBr]: [bpy]: [2-Br-EA] = 1:2:1

b) [CuBr]: [bpy]: [PBMA-Br] = 1:2:1

c)  $W_F$  represents fluorine content obtained from fluorine element analysis

d) This value is not accurate

e) The molecular weight of polymer calculated from  $BMA_xFMA_y$

Table 2. Characteristics of random copolymer PBMA-*r*-PFMA synthesized by radical polymerization.

Sample	$M_n$ ( $\times 10^{-4}$ )	MWD	FMA (mol%) <sup>a)</sup>
Sample-r-1	4.06	1.69	0.59
Sample-r-2	3.79	2.20	2.15
Sample-r-3	3.76	1.75	3.92
Sample-r-4	3.87	1.71	8.90
Sample-r-5	3.54	1.81	13.01
Sample-r-6	3.33	2.13	17.40

a) Determined by  $^1\text{H}$  HNR.

$$W_F(\%) = (17 \times 19 \times y) / (M_{n,BMA} + 532 \times y)$$

Each fluorinated monomer FMA contains 17 fluorine atoms, fluorine atomic weight is 19. The results showed that the polymerization degree ( $y$ ) of PFMA was very low. The most value of  $y$  is only 1-2, which is similar to the structure of fluorocarbon-terminated poly(butyl methacrylate). This polymer matched what we had designed very well.

As comparison, relative random copolymers PBMA-*r*-PFMA were synthesized by free radical polymerization. Since the content of fluorinated monomer was much higher, both FTIR and  $^1\text{H}$  NMR were employed to characterize the random copolymers. Peaks at 1250, 1180, 660, 714  $\text{cm}^{-1}$  in the 650 ~1500  $\text{cm}^{-1}$  region were observed in FTIR spectrum of PBMA-*r*-PFMA. The bonds at 1250, 1180  $\text{cm}^{-1}$  were

associated with stretching vibration of the  $\text{CF}_2$  group, that at  $660$  and  $714\text{ cm}^{-1}$  result from a combination of rocking and wagging vibrations of  $\text{CF}_2$  groups. The  $^1\text{H}$  NMR spectrum for PBMA-*r*-PFMA exhibited two peaks at  $4.23$  and  $3.93$  ppm, which were attributed to the two protons of  $-\text{OCH}_2\text{CH}_2-(\text{CF}_2)_7\text{CF}_3$  in FMA and the two protons of  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  in BMA, respectively [14]. The fluorinated monomer content in the random copolymer could be calculated by  $^1\text{H}$  NMR. The characteristics of the random copolymers were presented in Table 2.

#### *Surface properties of the end-capped poly(butyl methacrylate) PBMA-ec-FMA*

It is well known in multicomponent systems, small molecule or polymeric, that composition in the vicinity of an interface differs from the average bulk composition. However, surface wettability is controlled by the structure of the outermost layers. Contact angle measurement is one of the most sensitive methods for providing information on the outer few angstroms of polymer surfaces [29-31]. The effect of the fluorinated monomer on polymer surface was studied by measuring the wettability of the copolymer surface. Figure 1 shows the effect of FMA content on contact angle of water of end-capped PBMA and random copolymers. The contact angles of water on the surface of PBMA-ec-FMA increased dramatically with a little increasing of FMA content and reached maximum value  $118^\circ$  as the content of FMA is  $0.34\text{ mol}\%$  (the average polymerization degree of PFMA is 1), approaching that of poly(2-perfluorooctylethyl methacrylate) homopolymer [24,32]. However, that on random copolymer increased gradually with increasing of FMA content and reached maximum value as  $9.0\text{ mol}\%$  of FMA content in the random copolymer. The effect of FMA content on the contact angles of paraffin oil on the surface of polymer was

