Preparation and Surface Properties of Fluorine-Containing Diblock Copolymers PLMA-Block-PFAEA

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Preparation and Surface Properties of Fluorine-Containing Diblock Copolymers PLMA-Block-PFAEA

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A series of fluorine-containing diblock copolymers based on lauryl methacrylate and 1H,1H,2H,2H-perfluoroalkyl acrylate have been prepared by atom transfer radical polymerization (ATRP). The preparation process of PLMA-Br macroinitiators was controlled within a reasonable time corresponding to the ln $[M_0]/[M_t] \sim$ time plot of the reaction. FTIR, ^{1}H-NMR, GPC and fluorine-element analysis (FEA) were used to characterize the synthesized block copolymers. The solid surface activity of these polymers was demonstrated by contact angle measurement. The polymer films prepared by block copolymers with more than three fluorinated units showed low dispersion force contributions to the surface energy indicating the presence of the fluorinated block at the surface. The surface activity in solutions was measured by drop-weight method. Ii is interesting to find, when the fluorine weight percentage is controlled constant, that PLMA-b-PFAEA with larger molecular size is more prominent in exploiting the fluorinated structure to reduce the surface tension of solutions. The block copolymer's ability in reducing surface tension of solutions also depends on the type of solvent.

Keywords: atom transfer radical polymerization (ATRP); diblock copolymers; fluoropolymers; lauryl methacrylate; surface properties

1 Introduction

It is known that the properties of thermoplastics can be varied by incorporating a small amount of fluorinated monomer in order to reduce surface friction and offering applications such as oil and water repellent coatings (1). Semi-fluorinated block copolymers are of potential interest, e.g. as emulsifiers in liquid and supercritical carbon dioxide (2) and as surfactants for the nucleation and stabilization of polyurethane foams (3).

Fluorochemicals have been known to exhibit both water- and oil-repellency since the late 1950′s. 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 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 properties, one approach is to increase the fluorine content of the fluorinated copolymer. 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 (4).

Atom transfer radical polymerization (ATRP) is one of the most widely used controlled radical polymerization (CRP) techniques. Polymers synthesized by ATRP are typically end-capped by a halogen atom, which can act as a macroinitiator for the synthesis of another block. The polymerization of pentafluorostyrene, perfluoroalkyl (meth) acrylates with ATRP has been reported (5−8).

Previously, we have reported the synthesis and characterization of poly(butyl methacrylate) PBMA-based and poly(methyl acrylate) PMA-based semifluorinated block copolymers (9, 10). In this article, we report the synthesis of poly(lauryl methacrylate-block-perfluoroalkyl acrylate) PLMA-b-PFAEA by ATRP. LMA, with its side chain length 12, has been widely used in random copolymers of fluorine-containing (methyl) acrylates (11, 12). However, controlled synthesis of PLMA homopolymers and block copolymers is not easy by anionic techniques since LMA has limited solubility in solvents such as tetrahydrofuran below 0°C. In this paper, we also report the structure characterization, solid and solution surface properties of these polymers.

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2 Experiment

2.1 Materials

Monomer lauryl methacrylate (LMA) was washed with 5% NaOH and deionized water, dried through CaH$_2$, 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 (13).

N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA from Aldrich Co. 98%) was used as received. Perfluoroalkyl acrylate (FAEA) was kindly supplied from Clariant Company. FAEA was stirred over CaH$_2$ overnight at 40°C, then distilled under reduce pressure. The FAEA used in current study is a mixture of CH$_2$ = CHCO$_2$CH$_2$ CH$_2$ (CF$_2$)$_n$CF$_3$ with different n (n = 5, 7, 9, 11, and 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 0.0761 g, CuBr 0.0671 g, PMDETA 0.1031 g, LMA 20 ml, cyclohexanone 20 ml, and reaction temperature 70°C. The reaction time is set according to calculation on the ln [M$_0$]/[M$_t$]∼time plot and discussed in the Results and Discussion section. The reaction flask was deoxygenated via three freeze-pump-thaw cycles. 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 150°C gel permeation chromatography equipped with Ultrastyragel columns of 100, 10 000 Å porosities using THF as eluant at 25C. 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. ^{1}H-NMR spectra were recorded using a Bruker 500 Hz spectrometer. Fluorine percent was obtained through fluorine-element analysis of the ignition method. A laser light-scattering spectrometer (Malvern Autosizer 4700) equipped with a multi-τ digital time correlation (Malvern PCS7132) and Compass 315M-100 Diode-Pumped Laser (output power ≥100 mW, CW at λ_0 = 532 nm) as a light source was used for the DLS measurements. The DLS measurements were done at 25.0 ± 0.1°C and at a scattering angle of 90°. The measured time correlation functions were analyzed by Automatic Program equipped with the correlator.

2.4 Measurement of Contact Angles and Surface Tension of Copolymer Solutions

Glass microscope slides were etched (H$_2$SO$_4$ 200 ml) at 120°C. Polymer solutions were prepared up to 5 wt% in petroleum ether (boiling range 30–60°C). The slides were coated with a thin film by the scratch casting method and left to dry in vacuum. The slides were also annealed in an oven at 120°C for 10 h. The thickness of the coat is about 200 µm. Contact angle measurements of a 0.5 µL water or oil drop on the surfaces were performed with JC-2000-series surface tension instrument (Shanghai Zhongchen Digital Equipment Ltd. Co.). The time lapsed between the drop application and the measurement was fixed at 4 sec. For each sample, at least seven 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 drop-weight method and analyzed with the following expression (14):

$$\gamma = \frac{m \cdot g}{2\pi r f}$$

Where m is the weight of drop, g is the gravitational acceleration, r is the capillary tip radius, and f is the so-called Harkins and Brown correction factor. The value of f can be calculated from the following equation (15):

$$f = 0.9045 - 0.7249(r/V^{1/3}) + 0.4293(r/V^{1/3})^2$$

Where V is the volume of the drop and was determined by the mass and density of the drops.

