

Polymer Communication

Preparation and surface properties of fluorine-containing diblock copolymers

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Abstract

Two series of semifluorinated fluorocarbon diblock copolymer poly(butyl methacrylate-*co*-perfluoroalkyl acrylate) have been synthesized by atom transfer radical polymerization (ATRP). The ¹H NMR, F-EA, GPC and FTIR were used to characterize copolymer structure. Contact angle measurements on the thin polymer films showed low critical surface tensions and low dispersion force contributions to the surface energy, which indicated the presence of the fluorinated block at the surface. The results showed that the water- and oil-repellency increased with the fluorine content in the diblock copolymers. After annealing at different temperatures or different times, the water- and oil-repellent properties of diblock copolymer were increased to approach maximum values. This phenomenon proves the propensity of polymer for fluorine enrichment at air–polymer surface. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Atom transfer radical polymerization; Perfluoroalkyl acrylate; Critical surface tension

1. Introduction

Many properties of a material are dependent on the surface structure and on the chemical composition of the outermost surface layer. Wetting and coating characteristics, fractional behavior and physiological compatibility are examples of such properties [1]. Fluorinated polymers are well known as low surface energy materials, which have oil- and water-repellent surface and have been proposed for coating of substrates such as textiles, papers, leather, wood, etc. When the surface is uniformly covered with a trifluoromethyl (CF₃) array, a very low energy surface can be achieved. These polymers critical surface tension γ_c will be much lower than that of the polytetrafluoroethylene. The surface component, orientation packing and end groups will affect the surface behavior of the polymer films [2,3].

There are many methods used for incorporation of fluorine content into polymer, such as plasma treatment, grafting reaction and living polymerization. The structure of polymer greatly influences its surface-active property, so controlling the distribution of fluorine atoms within the polymer is very important. Living anionic [4], living cationic [5], group transfer polymerization [6] and the method of iniferter polymerization have been used to prepare well-

defined fluorinated polymers [7]. But these techniques have their own disadvantages, such as rigorous reaction conditions or limited monomers and so on.

Fluorochemicals have been known to exhibit both water- and oil-repellency since the late 1950s. The fluorochemical compounds remain the most common active ingredients for water- and oil-repellent purpose. 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 copolymers. Thus fluorine content of the commercial products of fluoro-acrylate is very high, ranging from 30 to 55 wt%. The alternative approach is to change the molecular structure, and lead to the fluorinated blocks at the end of the molecular chain. By this means, the efficiency of fluorine can be increased to a maximum value [8].

In order to study the properties of fluorinated acrylate copolymers, two series of model block copolymers have been designed and synthesized by atom transfer radical polymerization (ATRP). The ATRP is a versatile method of synthesizing well-defined polymers [9,10]. In this paper, the ability to form well-defined copolymer containing fluorinated contents was investigated by ATRP, and the surface-active property of copolymer was studied by

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contact angle measurement and maximum bubble pressure method.

2. Experiment

2.1. Materials

Monomer butyl methacrylate (BMA) was washed with 5% NaOH and deionized water, dried through CaH₂, and then vacuum-distilled. Initiator ethyl 2-bromoisobutyrate (from Aldrich Co. 98%) was used as received. Catalyst CuBr was purified according to the procedure of Keller and Wycoff [11]. *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, from Aldrich Co. 98%) was used as received. Perfluoroalkyl acrylate (FAEM) was kindly supplied from Clariant Company. FAEM was stirred over CaH₂ overnight at 40 °C, then distilled under reduced pressure. The FAEM used in current study is a mixture of CH₂=CHCO₂CH₂CH₂(CF₂)_nCF₃ with different *n* (*n* = 5–13, average *n* ≈ 8.6).

2.2. General procedure

A typical reaction of preparing the macroinitiator has been carried out in a 100 ml flask under following conditions: ethyl 2-bromoisobutyrate 0.2629 g, CuBr 0.1935 g, PMDETA 0.4667 g, BMA 30 ml, cyclohexanone 30 ml, reaction temperature 70 °C, reaction time 24 h. A typical reaction of preparing the fluorinated copolymer has been carried out in a 30 ml flask under following conditions: macroinitiator (PBMA–Br) 4 g, CuBr 0.05738 g, PMDETA 0.1384 g, FAEM 0.4784 g, cyclohexanone 10 ml, reaction temperature 100 °C, reaction time 72 h. The reaction flask was deoxygenated via three freeze pump thaw cycles. The monomer BMA and solvent cyclohexanone were purged with nitrogen before used, and then introduced by syringe. The reaction mixture was immersed in an oil bath heated at desired temperature. When the reaction ended, the reaction mixture was dissolved in THF and precipitated into methanol after passing through an alumina column.

