Journal of Fluorine Chemistry 132 (2011) 9–14

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and characterization of a new fluorinated macroinitiator and its diblock copolymer by AGET ATRP

Yue Sun [a,b], Weiqu Liu [a,*]

[a] Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 20 July 2010
Received in revised form 29 September 2010
Accepted 22 October 2010
Available online 29 October 2010

Keywords:
Fluorinated macroinitiator
Diblock copolymer
AGET ATRP
Surface properties

ABSTRACT

A new fluorinated macroinitiator of poly 2,2,3,4,4,4-hexafluorobutyl methacrylate–Br (PHFMA–Br) was prepared via activator generated by electron transfer atom transfer radical polymerization (AGET ATRP), and then a series of fluorinated block copolymers with different fluorine content were successfully synthesized from the macroinitiator by the second step AGET ATRP. GPC, FTIR and ^{1}H NMR data obtained verified the synthesis. Contact angle measurement indicated that proper fluorine content could decrease the surface energy and increase the contact angle of the copolymer films. XPS characterization showed that the large difference in surface energy between the block and random copolymer film resulted from the difference of the fluorine content on the surface, although the fluorine content of the two copolymers in bulk was similar. The self-assembly behavior of the fluorinated block copolymer in selective solvents was evaluated by the TEM study, and the stable micelles with a core–shell structure were observed when the copolymer content was about 1 wt%.

1. Introduction

The block copolymers have unique microphase separation, which result in their broad applications including surfactant, adhesives, coatings, and polymer blend compatibilization [1–3]. Besides the common properties of block copolymers, fluorinated block copolymers have excellent chemical resistance, low surface energy, superior oil and water repellence as well as the low dielectric constant, so they have attracted significant attention over the years [4–6].

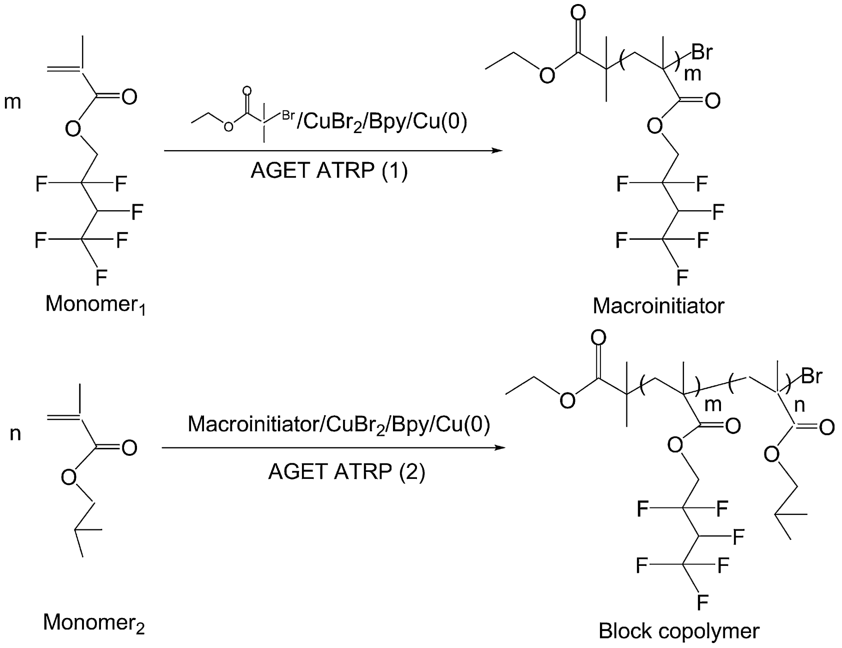
Many techniques have been used to synthesize the fluorinated block copolymers, one of the most important techniques is atom transfer radical polymerization (ATRP), because this method has been developed to obtain narrow polydispersity index, architectures, functionalities and well-defined compositions [7,8]. However, there are a few limitations for normal ATRP. For example, its catalyst is sensitive to air and the catalyst concentration is independently reduced [9,10]. They impede the use of ATRP in the commercial production of fluoropolymers. In order to overcome the drawbacks, activators generated by electron transfer (AGET) ATRP has been developed by Matyjaszewski and his coworkers [11]. In which Cu(I) complex used in normal ATRP can be generated in situ by the reduction of the air-stable Cu(II) complex with the reducing agents such as Cu(0) [12], tin(II)2-ethylhexanoate ($Sn(EH)_2$) [13], ascorbic acid [14]. Compared to the widely used normal ATRP, the controllability of AGET ATRP is worse [15]. However, as a technique for commercial prospects, AGET ATRP has undoubtedly greater advantages [11]. It only employs small amount of catalysts in higher oxidation state and its polymerization rate is higher than that of normal ATRP [10,15]. Especially, all agents of it can be thoroughly mixed in the presence of air and the reducing agent can be added at a controlled rate [16]. In short, AGET ATRP shows the advantages of facile preparation, storage, and handling of catalysts [9]. It is becoming one of the most powerful, versatile, simple and inexpensive methods in living/controlled free radical polymerization [10].