3 Results and Discussion

3.1 Synthesis and Characterization of Macroinitiator

The bromine end-capped macroinitiators PLMA-Br were prepared by ATRP of LMA in the presence of ethyl 2-bromoisobutyrate/cuprous bromide/PMDETA (1:1.2:1.5) at 70°C. To investigate the kinetic process during the preparation of PLMA-Br, the ln [M]$_0$/[M]∼time plot was made under 70°C (see Figure 1). As Figure 1 shows, the slope of the curve remained constant before 30 min (Conv. = 83.4%) and then a notable decline occurred. The reaction time of preparing macroinitiators should be less than the decline point of the slope of ln [M]$_0$/[M]∼time curve in order to guarantee the reactive species of the system remain constant. After the decline point, the conversion increased little, while the loss of bromine ends proceeded (16). The later block copolymerization was not satisfactory (the fluorine weight percentage of ultimate block copolymer was much less than designed) when initiated by the macroinitiators prepared in an excessively long time due to their loss of end functionalities. At the end of polymerization, the polymer solutions were added in petroleum ether (boiling range 30∼60°C and passed through an alumina column to remove the catalyst CuBr, then
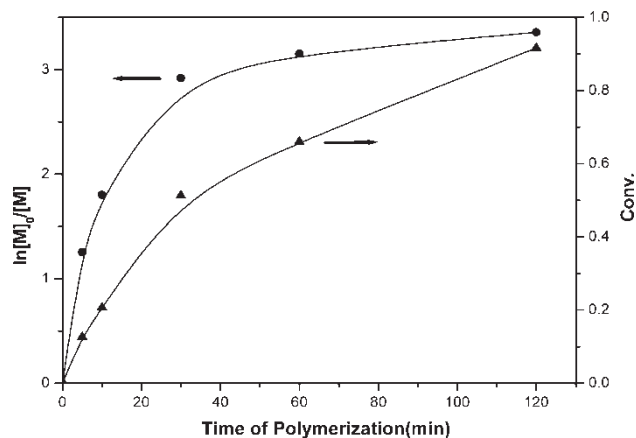
Fig. 1. Kinetics of solution ATRP of LMA in cyclohexanone at 70°C:[LMA] = 1.71M([EBiB]:[CuBr]:[PMDETA]:[LMA] = 1:1.2:1.5:75).

isolated by precipitation with methanol. The macroinitiator PLMA-Br was left to dry in vacuum at 40°C for several days. The molecular weight and molecular weight distribution of macroinitiators were measured by GPC.

3.2 Synthesis and Characterization of the Block Copolymer Containing the FAEA Segments

The block polymerization of fluorinated monomers was performed using the above bromine terminated PLMA-Br as macroinitiators. In order to achieve high conversion of FAEA, the reaction temperature of the second block was increased to 90°C which is higher than that of LMA. The experimental results show that the fluorinated monomer conversion will be highest if the reaction time is as long as 72 h (sample 1~6) (Table 1). Nos. 7, 8 and 9, with much less fluorine content, were obtained in the early stage of the FAEA block copolymerization. GPC

traces of the macroinitiator PLMA-Br and the resulting block copolymer PLMA-b-PFAEA are shown in Figure 2. The sample obtained after polymerization of FAEA is eluted earlier than the macroinitiator. 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 FAEA. The IR and ^{1}H-NMR results (see below) also indicated that the copolymer PLMA-b-PFAEA was readily obtained.

Figure 3 shows the IR spectra of (a) macroinitiator (PLMA-Br) and (b) diblock copolymer (PLMA-b-PFAEA). 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} (ν_a(CF$_2$) + r(CF$_2$)) and 1160 cm^{-1} (ν_s(CF$_2$) + δ(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 680 and 770 cm^{-1}, which results from a combination of rocking and wagging vibrations of CF$_2$ groups.

Figure 4 is a typical ^{1}H-NMR spectrum of PLMA-b-PFAEA. The -OCH$_2$- peak'd' (δ = 4.37) due to the second block PFAEA in the polymer chain is observed, and another -OCH$_2$- peak at 'c' (δ = 4.12) is assigned to the block of PLMA. The structure of the two blocks (FAEA and LMA) is somewhat similar, so overlaps did happen for some other protons (see Figure 4). 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 of fluorinated block copolymers PLMA-b-PFAEA as we concluded here and upon early studies of our group (9, 10). The equations are expressed as follows:

Table 1. Polymerization results of FAEA with bromine endcapped PLMA (T = 90°C, t = 72 h, [PLMA-Br]/[CuBr]/[PMDETA]/ = 1:1.2:1.5)