2.3. Characterization

The monomer conversion was determined gravimetrically. The molecular weight and molecular weight distribution were measured on Waters 150C gel permeation chromatography equipped with Ultrastaygel columns of 100, 10 000 Å porosities using THF as eluant at 30 °C. A series of monodisperse polystyrene standards were used for calibration. The IR spectra of the copolymers were measured on a Nicolet Nagma-IR 550 FTIR spectrometer. ¹H NMR spectra were recorded using a Bruker 500 Hz spectroscopy. Fluorine percent was obtained through fluorine-element analysis of ignition method.

2.4. Measurement of contact angles and copolymer solution surface tension

Glass microscope slides were etched (H₂SO₄ 200 ml) at 120 °C. Polymer solutions were prepared up to 1.5 wt% in 2-butanone. The slides were coated as a thin film and left dry in vacuum. The slides were also annealed in an oven at 120 °C for 24 h. Contact angle measurements were performed with JY-82-series instrument (ChengDe laboratory apparatus Inc.). The measurements were carried out in air at the room temperature by the sessile drop technique. For each sample, at least five measurements were performed, by placing the liquid drops in different parts of the sample surface.

The surface tension of copolymer solution, γ , was measured using the maximum bubble pressure method and analyzed with the following expression [12]

$$\Delta P_{\max} = \frac{2\gamma}{R}$$

where ΔP_{\max} is the maximum pressure difference and *R* is the radius of the capillary column.

3. Results and discussion

ATRP is a versatile method of synthesizing well-defined polymers. In this process, the control available from living polymerization is combined with the versatility and robust character of free radical process. ATRP also gives a good control over chain topologies, composition, functionalities and uses different initiators and macroinitiators with halogen atoms activated by aryl, allyl, sulfone or carbonyl groups. Macroinitiator method is a strong tool to prepare block copolymers. This method involves the isolation and purification of the first block polymer, then using it as a macroinitiator.

The simple amine PMDETA has been used as ligand for the copper catalyst system. Due to the following three reasons, we substituted PMDETA for 2,2'-bipyridine (bipy). First, the PMDETA is less expensive, more accessible and more tunable than bipy. Secondly, due to the absence of the extensive π -bonding in the PMDETA, the subsequent copper complexes are less colored. The third is that the coordination complexes between the copper and the simple amine tend to have lower redox potential than the copper–bipy complex, and therefore, the employment of PMDETA as the ligand in ATRP may lead to faster polymerization rates [13,14]. In this paper, a ATRP system with faster rate, better control and fewer side reactions has been discovered not only for the polymerization of BMA but also for fluorinated monomer (FAEM).

3.1. Synthesis and characterization of macroinitiator

The bromine endcapped macroinitiators PBMA–Br were prepared by ATRP of BMA in the presence of ethyl

Table 1
Polymerization results of FAEM with bromine endcapped PBMA ($T = 100\text{ }^\circ\text{C}$, $t = 72\text{ h}$, $[\text{Cu}]/[\text{PMDETA}]/[\text{PBMA-Br}] = 1:2:1$)

Samples	PBMA-Br ($M_n \times 10^{-4}$)	PBMA- <i>b</i> -FAEM ^a ($M_n \times 10^{-4}$)	Conv. of FAEM ^b (%)	W_F ^c (%)	BMA _x FAEM _y	M_w/M_n ^d
No. 1	0.69	0.81	95	9.0	BMA ₄₉ FAEM _{1.9}	1.29
No. 2	1.09	1.26	90	6.4	BMA ₇₆ FAEM _{2.1}	1.44
No. 3	1.36	1.49	92	5.5	BMA ₉₆ FAEM _{2.1}	1.41
No. 4	1.36	1.55	95	7.6	BMA ₉₆ FAEM _{3.1}	1.40
No. 5	1.36	1.63	90	10.6	BMA ₉₆ FAEM _{4.5}	1.36
No. 6	1.36	1.85	93	17.0	BMA ₉₆ FAEM _{8.2}	1.38
No. 7	1.36	1.97	75	19.9	BMA ₉₆ FAEM _{10.2}	1.32
No. 8	1.52	2.33	62	22.5	BMA ₁₀₇ FAEM _{13.7}	1.28
No. 9	2.50	2.61	86	2.8	BMA ₁₇₆ FAEM _{1.9}	1.31

^a The molecular weight of copolymer calculated from BMA_xF_y.

^b FAEM represents FLUOWET ($\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}_2(\text{CF}_2)_x\text{CF}_3$, $x = 3, 5, 7, 9, 11$) monomer.

^c W_F represents fluorine content obtained from fluorine element analysis.

^d The polydispersity of macroinitiator was gained from GPC, calibrated by polystyrene standards. The parameters of MHS equation were those of PBMA.