There are two approaches for the synthesis of fluorinated block copolymers by ATRP. While one is a sequential preparation of nonfluorinated segment followed by the polymerization with fluorinated monomers, the other is the reversal procedure; that is, preparation of fluorinated segment firstly and then polymerization with nonfluorinated monomers. It is reported that by the introduction of even only a few fluorinated units, the performance of the block copolymer can be significantly improved [17]. Therefore, although fluorinated monomers are somewhat expensive, it would be possible to realize desired properties by a small fluorine content in the block copolymer. Compared with the former approach used by many scientists, the latter one is better to

---

* Corresponding author at: Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, China. Tel.: +86 20 85231660;
fax: +86 20 85231660.
E-mail address: liuwq@gic.ac.cn (W. Liu).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.10.004



Scheme 1. Synthesis of macroinitiator PHFMA–Br and its block copolymer PHFMA-b-IBMA via two-step AGET ATRP.

control the fluorine content in the block copolymer. Furthermore, since the reactivity of macroinitiator is lower than that of the small-molecule initiators, the latter approach has been widely used in the synthesis of various fluoropolymers [18–25]. Among these, fluorinated acrylate is an important chemical raw material; the block copolymers composed of it have been broadly applied to high-performance paint and varnish in the textile, paper, leather, construction, automotive and aerospace industries [26–28]. Xia et al. converted 1,1-dihydroperfluorooctyl methacrylate (FOMA) into macroinitiator, and then used it to polymerize successfully with methyl methacrylate (MMA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) [21]. Hansen et al. transformed 2,2,2-trifluoroethyl methacrylate (TFEMA) into macroinitiator and then initiated the polymerization of 1,1,4,7,10,10-hexamethyltriethylenetetramine to prepare block copolymers (HMTETA) [23]. Li et al. successfully synthesized homopolymer of 2,3,5,6-tetrafluorophenyl methacrylate (TFPM) by ATRP and used it as macroinitiator to synthesize fluorinated block copolymers [25]. However, the block copolymers synthesized from fluorinated macroinitiator were mostly prepared via normal ATRP.

Consider that AGET ATRP have more advantages than normal ATRP on commercial prospects and 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFMA) have not been used as initiator for ATRP. We synthesized a new macroinitiator of PHFMA–Br by AGET ATRP in this paper, and then a series of well-defined diblock copolymers of poly 2,2,3,4,4,4-hexafluorobutyl methacrylate-block-poly (isobutyl methacrylate) (PHFMA-b-PIBMA) were successfully prepared from the macroinitiator by the second step AGET ATRP. The experiments provided an opportunity for the commercial products of block copolymers with fluorinated acrylate blocks. Polymers derived from HFMA and IBMA were characterized by GPC. The structure elucidations of the macroinitiator and its diblock copolymer were carried out by FTIR and ^{1}H NMR measurements. The surface properties of the diblock copolymers were also studied by contact angle and XPS. The self-assembly behavior of the diblock copolymers was investigated by TEM as well.

2. Results and discussion

2.1. Synthesis and characterization of PHFMA–Br and PHFMA-b-PIBMA

After HFMA was transformed into a macroinitiator PHFMA–Br in the first step AGET ATRP, the macroinitiator was then used to initiate the polymerization of IBMA to get a series of diblock copolymer PHFMA-b-PIBMA. The general synthetic process is shown in Scheme 1.