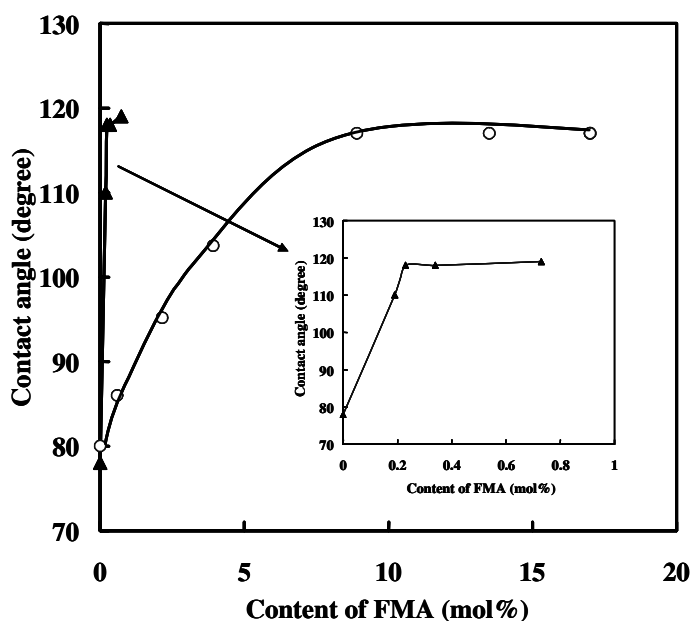


Figure 1. Dependence of contact angles of water on the content of FMA in PBMA-ec-FMA (▲) and in random copolymers (○).

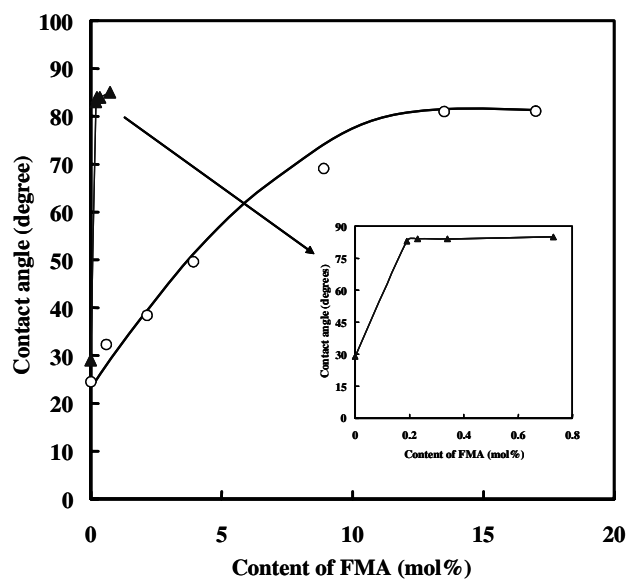


Figure 2. Dependence of contact angles of paraffin oil on the content of FMA in PBMA-ec-FMA (▲) and in random copolymers (○).

shown in Figure 2. Similarly, paraffin oil contact angles of the end-capped PBMA reached  $84^\circ$  of maximum value when the content of FMA is 0.34 mol%, same as the reported value of poly(2-perfluorooctylethyl methacrylate) homopolymer. However, 13 mol% of FMA is required for the relative random copolymer to reached this value.

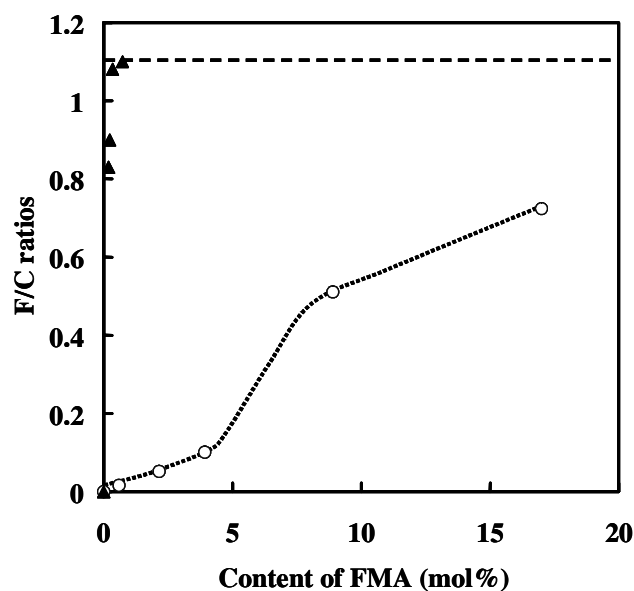


Figure 3. F/C ratio determined by XPS at the surface as a function of mol% FMA in PBMA-ec-FMA (▲) and in random copolymers (○).