2-bromoisobutyrate/cuprous bromide/PMDETA (1:1:2) at $70\text{ }^\circ\text{C}$. At the end of polymerization, the polymer solutions were added in THF and passed through an alumina column to remove the catalyst CuBr, then isolated by precipitation with methanol. The macroinitiator PBMA-Br left to dry in vacuum at $40\text{ }^\circ\text{C}$ for several days. The molecular weight and molecular weight distribution of macroinitiator were measured by GPC.

3.2. Synthesis and characterization of the block copolymer contain the FAEM segments

The block polymerizations were performed using the above bromine terminated PBMA as macroinitiators. The block copolymerizations of fluorinated monomer FAEM were performed at higher temperature than that of BMA. In order to achieve high conversion of FAEM, the reaction temperature of the second block was increased to $100\text{ }^\circ\text{C}$. The experimental results show that the fluorinated monomer

conversion will be mostly high if the reaction time is as long as 72 h (sample 1–6 and 9) (Table 1). In order to obtain much longer fluorinated block, we add an excessive amount of fluorinated monomer in the recipe of the sample Nos. 7 and 8. So the conversions in the case of Nos. 7 and 8 are much lower than those of others within the fixed reaction time. The polymerizations of fluorinated monomer FAEM initiated by bromine-endcapped PBMA have been studied in order to examine the ability to form well-defined copolymer of this ATRP system. GPC traces of the PBMA macroinitiator and the resulting block copolymer PBMA-*co*-PFAEM are shown in Fig. 1. The sample obtained after polymerization of FAEM is eluted earlier than the macroinitiator designating a formation of block copolymer. The monomodal in GPC trace of the copolymer indicated the absence of unreacted homopolymer and the efficient initiation of the macroinitiator for the copolymerization of the FAEM. The reaction solution was sampled periodically and the aliquots were analyzed by gravimetry and the GPC to obtain their conversion and molecular weight distribution. The molecular weight of fluorinated copolymer is determined by fluorine analysis method. The results are shown in Fig. 2. The M_n of copolymer increases linearly with the conversion and the polydispersity decreases gradually. Furthermore, the IR and H NMR results indicated that the copolymer PBMA-*co*-PFAEM was readily obtained (see below).

Fig. 3 shows the IR spectra of (a) macroinitiator (PBMA-Br) and (b) diblock copolymer (PBMA-*co*-PFAEM). Compare the IR spectra (a) with (b). The first region of interest lies between 1500 and 1000 cm^{-1} of IR spectroscopy (a), which is dominated by bands associated with motions of the CF_2 group at 1260 cm^{-1} ($\nu_a(\text{CF}_2) + r(\text{CF}_2)$) and 1160 cm^{-1} ($\nu_s(\text{CF}_2) + \delta(\text{CF}_2)$). In addition, the band at 1220 cm^{-1} is attributed to stretching and bending of the carbon skeleton of the fluorocarbon helix. The second region of interest is that between 600 and 800 cm^{-1} . There are two medium bands at 660 and 710 cm^{-1} , which

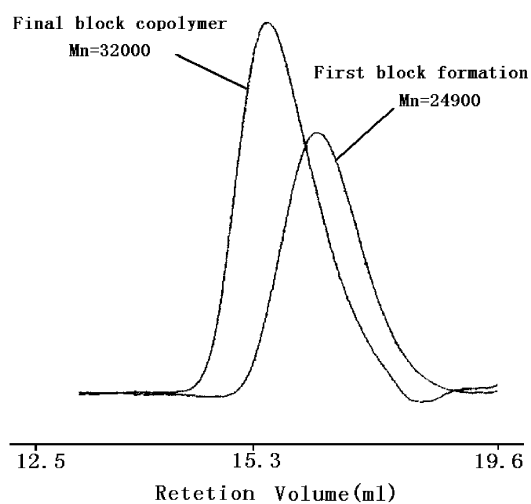


Fig. 1. GPC curves of PBMA-Br and PBMA-*co*-PFAEM (the sample is BMA₁₇₆FAEM_{11.9}).

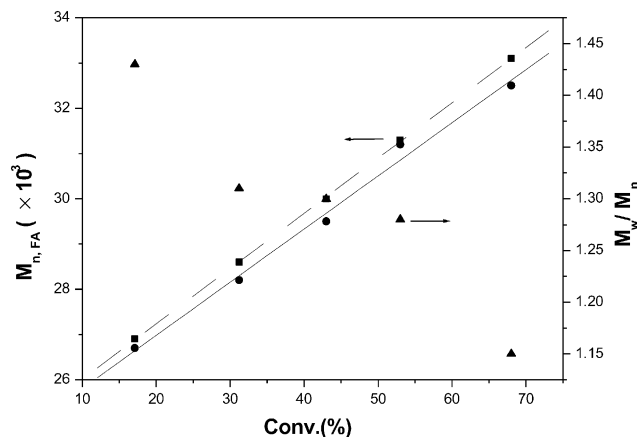


Fig. 2. Dependence of $M_{n,th}$, $M_{n,FA}$ and M_w/M_n of P(BMA-*b*-FAEM) on the conversion of fluorinated monomer initiated by macroinitiator PBMA. ((PBMA-Br)₀ = 0.0139 mol dm⁻³, (FAEM)₀ = 0.278 mol dm⁻³) ■ $M_{n,th}$; ● $M_{n,FA}$ (determined by fluorine analysis method); ▲ M_w/M_n (determined by GPC method).