The molecular weights and polydispersity index of the polymers were characterized by GPC. The data is shown in Table 1. As can be seen, the polydispersity index of all polymers was narrow, that indicated the well controlling of AGET ATRP technique. The typical molecular weight distributions for PHFMA–Br and PHFMA-b-PIBMA were shown in Fig. 1. The elution time for PHFMA-b-PIBMA was shorter than that for PHFMA–Br,

Table 1
Molecular weight, polydispersity index of the polymers and the relative weight for HFMA and IBMA.

Polymer	Mn[a]	PDI[b]	[PHFMA]:[IBMA]	
			Before reaction	In the polymer obtained[c]
PHFMA	5300	1.12	0:100	0:100
PHFMA-b-PIBMA(1)	167,833	1.23	3:97	2.8:97.2
PHFMA-b-PIBMA(2)	124,550	1.24	4:96	3.6:96.4
PHFMA-b-PIBMA(3)	101,710	1.22	5:95	6.2:93.8

[a] Mn: the number-average molecular weight, determined by GPC.
[b] PDI: the polydispersity index, determined by GPC.
[c] The data determined by ^{1}H NMR.

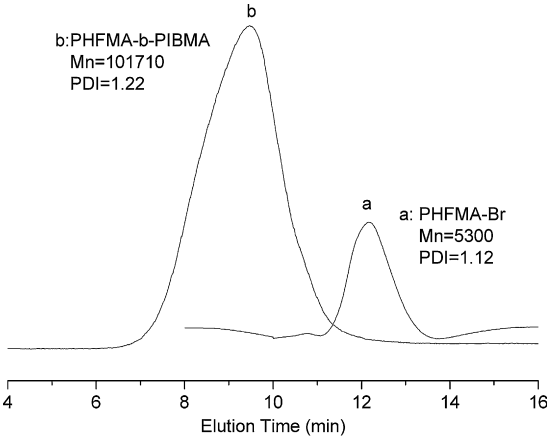


Fig. 1. GPC traces of the macroinitiator PHFMA–Br (a) and the block copolymer PHFMA-b-IBMA (b).

showing that its molecular weight was larger than that of PHFMA–Br. The monomodal GPC curve of the copolymer suggested the formation of block copolymer without homopolymerization. No observable peak of the macroinitiator from the GPC curve of the block copolymer indicated the complete initiation of the macroinitiator.

Based on the FTIR and ^{1}H NMR data structures of PHFMA–Br and PHFMA-b-PIBMA were analyzed. The FTIR spectra of monomer HFMA (trace a), macroinitiator PHFMA–Br (trace b) and the copolymer PHFMA-b-PIBMA (trace c) are shown in Fig. 2. The peak of trace a are very similar to that of trace b, they both exhibit the characteristic peaks at 1190 and 690 cm^{-1} which are ascribed to the characteristic absorbance of $–CF_2$ and $–CHF–CF_3$, respectively [6,29]. Comparing trace a with trace b, unambiguous disappearance of the characteristic peak of C=C at 1642 cm^{-1} (trace a) and the appearance of the characteristic peak of C–Br at 523 cm^{-1} (trace b) were observed, this indicated the completion of the polymerization and the successful preparation of the macroinitiator PHFMA–Br. Trace c showed the spectrum of the PHFMA-b-PIBMA. The characteristic peaks of C–F mentioned above became faintness, and the peak at 1150 cm^{-1} can be seen, it was ascribed to the characteristic absorbance of $–CH(CH_3)_2$ in IBMA.