At the same time, it also found that with a little increasing of FMA content, the surface free energy of PBMA-ec-FMA decreased sharply. At a FMA content over 0.34 mol%, the surface free energy was constant at about 8.8 erg/cm<sup>2</sup> which was very close to that of perfluoroalkyl methacrylate homopolymer (8.5 erg/cm<sup>2</sup>)[24].

The atomic ratio of fluorine to carbon (F/C) near the surfaces of end-capped PBMA and random copolymers are shown in Figure 3. With FMA up to 0.34 mol% resulted in a dramatic increase in F/C ratio near PBMA-ec-FMA surfaces. The surface F/C ratio in the end-capped PBMA with a FMA content of more than 0.34 mol% was constant about 1.1, very close to F/C ratio (1.2) of homopolymer PFMA. However, the surface F/C ratio of the random copolymer increased gradually with increasing FMA content and reached 0.72 even if FMA content was 17 mol%.

#### *Environmental stability of PBMA-ec-FMA surface*

The samples were prepared as previously described, immersed in water for controlled time intervals, and then dried with nitrogen stream. Figure 4 and 5 show the water and paraffin oil contact angles of the PBMA-ec-FMA with 0.34 mol% FMA and the random copolymer with 13 mol% FMA after exposure to water at 60°C, respectively. Regardless of liquids, the contact angle on random copolymer drops almost immediately after a short water exposure, which indicates that the copolymer chain surface reconstruct. However, the contact angle on the end-capped PBMA decreases gradually with water exposure time. For example, after water immersion for 30 min, paraffin oil contact angle on the PBMA-ec-FMA with 0.34 mol% decreases only by 16°, which represents the decreases in oil contact angle of 19% from the values measured before the water exposure. However, that on the random copolymer with 13 mol% FMA decreases by 41°, which represents the decreases in oil contact angle of

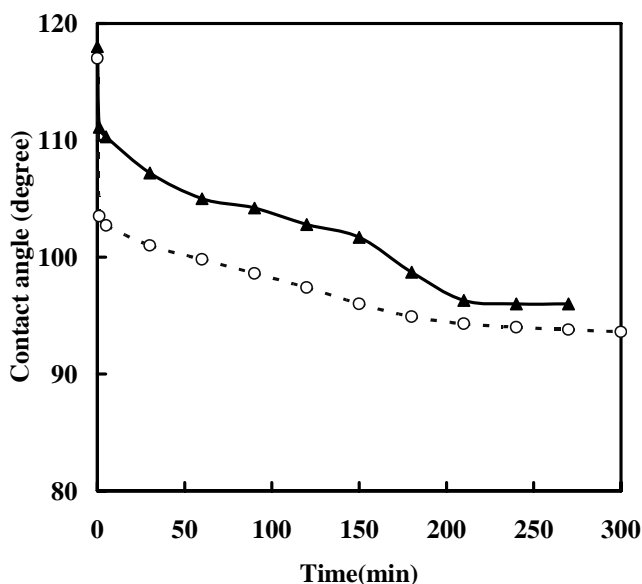


Figure 4. Dependence of the water contact angle of the end-capped PBMA Sample-ec-3 (▲) and the random copolymer Sample-r-5 (○) on the exposure time of the polymer to water. Temperature: 60°C.



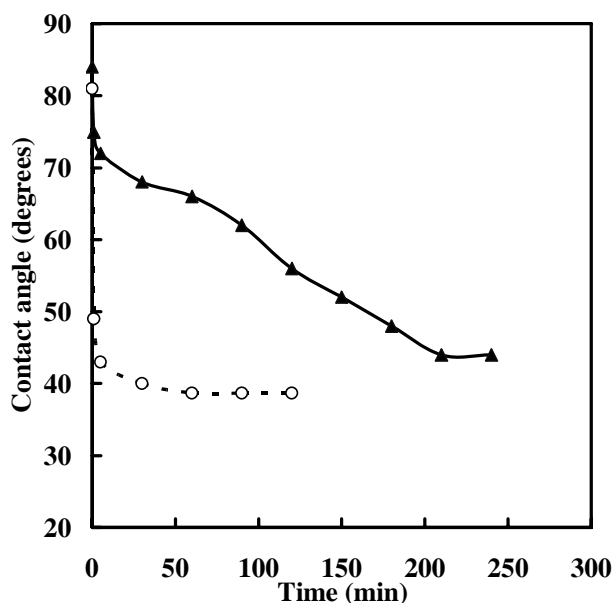


Figure 5. Dependence of the paraffin oil contact angle of the end-capped PBMA Sample-ec-3 (▲) and the random copolymer Sample-r-5 (○) on the exposure time of the polymer to water. Temperature: 60°C