result from a combination of rocking and wagging vibrations of CF₂ groups. Fig. 4 is a typical ¹H NMR spectrum of PBMA-*co*-PFAEM. A -OCH₂ peak at δ4.37 due to the second block PFAEM in the polymer chain is observed, and another -OCH₂ peak at δ3.92 is assigned to the block of PBMA. The structure of FAEM and BMA is so similar that other proton peaks almost overlap. Through IR spectroscopy and NMR results, the formation of fluorinated copolymer can be confirmed.

According to the experimental data, there are three methods to calculate the polymerization degree (*m*) of fluorinated block copolymers PBMA-*co*-PFAEM. The equations are expressed as follows.

1. GPC method:

$$m_1 = (M_{n,COP} - M_{n,BMA})/598 \quad (1)$$

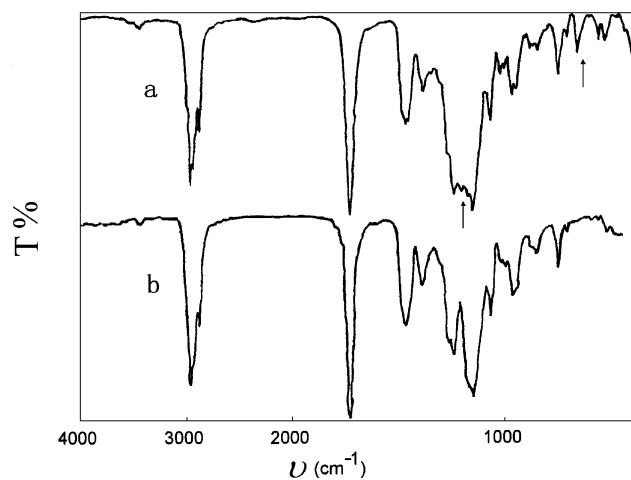


Fig. 3. IR spectra of PBMA-*co*-PFAEM (a) (the sample is No. 7) and PBMA-Br (b).

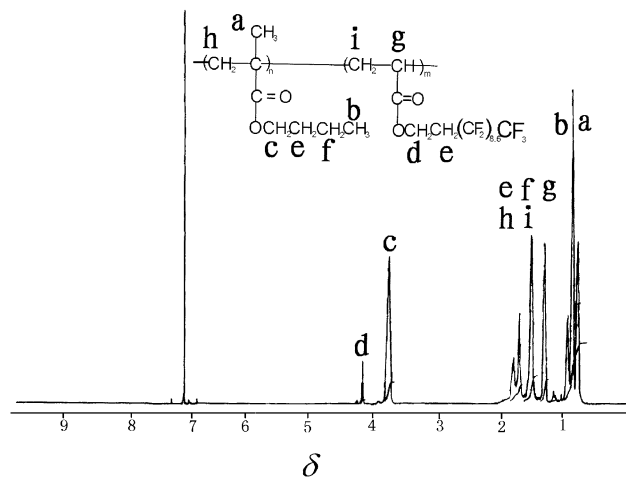


Fig. 4. ¹H NMR spectrum of PBMA-*co*-PFAEM (the sample is No. 7).

$M_{n,COP}$ and $M_{n,BMA}$ are the molecular weight of copolymer and PBMA measured by GPC. The molecular weight of fluorinated monomer FAEM is 598.

2. GPC—element analysis method:

$$m_2 = (M_{n,COP} \times F\%)/(20.2 \times 19) \quad (2)$$

F% is the fluorine content of copolymer measured by fluorine-element analysis of ignition method.

3. Fluorine analysis method:

$$F\% = (20.2 \times 19 \times m_3)/(M_{n,BMA} + 598 \times m_3) \quad (3)$$

Each fluorinated monomer FAEM contains 20.2 fluorine atoms on average. Fluorine atomic weight is 19. m_1 , m_2 , m_3 are polymerization degree of the PFAEM block.

Martin found that the GPC traces of the fluorinated copolymer had a higher molecular weight peak along with the expected normal molecular weight peak [6]. Christopher also observed the relatively broad higher molecular weight peak of some fluorinated samples [15]. When the temperature was increased or the polymer solutions were diluted, the higher molecular weight peak might disappear while the normal molecular weight peak did not [16]. The appearance of such peak suggested the formation of micelles in solution. Zhang has calculated the molecular weight of fluorinated copolymer by GPC [17]. The results showed the experimental molecular weight was different from the theoretical value [18,19]. They also attributed this difference to the aggregation of fluorinated blocks in solution.