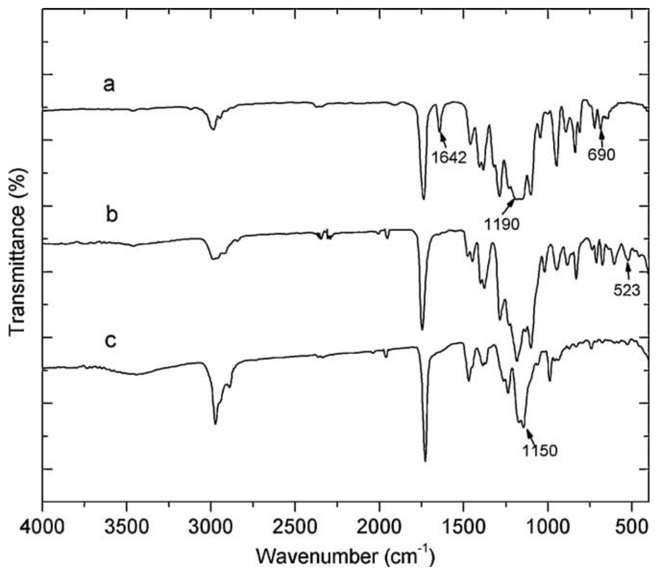


Fig. 2. FTIR spectra of HFMA (a), PHFMA–Br (b) and its block copolymer PHFMA-b-IBMA (c).

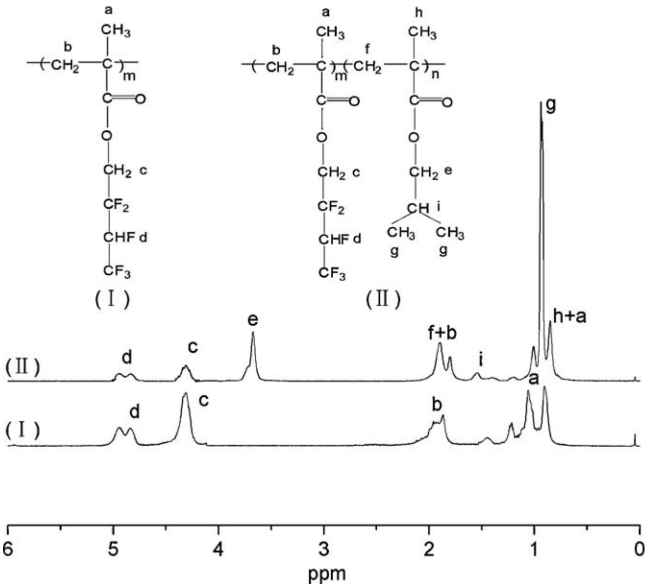


Fig. 3. ^{1}H NMR spectra of macroinitiator PHFMA–Br (I) and its block copolymer PHFMA-b-IBMA (II).

The ^{1}H NMR spectra of PHFMA–Br and PHFMA-b-PIBMA are shown in Fig. 3. From trace I, peaks at 0.7–1.2 ppm and 1.8–2.1 ppm are assigned as $–CH_3$ (a) and $–CH_2$ (b), respectively, while peaks at 4.3–4.5 and 4.8–5.0 ppm are corresponding to $–OCH_2$ (c) and –CHF (d). Two additional small peaks at ~1.2 and ~1.5 ppm in Fig. 3(I) represent the $–CH_3$ (a) protons of isotatic (mm) triad [4]. Peaks at ~4.8 ppm are designated to the splitting of –CHF (d), which may result from the coupling of proton with nuclei of fluorine atoms [4]. In trace I, olefinic proton signals derived from unreacted HFMA could not be detected. For PHFMA-b-PIBMA (as shown in trace II), some new peaks compared with trace I appeared. Peaks at 3.6–3.8 ppm and 1.5–1.6 ppm are assigned as $–COOCH_2$ (e) and –CH (i) in the PIBMA segments, respectively, while peaks at ~0.9 ppm are corresponding to $–CH_3$ (g) of IBMA. From the FTIR and ^{1}H NMR data, PIBMA-b-PHFMA was successfully synthesized via AGET ATRP.

2.2. The surface property of the diblock copolymer

Low surface energy of fluorinated polymers is well known. In this study, a series of PHFMA-b-PIBMA were designed to see the factors affecting surface energy of the polymer film by comparing with PHFMA. The contact angles of the water and dodecane on the block or random copolymer films are shown in Table 2, and the fluorine content of the copolymers are also listed in Table 2. As expected, the water contact angles were dependent on the fluorine content in polymers. They increased with the gradual increase in fluorine content in both the block copolymers and the random copolymers. While the change of contact angle of the block copolymer was smaller than that of the random copolymers. The contact angle value for dodecane on the polymers film exhibited the same phenomenon. This may result from the push-me/pull-you architectures of fluorinated block polymers [17], which indicated that the polymers have an ordered and close-packed structure on the surface. However, it is unlikely for the random copolymer to form the ordered structure [17].