51% from the values measured before the water exposure even though this sample have much higher FMA content. Moreover, by comparing the data from various copolymer, it is evident that the end-capped PBMA with low FMA content exhibit not only excellent surface properties, but also better stability and resistance to polar environment. This response is presumably associated with better packing of the longer fluorocarbon chain.

Most polymers were in hydrophobic environments before being used in which the interface was an air-polymer interface. When a polar liquid such as water contacted a polymeric surface, the original structure favored at an air-polymer interface will no longer be stable, and the new interface will attempt to reconstruct and re-equilibrate in response to its new environment [11]. Polar molecules in the region of the surface will rearrange or reconstruct, and facilitate the migration of polar groups toward the water-polymer interface [33]. So fluorinated polymers usually reconstruct at their surface and lose their low-energy surface properties when exposed to polar liquids.

Why does poly(butyl methacrylate) end-capped with 2-perfluorooctylethyl methacrylate units (PBMA-ec-FMA) has higher water and oil contact angle and exhibit better stability and resistance to polar environment even though the polymer has only one constitutional unit of FMA ? It was reported [19] that the surface reconstruction can be minimized or completely avoided if  $-C_nF_{2n+1}$  chain on the surface was manipulated to form very closely packed arrays. Therefore, the reason was attributed to the structure of end-capped PBMA. As shown in Scheme 1, low-surface-tension functional groups  $-(CF_2)_7CF_3$  were incorporated into one chain end of PBMA-ec-FMA and high-surface-tension groups  $-COOCH_2CH_2CH_2CH_3$  were incorporated into BMA unit of long chain of PBMA block in this type the end-capped PBMA. In order to minimize the interface free energy, fluorocarbon group will segregate to air-polymer

interface whereas PBMA block will segregate to glass-polymer interface, namely, the so-called push-me/pull-you structures. During the film formation, monolayers of semifluorinated self-assembled monolayers at air-polymer interface are formed by physical forces through self-assembly process that are governed by push-me/pull-you structures of the polymers as shown in Scheme 1. The sample-ec-3 have surface free energy of about  $8.8 \text{ mJ/m}^2$ , a value near that of a perfectly closed-packed crystalline array of  $-\text{CF}_3$  groups (about  $6 \text{ mJ/m}^2$ ). This is presumably associated with better chain alignment and packing of the longer  $-(\text{CF}_2)_7\text{CF}_3$  moieties. These also were confirmed by XPS that the surface F/C ratio in PBMA-ec-FMA with a FMA content of 0.34 mol% was about 1.1, very close to F/C ratio (1.2) of homopolymer PFMA. The packing density of the self-assembled monolayers not only determines their surface energies but ultimately influences the stability of the monolayer and its resistance to surface reconstruction [20,34]. However, it is hard for the relative random copolymer to form this kind of ordered structure.

### Conclusions

A series of end-capped PBMA with few fluorinated monomer units have been synthesized by ATRP and their surface properties was investigated. Surprisingly, the contact angles of water and paraffin oil on the surface of PBMA-ec-FMA were  $118^\circ$  and  $84^\circ$ , respectively, approaching that of poly(2-perfluorooctylethyl methacrylate) homopolymer, even though the content of FMA was 0.34 mol% (the average polymerization degree of PFMA is 1). However, more than 9 mol% was necessary for random copolymer to reach these values of the contact angles. Regardless of the wetting properties, the end-capped polymer has better resistance to surface reconstruction than PBMA-*r*-PFMA random copolymer even though FMA content in the end-capped PBMA is much lower than that in random copolymer. This was attributed to the structure of PBMA-ec-FMA, namely, the so-called push-me/pull-you structures. This structure was in favorable of the longer  $-(\text{CF}_2)_7\text{CF}_3$  moieties self-assembling on the end-capped polymer surface during film formation, which resulted in better chain alignment and packing of the longer  $-(\text{CF}_2)_7\text{CF}_3$  moieties. Therefore, it is possible way to prepare easily the film with low-energy surface properties and better resistance to surface reconstruction with lower fluorine content by the end-capped polymer having push-me/pull-you structures.