Samples	PLMA-Br ($M_n \times 10^{-4}$)	M_w/M_n^a	PLMA-b-FAEA^b ($M_n \times 10^{-4}$)	Conv. of FAEA^c (%)	W_F^d(%)	LMA$_x$FAEA$_y^d$
No.1	1.47	1.75	2.67	96.00	28.82	LMA$_{57}$FAEA$_{20.0}$
No.2	2.62	1.33	4.39	85.46	25.94	LMA$_{102}$FAEA$_{29.6}$
No.3	2.97	1.36	5.20	91.90	27.57	LMA$_{116}$FAEA$_{37.2}$
No.4	4.13	1.43	6.99	87.90	26.37	LMA$_{161}$FAEA$_{48.0}$
No.5	4.36	1.46	7.61	91.37	27.41	LMA$_{171}$FAEA$_{54.3}$
No.6	2.97	1.36	8.13	90.40	40.69	LMA$_{116}$FAEA$_{86.3}$
No.7	2.97	1.36	3.82	71.15	14.23	LMA$_{116}$FAEA$_{14.2}$
No.8	2.97	1.36	3.13	33.30	3.33	LMA$_{116}$FAEA$_{2.7}$
No.9	2.97	1.36	3.03	26.20	1.31	LMA$_{116}$FAEA$_{1.0}$

^{a}The polydispersity of macroinitiator was gained from GPC, calibrated by polystyrene standards.
^{b}The molecular weight of copolymer was calculated from LMAxFAEAy.
^{c}FAEA represents FLUOWET (CH$_2$=CHCO$_2$CH$_2$CH$_2$(CF$_2$)$_n$CF$_3$, n = 5, 7, 9, 11, and 13; average n ≈ 8.6) monomer.
^{d}W$_F$ represents fluorine content obtained from fluorine element analysis.
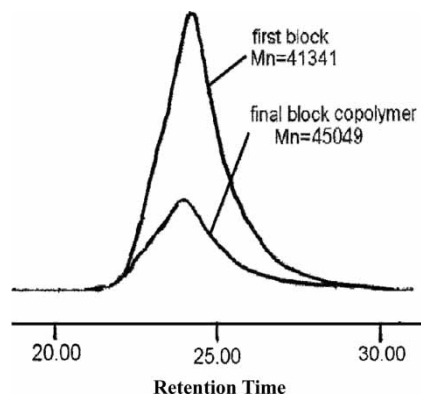
Fig. 2. GPC Curves of the PLMA-Br and PLMA-b-PFAEA (the sample is LMA$_{161}$FAEA$_{48.0}$).

3.2.1 GPC Method, Equation 1

$$DP_F = (M_{n,cop} - M_{n,LMA})/598 \qquad (1)$$

$M_{n,cop}$ and $M_{n,LMA}$ are the molecular weight of copolymer and PLMA measured by GPC. DP_F is the polymerization degree of fluorinated block. The molecular weight of fluorinated monomer FAEA is 598.
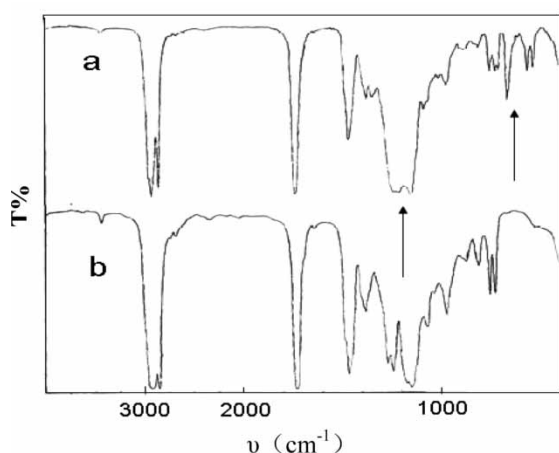
3.2.2 GPC–^{1}H-NMR Method, Equation 2

$$DP_F = \frac{A_{F,-OCH2-}/2}{A_{LMA,-OCH2-}/2} \times DP_{LMA} \qquad (2)$$

$A_{F,-OCH2-}$ and $A_{LMA,-OCH2-}$ are the areas of -OCH$_2$- of FAEA and LMA in the ^{1}H-NMR spectra. DP_{LMA} is the polymerization degree of LMA block.
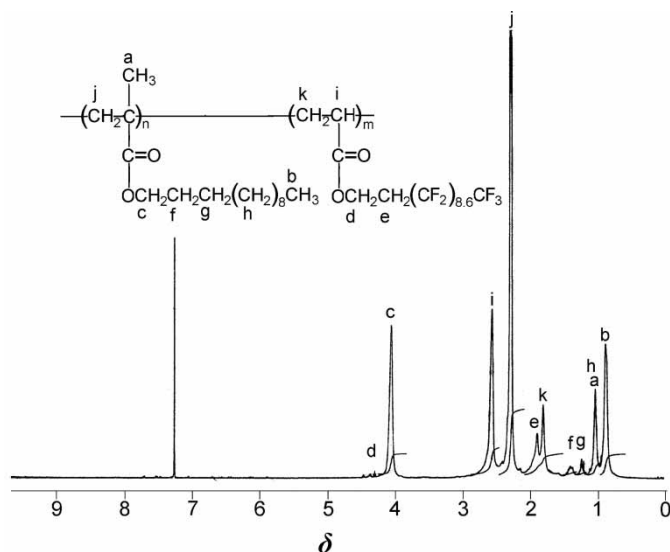
3.2.3 GPC–Fluorine Analysis Method, Equation 3

$$F\% = (20.2 \times 19 \times DP_F)/(M_{n,LMA} + 598 \times DP_F) \qquad (3)$$

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

Fig. 3. IR spectra of PLMA-b-PFAEA (a) (the sample is LMA$_{161}$-FAEA$_{48.0}$) and PLMA$_{161}$-Br (b).

Fig. 4. ^{1}H-NMR spectrum for PLMA-b-PFAEA (the sample is LMA$_{161}$FAEA$_{48.0}$).

fluorinated monomer FAEA contains 20.2 fluorine atoms on average. Fluorine atomic weight is 19.