We obtained indirectly surface energy from the water contact angle. An equation, $1 + \cos\theta = 2(\gamma_S/\gamma_L)^{1/2}\exp[-\beta(\gamma_L - \gamma_S)^2]$ [30–32] was applied to calculate the surface energy. β is a constant with a value of 0.0001247 $(m^2/mJ)^2$ [31]; θ, γ_S and γ_L are the contact

Table 2
The fluorine content, contact angle and surface energy of a series of copolymers.

Sample	Copolymer	[PHFMA–Br]:[IBMA][a]	W_F[b] [%]	Contact angle [°][c]		γ_S[d] [mN/m]
				$C_{12}H_{26}$	H_2O	
1	PIBMA	0:100	0	16.1	86.5	31.4
2	PHFMA-b-PIBMA(1)	3:97	1.5	27.1	96.2	25.4
3	PHFMA-b-PIBMA(2)	4:96	1.9	28.3	97.9	24.4
4	PHFMA-b-PIBMA(3)	5:95	2.2	30.0	98.4	24.1
5	PHFMA-r-PIBMA(1)	3:97	1.2	20.8	89.1	29.8
6	PHFMA-r-PIBMA(2)	4:96	1.8	21.2	89.7	29.4
7	PHFMA-r-PIBMA(3)	5:95	2.3	24.3	92.8	27.5
8	PHFMA-r-PIBMA(4)	15:85	4.9	26.8	95.0	26.1
9	PHFMA-r-PIBMA(5)	30:70	13.0	32.0	100.5	22.8
10	PHFMA	100:0	39.4	37.2	102.2	21.7

[a] The relative weight for the macroinitiator PHFMA–Br and the IBMA before the reaction.
[b] The fluorine content of copolymer in bulk.
[c] The contact angle on the air-side surface of the copolymers films.
[d] Surface energy obtained indirectly from the water contact angle.

angle, the surface energy of the solid and the surface energy of the tested liquid, respectively. A data summary is shown in Table 2. The surface energy of both the block copolymers and the random copolymers decreased gradually with the increase in fluorine content. When the fluorine content was 2.2%, the surface energy of the block copolymer dropped to 24.1 mN/m, which was slightly higher than that of random copolymers with 13% fluorine content (22.8 mN/m), and the value was much lower than that of IBMA homopolymers (31.4 mN/m).