These literatures suggest that the molecular weight of PBMA-*co*-PFAEM measured by GPC is less accurate because of the special property of fluorinated polymers. In addition, the structures of BMA and FAEM are so similar that most of the proton peaks are overlapping. Thus ¹H NMR method is not suitable for distinguishing them from each other. From what has been discussed, using Eq. (3) to calculate the molecular weight is a reasonable choice. The

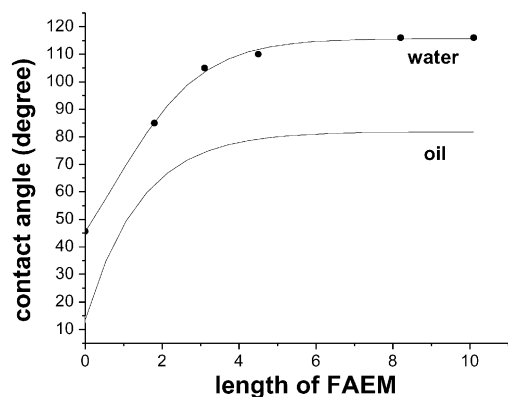


Fig. 5. Dependence of contact angles on length of FAEM (the samples used in this figure are Nos. 3–7).

calculated volume ratio of PBMA and PFAEM matched what we had designed very well (Table 1).

3.3. The effect of fluorine content on the water- and oil-repellency

The effect of the fluorine content has been studied by measuring the wettability of the copolymer surface. The wettability measurements can provide much useful information about the structure of polymeric surface. Similarly, polymers with well-defined surface can give considerable insights into interactions that control wetting. In order to study the relationship between the wettability and fluorine content of copolymer, one series of samples with fixed length of PBMA of variable length of PFAEM have been synthesized by ATRP through macroinitiator technique. The other samples with fixed PFAEM of variable length of PBMA have also been synthesized.

The relationship between contact angle and surface tension can be expressed by the following equation

$$\cos \theta = 1 - b(\gamma_{sv} - \gamma_{lv}) \quad (4)$$

where θ is the contact angle, b a constant, γ_{sv} the surface tension of solid and γ_{lv} is the surface tension of the wetting liquid. The fluorinated copolymers have low surface energy

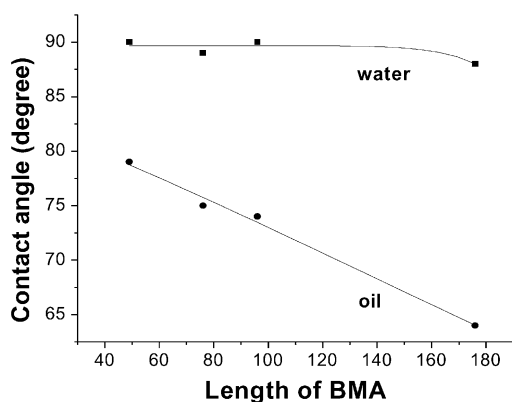


Fig. 6. Dependence of contact angles on length of BMA (the samples used in this figure are Nos. 1–3, 9).

property. Incorporation of fluorinated moieties into a polymer film has been shown to be effective for reducing the surface energy to produce nonwetable surfaces. Fig. 5 shows that the contact angles of water and paraffin oil are dependent on PFAEM length. For these samples, the length of PBMA block was fixed at the polymerization degree of 96 by macroinitiator technique. The contact angles of the pure PBMA with water and paraffin oil are around 45.6 and 13.3°, respectively. When the fluorinated monomers are incorporated in the copolymer chains, the fluorinated copolymer will show very high contact angle comparing to that of homopolymer PBMA. Because fluorine atom has extremely low surface free energy and self-aggregated property, this property causes the fluorinated segment to be absorbed and oriented to the surface of the systems so as to decrease surface tension. Therefore, contact angle θ increases with an increase in PFAEM content of copolymer. According to the above equation, the γ_{sv} (the surface tension of solid) will decrease with increasing PFAEM content. Especially, in the region of PFAEM length < 4 (fluorine wt% < 10), water and paraffin oil contact angles initially increase rapidly with an increase in the PFAEM content and in the region of PFAEM length > 4.5 (fluorine wt% > 10.6) increase slowly. Increment of contact angle indicated the enrichment of fluorinated structure at the polymer surface. At the higher fluorine percentage, the tendency of incremental contact angle begins to weaken. It indicates the PFAEM group enrichment has reached a maximal value. Under this condition, to enhance fluorine content will have little influence on the surface-active property of copolymer.