For fluorinated polymers, it has been pointed out by many researchers that aggregations really formed in GPC solution (17–19) and the GPC results were different from the theoretical values (20, 21). In this investigation, taking No. 4 (see Table 1) as an example, the DP$_F$ value calculated from GPC results was 6.2 much less than the GPC–FEA result 48.0, which is closer to the value obtained gravimetrically. Therefore, the GPC method is less accurate for fluorine-containing block copolymers because of the poor solubility and low hydrodynamic volume in THF of fluorinated block. GPC–^{1}H-NMR method is also unsuitable for distinguishing the polymerization degree of fluorinated block because of the overlapping proton peaks of LMA and FAEA and moreover, aggregations in the NMR solution bring a shielding effect to -OCH$_2$- of FAEA (10). Still taking sample No. 4 as example, the DP$_F$ value calculated from GPC–^{1}H NMR method was 3.5 acting as an obvious deviation from the GP–FEA result 48.0. This shielding effect has also been discussed by Frechet in the investigation on benzyl ether dendrimers (22, 23). The GPC–fluorine analysis method is a reasonable choice for calculating the molecular weight of PLMA-b-PFAEA and the calculated volume ratio of PLMA and PFAEA matched the designed ones well. (Table 1).

3.3 ^{1}H-NMR and DSL Study for PLMA$_{161}$-b-PFAEA$_{48}$ in Mixed Solvents CDCl$_3$/C$_2$F$_3$Cl$_3$

The decreased mobility of protons in polymer chains/blocks with hindered motion causes broadening of the respective NMR lines and even disappearance of the corresponding signal when the polymer/block is in the glassy state. These phenomena have already been observed in the early 80's by Spevacek (24) for PS–PB in a selective solvent for the
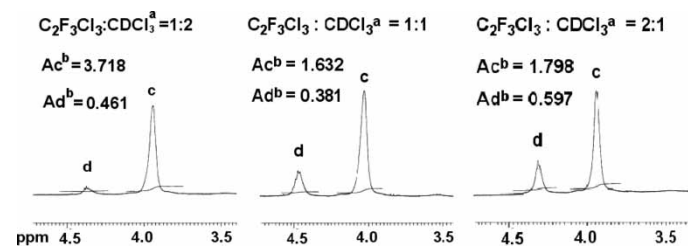
aliphatic block. The aromatic signal of PS could not be detected at all in high resolution spectra at 26°C, demonstrating that the PS in the aggregates' core is in the glassy state.

In order to improve the solubility of the synthesized fluorinated block copolymers PLMA-b-PFAEA and to confirm the aggregation also with a glassy core of these copolymers in CDCl$_3$ solvents, 1, 1, 2-trichlorotrifluoroethane was adopted in the ^{1}H-NMR characterization of PLMA$_{161}$-b-PFAEA$_{48}$ (No. 4, see Table 1).

Figure 5 shows that the apparent DP$_F$ value (degree of polymerization of fluorinated block calculated according to equation (2)) by the GPC$-$^{1}H-NMR method increases with the rising of the fluorinated solvent content (C$_2$F$_3$Cl$_3$:CDCl$_3$ (V:V)) in the mixed solvents for NMR measurements. It indicates that the fluorinated block of the investigated copolymer turns out to be more soluble when the fluorinated component is added, so the fluorinated part of these polymers can be better detected by NMR measurements. Here the aggregation behavior of the synthesized fluorine-containing block copolymers in CHCl$_3$ can be further confirmed.

The DP$_F$ values are calculated as 20.0(C$_2$F$_3$Cl$_3$:CDCl$_3$ (V:V) = 1:2), 37.6(C$_2$F$_3$Cl$_3$:CDCl$_3$ (V:V) = 1:1) and 53.5(C$_2$F$_3$Cl$_3$:CDCl$_3$ (V:V) = 2:1), respectively. It is obvious that the DP$_F$ value 53.5 is very close to GPC$-$FEA (fluorine element content analysis) result 48.0, when the C$_2$F$_3$Cl$_3$:CDCl$_3$ (V:V) ratio is raised to 2:1, which proves the existence of molecularly dispersed block copolymers with flexible FAEA blocks in the NMR solutions. However, the GPC$-$^{1}H-NMR method with mixed solvents is not encouraged in determining the structures of fluorine-containing block copolymers, since the suitable fluorinated solvent content of the mixture solution for ^{1}H-NMR measurements cannot be determined beforehand without fluorine element content analysis, furthermore, an excess amount of fluorinated solvent may lead to higher DP$_F$ values since the reduced solubility of non-fluorine blocks.

The DSL analysis of PLMA$_{161}$-b-FAEA$_{48}$ in the mixed solvent of CHCl$_3$ and C$_2$F$_3$Cl$_3$ was performed for the further confirmation of the existence of aggregates in pure CHCl$_3$ solvent and molecularly dispersed block copolymers in mixed solvent of CHCl$_3$/C$_2$F$_3$Cl$_3$. The detected average