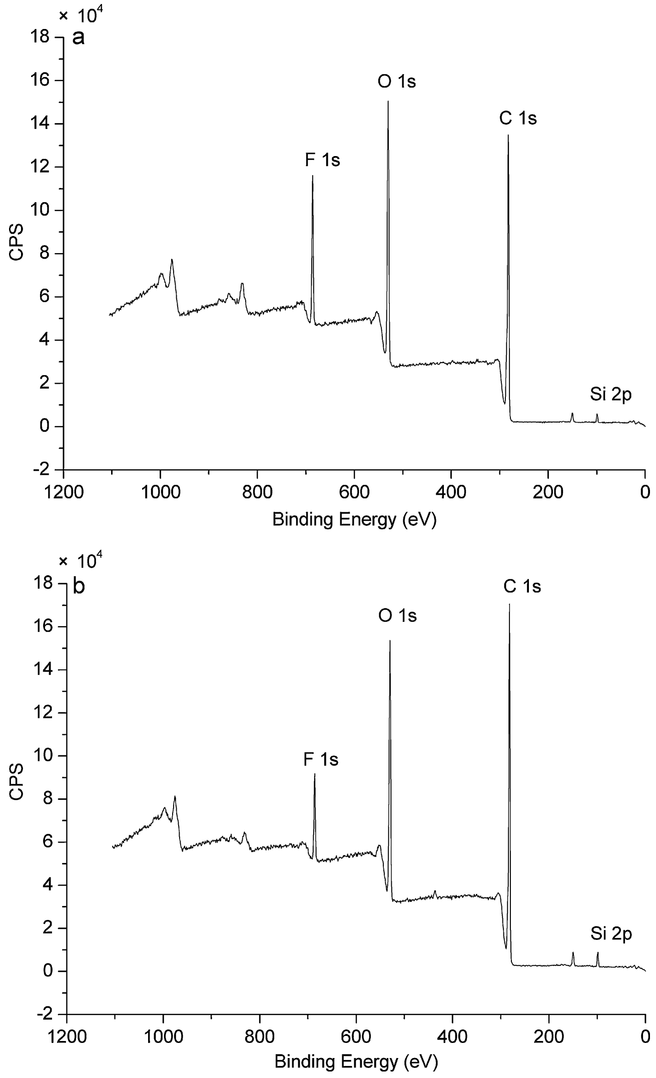


Fig. 4. XPS broad scan of the binding energy spectrum diblock copolymer: (a) sample 4 and (b) sample 7.

2.3. Surface composition characterization

Somewhat unusual phenomenon was observed. That is, as shown in Table 1, the fluorine content in their bulk of sample 4 and sample 7 was approximately the same, but the water contact angle and the surface energy were quite different. It was reported that the composition at the polymer–air interface is different from that in the bulk [31]. Therefore, the surface compositions of the two samples were studied by XPS. The broad scan of the binding energy (BE) spectrum for sample 4 block copolymer is shown in Fig. 4a. It is comprised of three strong and one weak peaks, at approximately 687, 532, 285 and 102 eV, which result from direct photoionization from F1s, O1s, C1s, and Si2p core levels, respectively. Fig. 4b is a broad scan of the BE spectrum of sample 7, which is a random copolymer. There are also three strong and one weak peaks, which is at approximately 687, 532, 285, 102 eV corresponding to direct photoionization from F1s, O1s, C1s, Si2p core levels, respectively.

XPS characterization showed the surface compositions of sample 4 and sample 7, which are listed in Table 3. We can see the great difference in surface energy possibly due to the difference of the fluorine enrichment on the surface. The fluorine content of sample 4 with a surface energy of 24.1 mN/m was about 5.8%, which was much higher than 3.1% of sample 7 with a surface energy of 27.5 mN/m, although their fluorine content in bulk is similar.

2.4. Self-assembly behavior

The self-assembly behavior of the fluorinated diblock copolymers in selective solvents is one of their important properties, which is a basic element for the variety of applications. To investigate the self-assembly behavior of the block polymer in water, TEM study was conducted using 1.0 wt% sample. As shown in Fig. 5, micelles with the diameter of 100–150 nm have been formed. All these micelles had a core–shell structure. This may be attributed to the good hydrophobicity of fluorinated segments;

Table 3
Surface compositions of the diblock copolymers, measured by XPS.

Sample	F (in bulk) [%]	C1s [%]	O1s [%]	F1s [%]
PHFMA-b-PIBMA(3)	2.2	73.9	17.5	5.8
PHFMA-r-PIBMA(3)	2.3	76.6	15.6	3.1

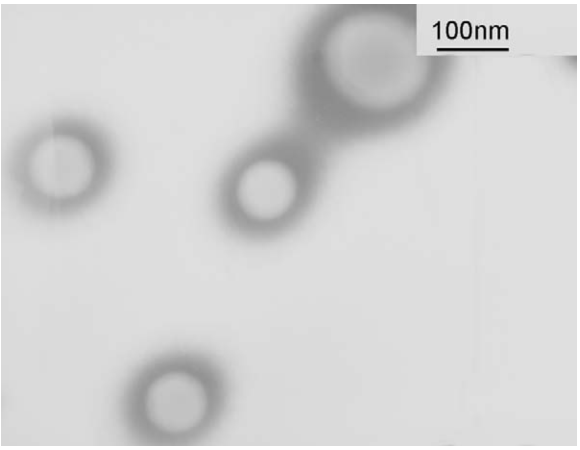


Fig. 5. The typical TEM pictures of the aggregates formed by the diblock copolymer PHFMA-b-PiBMA(3). Concentration of the polymer was 1 wt%.

they associated with each other and form the core of the micelles, while the hydrophilic nonfluorinated segments extended from outer surfaces to form the shell [33]. Indicated by TEM, the core phase and the shell phase are compatible to a certain degree and the interface between them is clear.