To study the relation between the surface-active property and composition of copolymer carefully, contact angles on some samples with fixed PFAEM block and variable PBMA block size were examined. Fig. 6 summarizes the dependence of contact angle values on PBMA length. As far as these samples are concerned the lengths of fluorinated block were fixed, the degree of polymerization of fluorinated block ranging from 1.9 to 2.1. With the length of PBMA block increasing, in other words, with the fluorine relative content decreasing, the contact angles of water keep stable, whereas the contact angle of paraffin oil decreases gradually. This tendency suggests the oil-repellency of copolymer is weakened. The reason of this phenomenon can be attributed to the hydrophobic property of PBMA units and PFAEM units. The hydrophobic PBMA units can maintain the water-repellency under the condition of PFAEM content declining. On account of lipophilic property for the PBMA unit, the contact angle of paraffin oil decreased gradually is reasonable. This suggests that incorporation of fluorinated units affected the lipophobic property of copolymer much more remarkably than the hydrophobic property.

3.4. Effect of heat treatment on the surface property of PBMA-co-PFAEM

The block copolymers are also likely to be useful in a

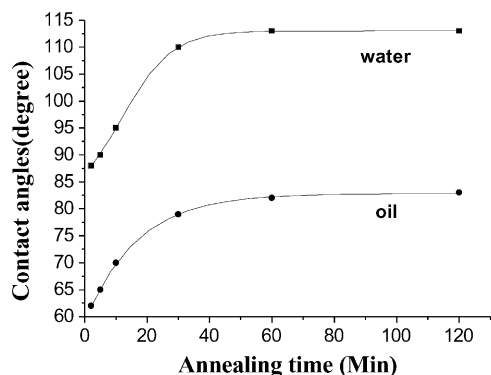


Fig. 7. The effect of annealing time on the contact angles of water and oil (annealing temperature is 120 °C, the sample is No. 7).

number of applications if the block chains with highly fluorinated side could segregate to the surface. A small amount of such an interfacial-active polymer can dramatically alter the interfacial energy of a polymer/polymer and/or of a polymer/nonpolymer system. Considering the PBMA-co-PFAEM diblock copolymer in a PBMA matrix, the PBMA block will be miscible with the matrix while the PFAEM blocks tend to segregate to the surface, and then minimize the surface energy of the system. The segregation will be driven both by the unfavorable enthalpic interactions between the fluorinated units FAEM and the PBMA block and by the decrease in the surface energy produced by substituting the PBMA block. The segregation of the fluorinated units is a process of fluorinated chains moving to air-polymer surface actually. The heat treatment affects the copolymer chains movement remarkably, so the heat treatment will make an impact on the segregation of fluorinate units dramatically.

Figs. 7 and 8 show how the heat treatment temperature and time affect the fluorinated copolymer surface-active property. It can be expected that the segregation of fluorinated units will be very slow at ambient temperature because the T_g of PBMA-co-PFAEM is near room temperature. (The T_g of the samples used in this paper are around

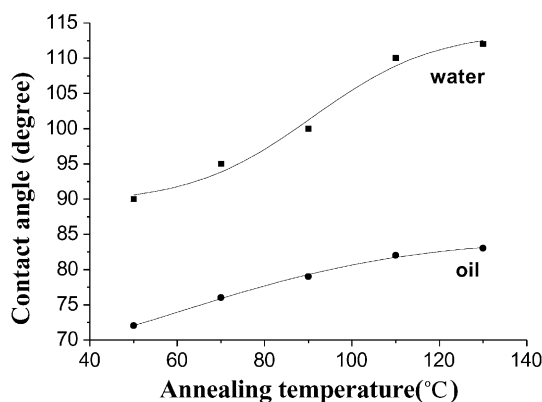


Fig. 8. The effect of annealing temperature on the contact angles of the water and oil (annealing time is 30 min and the sample is No. 7).

32 °C). Fig. 7 shows that the contact angle of water and paraffin oil for copolymer surface increased rapidly with increasing annealing time at the same annealing temperature. This tendency suggested the surface excess of fluorinated block increased gradually and reached a maximal value finally. The data from Fig. 8 indicate that the movement of fluorinated chains and segregating to air-polymer surface are much faster at higher annealing temperature. It takes less time to reach maximal surface excess value.

3.5. Surface properties of diblock copolymer

Thermodynamic wetting is a function of four parameters given by the well-known Yong's equation [20].