⟨D$_h$⟩ values of DLS measurements of molecularly dispersed LMA$_{161}$-b-FAEA$_{48}$ are 27 nm (C$_2$F$_3$Cl$_3$:CDCl$_3$ (V:V) = 1:2), 30 nm(C$_2$F$_3$Cl$_3$:CDCl$_3$ (V:V) =1:1), and 29 nm(C$_2$F$_3$Cl$_3$:CDCl$_3$ (V:V) =2:1). However, in pure CHCl$_3$ solvent, there was no ⟨D$_h$⟩ signal in the range of molecularly dispersed block copolymers, even in the dilute solution (the concentration is tenth of the normal NMR solutions), but only an average ⟨D$_h$⟩ value of more than 250 nm with high PDI was detected, which corresponds to the aggregates of the block copolymers.
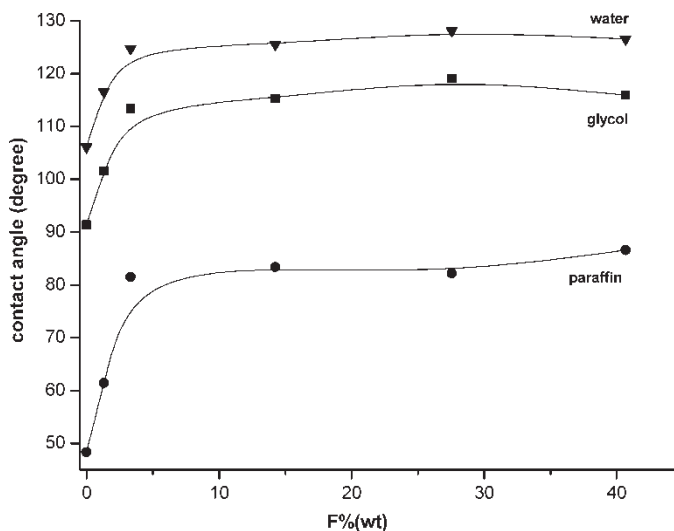
3.4 The Effect of Fluorine Content on the Water-, Alcohol-, and Oil-Repellency

In order to study the relationship between the wettability and fluorine content of block copolymers, a series of samples with a fixed length of PLMA and variable length of PFAEA have been synthesized by ATRP through the macroinitiator technique.

The relationship between contact angle and surface tension can be expressed by the following Equation (4):

$$Cos\ \theta = 1 - b(\gamma_s - \gamma_l) \qquad (4)$$

Where θ is the contact angle, b a constant, γ_s the surface tension of solid and γ_l is the surface tension of the wetting liquid. The fluorinated copolymer film has been shown to be effective for reducing the surface energy to produce non-wettable surface (Figure 6) shows that the contact angles of water, glycol and paraffin oil are dependent on the fluorine content. For these samples, the length of PLMA block was fixed at 116 by the macroinitiator technique. The contact angles of the pure PLMA with water, glycol and paraffin oil are around 106°, 92°, and 48°, respectively. Remarkable elevation of contact angles was observed when FAEA monomers are incorporated into the copolymer chains.

Fig. 5. ^{1}H-NMR spectra for PLMA$_{161}$-b-FAEA$_{48}$ (in the mixed solvent of CDCl$_3$ and C$_2$F$_3$Cl$_3$) [a]CDCl$_3$:C$_2$F$_3$Cl$_3$ here represents the volume ratio. [b]Ac and Ad delegate the area of peak c and peak d respectively in the ^{1}H-NMR spectra. Peak c is for the structure of -OCH$_2$- assigned to the block of PLMA and peak d is for -OCH$_2$- of block PFAEA.

Fig. 6. Dependence of contact angles on the weight percentage of Fluorine (the samples used in this figure are Nos. 3, 6−9 and their macroinitiator PLMA$_{116}$-Br).

The fluorinated segments of block copolymers move to the film surface and form into regular structures spontaneously (19). As Figure 6 shows, contact angle values of water, glycol and paraffin oil all exhibit an increasing trend with an increase in fluorine composition. In the range of F% (wt) <3.3% (PFAEA length <3) contact angles increase rapidly, while in the region of F% (wt) >3.3% (PFAEA length >3) the increase slows down. It indicates a distinct enrichment of the PFAEA segments to the film surface before the PFAEA length reaches 3 and the enrichment effect has come to a maximal value at higher fluorine percentage. Furthermore, incorporation of fluorinated monomers seems to be fruitless in elevating the copolymers' surface-active property.