3. Conclusion

A new fluorinated macroinitiator PHFMA–Br was prepared by AGET ATRP. Then the maroinitiator initiated the polymerization of IBMA to form the diblock copolymer PHFMA-b-PIBMA by the second AGET ATRP. The macroinitiator and its well-defined block copolymers were characterized by means of GPC, FTIR and ^{1}H NMR. Contact angle measurement indicated that the proper fluorine content could decrease the surface energy and increase the contact angle. When the surface properties of the block copolymers were compared with that of the random copolymers synthesized by the same monomer, XPS characterization showed that the great difference in surface energy between them resulted from the difference of the fluorine enrichment on the surface, although the fluorine content of the two copolymers in bulk are similar. Finally, the self-assembly behavior of the fluorinated diblock copolymer in water was carried out by TEM study, and the stable micelles with a diameter of 100–150 nm having core–shell structure were observed. These results would provide an economical and facile method for the synthesis of fabricating fluorinated block copolymers.

4. Experimental

4.1. Materials

2,2,3,4,4,4-Hexafluorobutyl methacrylate (HFMA) was purchased from Xeogia Fluorine-Silicon Chemical Co. Ltd. (Harbin, China); isobutyl methacrylate (IBMA), 2,2′-azobisisobutyronitrile (AIBN) and butanone were obtained from Kemiou Chemical Co. (Tianjin, China); 2,2′-bipyridine(Bpy), ethyl 2-bromoisobutyrate (EbiB, 98%) and copper(0) powder were from Alfa Aesar Chemical Co.; copper(II) bromide was purchased from Zhenxin Chemical Co. (Shanghai, China).

HFMA and IBMA were prepared according to the literature [31,34]. All other chemicals are used without further purification. All solvents were reagent grade except EbiB.

4.2. Sample preparation

4.2.1. Preparation of PHFMA–Br macroinitiator by AGET ATRP

The reagent with a molar ratio HFMA/EbiB/$CuBr_2$/bpy = 100/1/0.1/0.2 was dissolved in butanone in the reaction flask [12]. Then the flask was thoroughly purged by vacuum and flushed with nitrogen (three cycles) to eliminate oxygen in the solution. The flask was immersed in an oil bath thermostated at 80 °C, and Cu(0) powder (with a molar ratio $CuBr_2$/Cu(0) = 0.1/0.2) was added to initiate the polymerization. The reaction was carried out under nitrogen atmosphere all the time. After 8 h, the flask was placed in an ice bath to stop the reaction. The product PHFMA–Br macroinitiator was obtained after precipitation in water, filtration, washing with methanol, and drying under high vacuum to constant weight.

4.2.2. Synthesis of PHFMA-b-PIBMA by the second step AGET ATRP

The PHFMA–Br macroinitiator was firstly dissolved in butanone in a 100 ml three-necked flask equipped with a mechanical stirrer, a thermometer and an inlet system of nitrogen. Then, the reagent with a molar ratio iBMA/$CuBr_2$/bpy = 100/0.1/0.2 was injected into the reaction flask. The relative weight for the macroinitiator and IBMA is shown in Table 1. After the reaction mixture was thoroughly purged by vacuum and flushed with nitrogen three times, the flask was immersed in an oil bath at 90 °C. Finally Cu(0) powder (with a molar ratio $CuBr_2$/Cu(0) = 0.1/0.2) was added to initiate the polymerization of IBMA, and the reaction was conducted under nitrogen atmosphere all the time. After 8 h, the reaction was stopped and quickly cooled down to room temperature. The product PHFMA-b-IBMA was obtained according to the same procedure for PHFMA–Br.