$$\cos \theta \times \gamma_{lv} = \gamma_{sv} - \gamma_{sl} - \pi_e \quad (5)$$

where γ_{lv} , γ_{sv} , γ_{sl} are the interfacial tensions at liquid-vapor, solid-vapor and solid-liquid interfaces, respectively, π_e is the equilibrium pressure of adsorbed vapor of the liquid on the solid. Although θ and γ_{lv} are easily obtained from the experiments and the previous literatures. In order to understand and predict the wetting property, it is essential that something should be known about γ_{sv} , γ_{sl} . Zisman has made a useful approach to this problem [21]. He introduced the concept of critical solid surface tension of wetting (γ_c). This empirical quantity is defined as value of γ_{lv} at the intercept of the plot of $\cos \theta$ vs. γ_{lv} with the horizontal line, when $\cos \theta = 1$, $\gamma_c = \gamma_{lv} = (\gamma_{sv} - \gamma_{sl} - \pi_e)$. In view of many workers inclining to identify γ_c with γ_{sv} , Zisman also pointed out that γ_c is not equal to the solid surface energy (γ_{sv}). Because it is not certain that $\gamma_{sl} = 0$ and $\pi_e = 0$ when $\theta = 0$. Fowkes has suggested that the total free energy at a solid surface comprise the different intermolecular forces at the surface. Thus the surface free energy for solid can be written as following equation [22]

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \quad (6)$$

where the superscripts d and p refer to the dispersion and polar force components.

Fowkes has derived equation for the contact angle on a solid in terms of the polar and dispersion force from the Yong equation. Fowkes equation can be written as follows:

$$1 + \cos \theta = 2\sqrt{\gamma_{sv}^d} \left(\frac{\sqrt{\gamma_l^d}}{\gamma_{lv}} \right) + 2\sqrt{\gamma_{sv}^p} \left(\frac{\sqrt{\gamma_l^p}}{\gamma_{lv}} \right) \quad (7)$$

By measuring θ of two different liquids against a same polymer surface, simultaneous equations are obtained which can be solved for γ_{sv}^d , γ_{sv}^p .

Table 2 shows the comparison of surface free energies estimated from contact angle data for the surface of PBMA-co-PFAEM. As the wt% of the (perfluoroalkyl) acrylate is increased, both γ_c , γ_{sv} values declined gradually. For sample BMA₉₆FAEM_{10,2}, the dispersion force component of the surface energy is 13.04 mN m⁻¹. This value is similar to the surface energy for homopolymer of (perfluoroalkyl)

Table 2

Surface properties of resulting block copolymers (γ_c represents the critical surface tensions which were obtained according to Zisman plot from the wettability experiment of *n*-alkanes [24]; total surface free energies and their dispersion and polar components were calculated by Fowkes equation [25])

Sample	W_F (%)	θ (H ₂ O) (°)	θ (C ₂ H ₂ I ₂) (°)	γ_c (mN m ⁻¹)	γ^d (mN m ⁻¹)	γ^p (mN m ⁻¹)	γ_{sv} (mN m ⁻¹)
BMA ₉₆ FAEM _{2,1} ^a	5.5	90	66	25	22.56	2	24.56
BMA ₉₆ FAEM _{3,1}	7.6	105	84	18.7	14.24	1.73	15.97
BMA ₉₆ FAEM _{4,5}	10.6	106	86	18.3	13.3	1.70	15.00
BMA ₉₆ FAEM _{8,2}	17.0	112	88	15.4	12.96	0.92	13.88
BMA ₉₆ FAEM _{10,1}	19.7	113	88	15.0	13.04	0.83	13.87

^a The γ_c of sample BMA₉₆FAEM_{2,1} was obtained from the wettability experiment of a series of polar liquid [26].

Table 3

Surface concentration Γ and molecular area a_0 for toluene solution of diblock copolymer with perfluoroalkyl side chains

Sample	BMA ₉₆ FAEM _{2,1}	BMA ₉₆ FAEM _{3,1}	BMA ₉₆ FAEM _{8,2}	BMA ₉₆ FAEM _{10,2}
$\partial\gamma/\partial \ln C$	-1.075	-4.50	-1.39	-1.74
Γ^∞ ($\mu\text{mol m}^{-2}$)	0.297	1.19	0.295	0.348
a_0 (nm ²)	5.59	1.39	5.62	4.78

acrylate ($\gamma^d = 9.3$) [20]. Thus both γ_c and γ_{sv} suggest that a rather ordered packing of the perfluoroalkyl segments exposes the CF₃ groups at the outermost layer of the polymer surface. It is remarkable, however, the copolymer with only 7.6 wt% (perfluoroalkyl) ethyl acrylate show surface energy characteristics comparable to those of poly (tetrafluoroethylene) (18.5 mN m⁻¹) and poly (dimethylsiloxane) (21.3 mN m⁻¹) [23]. Such results showed an outstanding surface activity of the PBMA-*co*-PFAEM. In addition, this kind of fluorinated copolymer can be formulated into coatings, which offer unique repellent property.