*Acknowledgments.* The authors are grateful for the financial support from National Natural Science Foundation of China (Grant No. 50573069), the Natural Science Foundation of Zhejiang Province (Grant No. Y405490) and Education Committee of Zhejiang Province (Grant No. 20050785).

### References

1. Hung MH, Farnham WB, Feiring AE, Rozen S (1999) Fluoropolymers 1: Synthesis. (Hougham G, Ed., Plenum Press, New York, pp 51)
2. Hussain H, Budde H, Höring S, Busse K, Kressler J (2002) Macromol Chem Phys 203:2103
3. Matsumoto K, Kubota M, Matsuoka H, Yamaoka H (1999) Macromolecules 32:7122
4. Tanaka K, Kawaguchi D, Yokoe Y, Kajiyama T, Takahara A, Tasakic S (2003) Polymer 44:4171
5. Elman JF, Johs BD, Long TE, Koberstein JT (1994) Macromolecules 27:5341

6. Hunt MOJ, Belu AM, Linton RW, DeSimone JM (1993) *Macromolecules* 26:4854
7. Affrossman S, Hartshorne M, Kiff T, Pethrick RA, Richards RW (1994) *Macromolecules* 27:1588
8. Hopkinson I, Kiff FT, Richards RW, Bucknall DG, Clough AS (1997) *Polymer* 38: 87
9. Schaub TF, Kellogg GJ, Mayes AM, Kulasekera R, Ankner JF, Kaiser H (1996) *Macromolecules* 29:3982
10. Petitjean S, Ghitti G, Fayt R, Teyssie P, Jerome R (1990) *Bull Soc Chim Belg* 99:997
11. Koberstein J T (2004) *J Polym Sci Part B Polym Phys* 42:2942
12. Iyengar DR, Perutz SM, Dai CA, Ober CK, Kramer EJ (1996) *Macromolecules* 29:1229
13. Toselli M, Messoria M, Bongiovanni R, Malucelli G, Priola A, Pilatic F, Tonelli C (2001) *Polymer* 42:1771
14. Li K, Wu PP, Han ZW (2002) *Polymer* 43:4079
15. Andrade JD (1988) *Polymer Surface Dynamics*. (Plenum Press, New York, PP1-8)
16. Takahashi S, Kasemura T, Asano K (1997) *Polymer* 38:2107
17. Morita M, Ogisu H, Kubo M (1999) *J Appl Polym Sci* 73:1741
18. Schmidt DL, Brady RFJ, Lam K, Schmidt DC, Chaudhury MK (2004) *Langmuir* 20:2830
19. Genzer J, Efimenko K (2000) *Science* 290:2130
20. Wang J, Mao G, Ober CK, Kramer EJ (1997) *Macromolecules* 30:1906
21. Park IJ, Lee SB, Choi CK, Kim J (1996) *J Colloid Interface Sci* 181:284
22. Thunemann AF, Lochhaas KH (1998) *Langmuir* 14:4898
23. Wang J, Ober CK (1997) *Macromolecules* 30:7560
24. Nishino T, Urushihara Y, Meguro M, Nakamae K (2005) *J Colloid Interface Sci* 283:533
25. Nishino T, Urushihara Y, Meguro M, Nakamae K (2004) *J. Colloid Interface Sci* 279:364
26. Owens DK, Wendt RC (1969) *J Appl Polym Sci* 13:1741
27. Khongtong S, Ferguson GS (2001) *J Am Chem Soc* 123:3588
28. Bernhardt PV (1997) *J Am Chem Soc* 119:771
29. Van HSD, Hogt AH, Feijen J (1986) *J Colloid. Interface Sci* 114:167
30. Tingey KG, Andrade JD (1991) *Langmuir* 7:2471
31. Kwok DY, Neumann AW (1999) *Adv Colloid Interface Sci* 81:167
32. Katano Y, Tomono H, Nakajima T (1994) *Macromolecules* 27:2342
33. O'Rourke-Muisener PAV, Koberstein JT (2003) *Macromolecules* 36:771
34. Ulman A, *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self Assembly* (Academic Press, New York, 1991)