3.5 The Effect of Heat Treatment on the Surface Property of PLMA-b-PFAEA

The surface segregation of the fluorinated block of PLMA-b-PFAEA will be driven by the unfavorable enthalpy interactions between the fluorinated units FAEA and the PLMA block and by the decrease in the surface energy produced by substituting the PLMA block. The fluorinated units' movement to the air-polymer surface is affected by the heat treatment. Figures 7 and 8 show how the heat treatment time and temperature affect the fluorinated copolymer surface-active property. At the same temperature (120°C), contact angle values of water and paraffin oil show an increase trend with the time of heat treatment and the condition is similar when the time (30 min) was fixed and temperature was elevated. Compared to our previous investigation (9) on PBMA-b-PFAEA, the augmentation in contact angles through heat treatment is rather weak,
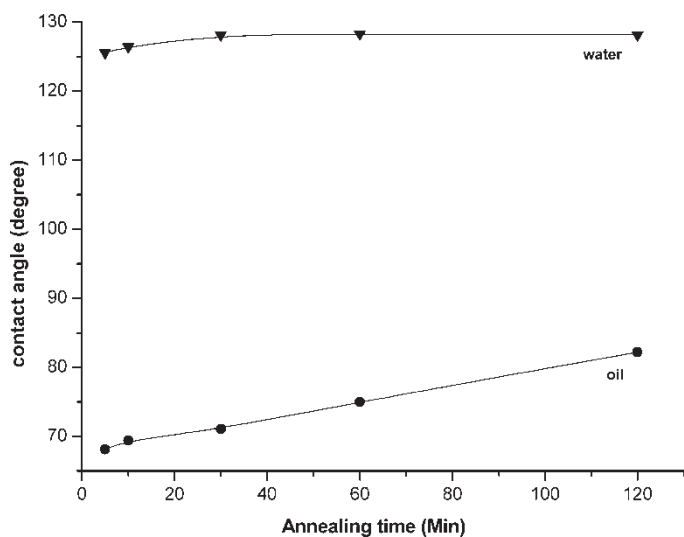
Fig. 7. The effect of annealing time on the contact angles of water and oil* Oil represnsts paraffin liquid ▼ Contact angles of the water; • Contact angles of the oil (Annealing temperature is 120°C, the sample is No. 3).
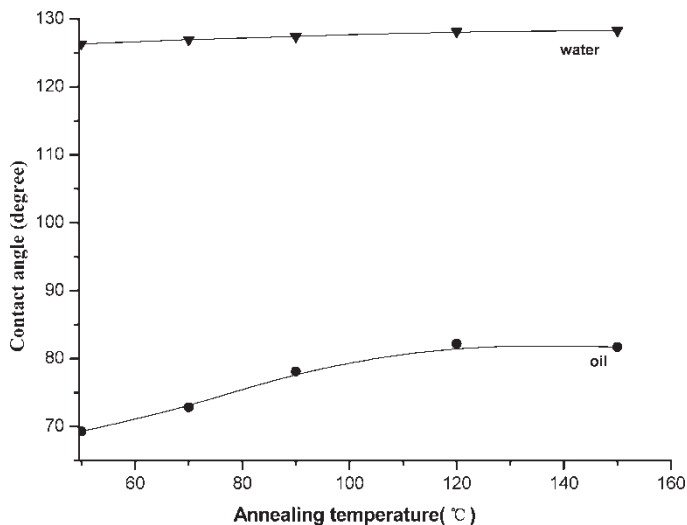
Fig. 8. The effect of annealing temperature on the contact angles of the water and oil* Oil represnsts paraffin liquid ▼ Contact angles of the water; • Contact angles of the oil (Annealing time is 30 min, the sample is No. 3).

especially in the case of water. This can be attributed to two aspects: (a) PLMA-b-PFAEA has a rather low Tg (Tg of the LMA blocks is around −35°C) and the segregation of fluorinated units would be rather sufficient even at room temperature; (b) The pure PLMA film has fairly good water-repellency (The contact angle of pure PLMA film with water is around 106°) due to the attachment of a long alkyl side chain. The fact that the effect of heat treatment on oil repellency is more obvious than on water can be explained by the hydrophobic and lipophilic nature of PLMA block. Furtermore, from the oil contact angle curves in Figures 7 and 8, the movement of fluorinated chains to air-polymer surface driven by heat treatment can be indicated.

3.6 Solid Surface Properties of PLMA-b-PFAEA Diblock Copolymer

Since the solid surface energy of polymer cannot be determined directly, the method of estimation by contact angles was employed in this paper. Fowkes assumed that the interactions which contribute to the work of adhesion are only those which operate across the interface. Moreover, he believes only dispersion interactions are important in this concept. So Equation (7) can be obtained upon the Rayleigh-Good Equation (5) and Young's Equation (6) to determine γ_s^d (the dispersive component of the solid surface tension) from the experimental contact angle values θ and γ_l and from the dispersive component γ_l^d of the liquid surface tension. In these equations, γ_l, γ_s and γ_{sl} are the interfacial tensions at liquid-vapor, solid-vapor and solid-liquid interfaces, respectively. It should be pointed out that Equation (7) is valid when both the

Table 2. Surface properties of resulting block copolymers (γ_s, γ_s^d and γ_s^p represent total surface energies, the dispersion and polar components respectively calculated by Owens and Wendt equation from the contact angle data of water and CH_2I_2)

Sample	W_F (%)	θ (H_2O) (°)	θ (CH_2I_2) (°)	γ_s^d (mN·m^{-1})	γ_s^p (mN·m^{-1})	γ_s (mN·m^{-1})
LMA$_{116}$	0	106	63	27.16	0.05	27.21
LMA$_{116}$FAEA$_{1.0}$	1.3	116	81	17.36	0.01	17.37
LMA$_{116}$FAEA$_{2.7}$	3.3	124	99	9.03	0.06	9.09
LMA$_{116}$FAEA$_{14.2}$	14.2	125	100	8.69	0.05	8.74
LMA$_{116}$FAEA$_{37.2}$	27.6	128	101	8.12	0.01	8.13
LMA$_{116}$FAEA$_{86.3}$	40.7	126	101	8.41	0.02	8.43

solid and the liquid are nonpolar, but it also gives a reasonable approximation when only one is nonpolar.

$$1 + \cos\theta = 2\sqrt{\gamma_s \gamma_l} \qquad (5)$$

$$\gamma_{sl} = \gamma_s - \gamma_l \cos\theta \qquad (6)$$

$$1 + \cos\theta = 2\sqrt{\gamma_s^d \left(\frac{\sqrt{\gamma_l^d}}{\gamma_l}\right)} \qquad (7)$$

Owens and Wendt (25) extended the ideas of Fowkes to those cases where both dispersive and polar intermolecular forces operate across the interface. The assumption is that the value of the surface tension is the sum of two components, $\gamma = \gamma^d - \gamma^p$ (where the superscript p stands for polar). The solid-liquid interfacial tension can then be written as:

$$1 + \cos\theta = 2\sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_l^d}}{\gamma_l}\right) + 2\sqrt{\gamma_s^p}\left(\frac{\sqrt{\gamma_l^p}}{\gamma_l}\right) \qquad (8)$$

From Equation (8), the components of the surface tension of the solid (and its total surface tension) can be obtained from the values of contact angles measured with a pair of testing liquids whose surface tension components (dispersive and polar) are known.