Surface activity of the fluorinated diblock copolymer in solution was investigated through maximum bubble pressure method. Surface tensions were measured in toluene. Fig. 9 shows the surface tension for the diblock polymers

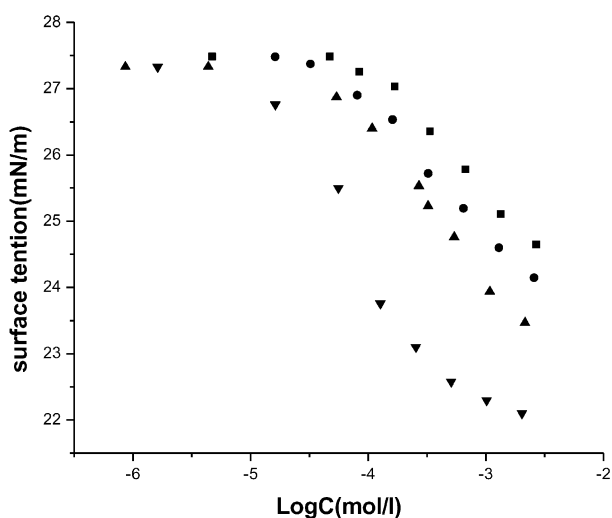


Fig. 9. Surface tension as a function of copolymer concentration for diblock copolymers with perfluoroalkyl side chains as measured in toluene ■ BMA₉₆FAEM_{2,1}; ● BMA₉₆FAEM_{3,1}; ▲ BMA₉₆FAEM_{8,2}; ▼ BMA₉₆FAEM_{10,1}.

as a function of copolymer mole percentage concentration (mole l⁻¹). All samples show a declining surface tension with polymer mole percentage concentration. Surface tension of sample BMA₉₆FAEM_{10,2} decreases strongest with the highest fluorine wt% among all samples. Sample BMA₉₆FAEM_{10,2} exhibiting unusually high values of surface activity, for its toluene solution with concentration greater than 5.1×10^{-4} mol l⁻¹, the surface tension measured is found to be less than 22.58 mN m⁻¹ (30 °C). This result can also be explained by the strong hydrophobic nature of fluorinated groups.

The data depicted in γ - C curves can also be employed for calculating the surface excess concentration Γ , and the occupied surface area of one molecule, a_0 . The Gibbs adsorption isotherm relates the Γ to the change of the surface tension Γ as the function of the solution concentration C [27]

$$\Gamma = -(\partial\gamma/\partial \ln C)/(RT) \quad (8)$$

where R is the gas constant and T is the absolute temperature. On a semilog plot relating Γ to the concentration, the number of adsorbed molecules per unit area can be obtained. Using the following expression, the area that per molecule occupies can be calculated. Because of no data about critical micelle concentration and unimer-micelle equilibrium, the Γ and a_0 -values as calculated from Eqs. (8) and (9) should be considered qualitatively. Nevertheless, these values of Γ and a_0 are valuable for investigating the surface-active property of fluorinated copolymer P(BMA-*co*-FAEM)

$$a_0 = 1/(N_{av}\Gamma) \quad (9)$$

where N_{av} is Avogadro's number. The Γ is surface excess concentration. The a_0 and Γ values obtained by above method are listed in Table 3. It showed the Γ of the copolymer is around $0.3 \mu\text{mol m}^{-2}$.

Due to the experimental error of $\partial\gamma/\ln C$ and defect of

mathematical model, the experimental data from the literature also showed some disorder [6]. The data from Table 3 showed that there was obvious deviation between the sample BMA₉₆FAEM_{3,1} and other samples. By making a comprehensive view of the experimental data and calculating results from Table 3, we found that when fluorinated copolymer PBMA-*co*-PFAEM adsorbed to maximal value at the air–solution interface, the occupied surface area of one molecule, a_0 , ranged from 4.8 to 5.6 nm².

4. Conclusions

In summary, ATRP polymerization of fluorinated monomer FAEM initiated by the bromine-endcapped PBMA was studied in detail. Efficient block copolymer formation had been demonstrated by FTIR and H NMR, and GPC. By combining the GPC and fluorine-element analysis, the molecular weight of the fluorinated copolymers were calculated more accurately. The experimental results matched the design very much. The (perfluoroalkyl) acrylate-containing acrylic copolymer was shown to be quite surface active in solution and, even more importantly, in the solid state. With incorporation of 7.6 wt% (perfluoroalkyl) acrylate FAEM, water- and oil-repellent surface were created obviously. The contact angles of the water and paraffin oil for polymer surface were larger than 100 and 75°, respectively. On the basis of contact angle measurements, how the length of fluorinated block and heat treatment affect the surface-active property was investigated systematically. Especially, in the region of PFAEM length < 4 (fluorine wt% < 10), water and paraffin oil contact angles initially increase rapidly with an increase in the PFAEM content and in the region of PFAEM length > 4.5 (fluorine wt% > 10.6) increase slowly. It indicates the process of the PFAEM group separating to polymer surface and reaching a maximal value. With the fluorine wt% higher than 7.6%, it could be estimated that surface tensions of copolymers were comparable to that of PTFE [22]. The block copolymer surface showed notable hydrophobic and lipophobic property.

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