Table 2 shows the comparison of γ_s values estimated from contact angle data for a series of PLMA-b-PFAEA copolymers. The γ_s values of PLMA-b-PFAEA are mainly composed of their dispersive components and show a decrease trend with increasing PFAEA block length. For sample LMA$_{116}$FAEA$_{2.7}$, in which only less than three fluorinated repetitive units per chain are incorporated (F% (wt) <3.33%), the γ_s^d value reached 9.03 mN·m^{-1}, similar to the values ($\gamma_s^d = 9.3$ mN·m^{-1}) of poly(perfluoroalkyl acrylate) reported by Owens and Wendt (25). The low γ_s values suggest a rather densely ordered packing of fluorinated alkyl side chain at the outermost layer of the film surface.

3.7 Surfactant Properties of PLMA-b-PFAEA Diblock Copolymer

The surfactant properties of PLMA-b-PFAEA diblock copolymers in solutions were studied with the drop-weight method. Surface tensions were measured in THF and

CHCl$_3$ as solvents, respectively. We initially attempted to adopt the maximum bubble pressure method, while, during the measurement, bubbles floated at the solution surface and were not easy to be eliminated. The drop-weight method is rather straightforward and precise in measuring the surface tension of solutions. Shinoda has investigated the surface tensions of fluorinated surfactant solutions through the drop-weight method and the data error was controlled less than 0.2 mN·m^{-1} (26). Parreira has pointed out the control of temperature should be emphasized in the accuracy of the drop-weight method (27). The temperature of the solution surface tension measurements in this paper is strictly set at 26°C.

Figures 9 and 10 show the surface tension data PLMA-b-PFAEA as a function of copolymer weight percentage concentration. All samples show a declining surface tension with polymer weight percentage concentration, which indicates surface enrichment of fluorinated structures. The γ-c plot for the series with perfluoroalkyl groups resembles the shape of curves typically encountered for 'polysoaps' (28) which are characterized by (a) a continuous decrease in surface tension with increasing polymer concentration and (b) the absence of a clear breakpoint at the CMC. From
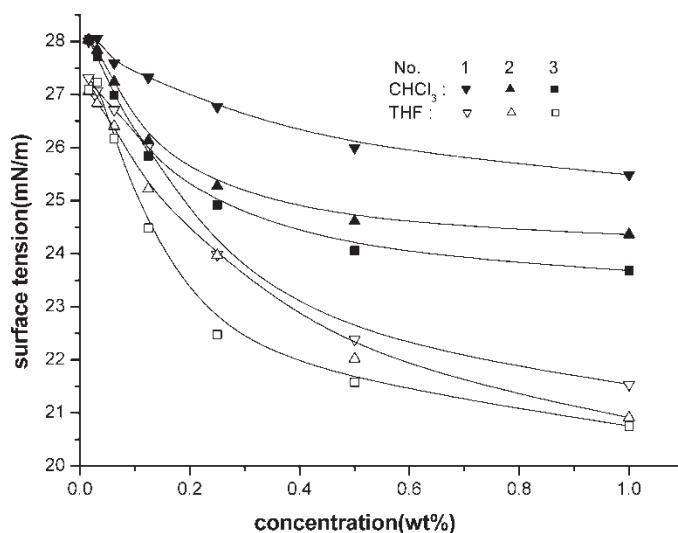
Fig. 9. Surface tension as a function of polymer concentration for diblock copolymers with perfluoroalkyl side chains as measured in solutions. ▼ ▽-No.1; ▲ △-No.2; ■ □-No. 3 (see Table 1).
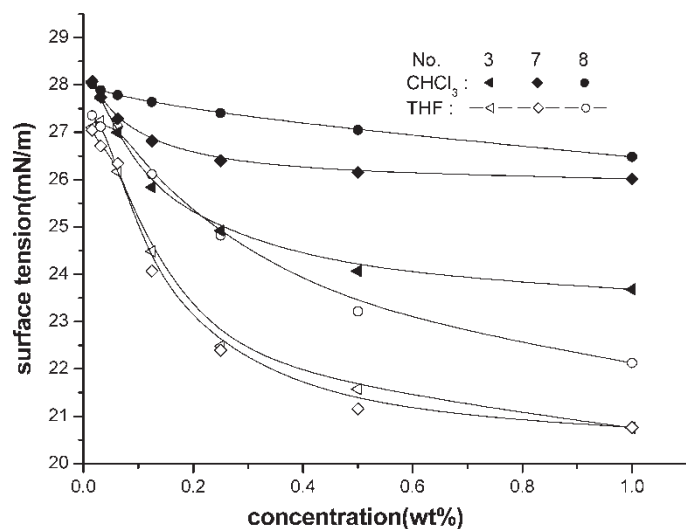
Fig. 10. Surface tension as a function of polymer concentration for diblock copolymers with perfluoroalkyl side chains as measured in solutions. ◀ ◁-No.3; ◆ ◇-No.7; ● ○-No.8 (see Table 1).

Figures 9 and 10, it is obvious that diblock copolymers have decreased the surface tension more successfully in THF solutions than in CHCl₃. This is attributed to the more ordered and dense packing of PFAEA blocks at the surfaces of their THF solutions. By comparing the data of surface area per molecule a_0 (see Table 3) this conclusion can be drawn more directly.

Nos. 3, 7 and 8 are based on the same macroinitiator PLMA$_{116}$-Br and decreased fluorinated block length. As Figure 10 shows, the block copolymer with longer fluorinated block can reduce the surface tension of solution more effectively.

In general concept, block copolymers with more fluorine content can show more potential in surface activity in solutions, but it is very interesting to find here that, when the fluorine weight percentage is constantly controlled, PLMA-b-PFAEA with higher molecular weight can also perform better in exploiting the fluorinated structure to reduce the surface tension of solutions. Such a series is composed of Nos. 1−3 whose fluorine weight percentages are similar (around 26−29%) while the molecular size increases. From their curves in Figure 9, it is obvious that polymers with fixed fluorine content, but larger molecular size, are attached with a stronger ability in decreasing the surface tension of solutions. The adsoprtion energy at an air-liquid interface of polymers with larger molecular size is higher than that of the smaller ones, which is similar to the Janus beads model investigated by Yoshimune Nonomura et al. (29) and can lead to such a molecular size dependence for surface tension.

By using the data depicted in γ-c curves, the surface excess concentration Γ and the occupied surface area of one molecule a_0 can be determined from the Gibbs adsorption isotherm (30, 31).

$$\Gamma = -(\partial\gamma/\partial\ln C)/(RT) \qquad (9)$$

where R is the gas constant, T the absolute temperature and $\partial\gamma/\partial$. In C the slope of the γ−plot. The occupied surface area a_0 can be calculated from Equation (10):

$$a_0 = 1/(N_{av}\Gamma) \qquad (10)$$

where N_{av} is the Avogardro number. There is no data about critical micelle concentration and unimer-micelle equilibrium, so Γ and a_0 values calculated from Equations (9) and (10) should be considered qualitatively. Nevertheless, these values of Γ and a_0 are really valuable for investigating the surface-active properties of PLMA-b-PFAEA.

The calculated Γ and a_0 values are listed in Table 3. For these block copolymers, Γ^{∞} values range from 0.814 μmol/m² to 1.07 μmol/m² and a_0 is between 1.55 nm² and 2.04 nm² in THF solutions, while the corresponding data in CHCl₃ are from 0.225 μmol/m² to 0.620 μmol/m² and from 2.68 nm² to 7.38 nm². The difference of solution properties in THF and CHCl₃ can be attributed to the different polarities of these two solvents. CHCl₃ has lower dielectric constant (4.81, 20°C) than THF (7.58, 20°C), so the block copolymer PLMA-b-PFAEA with blocks of rather low polarity can be dissolved more successfully and perform a more stretched form in CHCl₃. On the other hand, these polymers show stronger tendency towards aggregating in THF and their fluorinated blocks present more order and dense packing at THF surface. In this way, the higher Γ^{∞} and lower a_0 values of PLMA-b-PFAEA in THF than in CHCl₃ solutions can be explained reasonably. These Γ^{∞} and a_0 values correspond to the γ−C curves (Figures 9 and 10) well.

Table 3. Surface concentration Γ and molecular area a_0 for THF and CHCl₃ solution of diblock copolymer with perfluoroalkyl side chains

Sample	THF		CHCl₃	
	Γ^{∞} (μmol/m²)	a_0 (nm²)	Γ^{∞} (μmol/m²)	a_0 (nm²)
LMA$_{57}$FAEA$_{20}$	0.884	1.88	0.367	4.53
LMA$_{102}$FAEA$_{29}$	0.892	1.86	0.575	2.89
LMA$_{116}$FAEA$_{37}$	1.06	1.57	0.620	2.68
LMA$_{116}$FAEA$_{14.2}$	1.07	1.55	0.270	6.15
LMA$_{116}$FAEA$_{2.7}$	0.814	2.04	0.225	7.38

4 Conclusions

In this paper, atom transfer radical polymerization and the macroinitiator technique were investigated in detail in preparing well-defined PLMA homopolymers and their fluorinated block copolymers. The determination of reaction time during the preparation of macroinitiators, as a most important factor in conserving the bromine ends of PLMA-Br, was studied by detecting the kinetic process of the reaction. The structures of synthesized copolymers were verified by FTIR, ^{1}H NMR, GPC and FEA. Three routes have been discussed in calculating the molecular weight of PLMA-b-PFAEA, and the GPC−FEA method was concluded as the best choice. The glassy state of PFAEA block in the aggregates in pure $CDCl_3$ solutions and the existence of molecularly dispersed block copolymers in $CHCl_3/C_2F_3Cl_3$ mixed solutions are demonstrated by ^{1}H-NMR and DSL measurements. The surface of thin polymer films consisted mainly of the fluorinated block as demonstrated by contact angle measurements. Contact angle data show a distinct enrichment of the PFAEA segments to the film surface before PFAEA length reaches 3 (F% (wt) <3.3%) but above 3.3% this enrichment came to a maximum. PLMA-b-PFAEA block copolymers with more than 3 fluorinated units at one end showed excellent water-, alcohol- and oil-repellency. In the measurement of the surface activity in solution, the block copolymer with fixed PLMA block, while the longer fluorinated block can reduce the surface tension of solution more effectively, however, when the fluorine weight percentage is controlled constant, PLMA-b-PFAEA with larger molecular size is more prominent in exploiting the fluorinated structure to reduce the surface tension of solutions. These diblock copolymers have decreased the surface tension more successfully in THF solutions than in $CHCl_3$ due to more ordered and dense packing of PFAEA blocks at the surfaces of THF solutions.

5 Acknowledgements

6 References

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