4.2.3. Synthesis of series of random copolymers

The random copolymers were synthesized via conventional free radical polymerization (CFRP). The appropriate amounts of IBMA and HFMA were placed in a flask (see Table 2). AIBN in ethanol (20 ml) was added to the mixture. The final concentrations of the monomers and the initiator were 10 mmol and 0.25 mmol, respectively. The polymerization was carried out at 75 °C for 20 h.

4.3. Characterization

The molecular weight distributions of the polymer samples were measured at 30 °C by gel permeation chromatography (GPC) on a Waters 2410 instrument with THF as the solvent (1.0 ml/min) and polystyrene as the calibration standards.

The FTIR spectra were recorded on a WQF 410 Spectrophotometer made in Beijing, China. The films for FTIR were prepared by casting the polymer solution (20% w/w in butanone) onto KBr substrate. In order to remove the residual solvent completely, the films were placed in a vacuum oven at 60 °C for 3 h.

^{1}H NMR was performed on a 400 MHz Brüker NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane as an internal reference. Chemical shifts of the ^{1}H NMR were related to the $CDCl_3$ signal at 7.24 ppm.

The contact angle of water was measured on the air-side surface of the coating films with a contact goniometer (Erma Contact Anglemeter, Model G-I, 13-100-0, Japan) by the sessile drop method with a micro-syringe at 30 °C. The sample was prepared by casting the polymer onto a clean substrate disk from 20% (w/w) solution of butanone. The disk was put into an oven at 60 °C for 3 h and 60 °C for 3 h under vacuum. More than 10 readings were averaged to get a reliable value for each sample.

Fluorine content was obtained through fluorine-element analysis of ignition method.

XPS was carried out on Kratos Axis Ultra DCD systems equipped with an Al (mono) source and operating at 150 W. The sample for XPS was prepared with the same method for contact angle.

Transmission electron micrograph (TEM) images are obtained by JEM-100CXII at 200 kV. The sample was diluted by butanone and stained by phosphotungstic acid (PTA, aqueous solution) until the solid content was about 1 wt%.

Acknowledgements

Authors gratefully acknowledge the financial support from the Guangdong Natural Science Foundation, China (No. 07006841) and the Open Project of Key Laboratory of Cellulose and Lignocellulosics Chemistry, Chinese Academy of Sciences (No. LCLC-2010-11).

References

[1] Z. Shi, S. Holdcroft, Macromolecules 37 (2004) 2084–2089.
[2] J. Feng, H. Liu, Y. Huan, Fluid Phase Equilibr. 261 (2007) 50–57.
[3] D. Gromadzki, J. Lokaj, M. Š louf, P. Š tepa′nek, Polymer 50 (2009) 2451–2459.
[4] H. Hussain, B.H. Tan, C.S. Gudipati, Y. Xaio, Y. Liu, T.P. Davis, C.B. He, J. Polym. Sci. A: Polym. Chem. 46 (2008) 7287–7298.
[5] R. Kaplánek, O. Paleta, J. Michálek, M. Přádny, J. Fluorine Chem. 126 (2005) 595–600.
[6] S. Xu, W. Liu, J. Fluorine Chem. 129 (2008) 125–130.
[7] L. Bai, L. Zhang, J. Zhu, Z. Cheng, X. Zhu, J. Polym. Sci. A: Polym. Chem. 47 (2009) 2002–2008.
[8] K. Zhao, Z. Cheng, Z. Zhang, J. Zhu, X. Zhu, Polym. Bull. 63 (2009) 355–364.
[9] Z. Hu, X. Shen, H. Qiu, G. Lai, J. Wu, W. Li, Eur. Polym. J. 45 (2009) 2313–2318.
[10] H. Chen, Y. Liang, D. Liu, Z. Tan, S. Zhang, M. Zheng, R. Qu, Mater. Sci. Eng. C 30 (2010) 605–609.
[11] K. Min, H. Gao, K. Matyjaszewski, J. Am. Chem. Soc. 127 (2005) 3825–3830.
[12] K. Matyjaszewski, S. Coca, S.G. Gaynor, M. Wei, B.E. Woodworth, Macromolecules 30 (1997) 7348–7350.
[13] K. Min, S. Yu, H. Lee, L. Mueller, S.S. Sheiko, K. Matyjaszewski, Macromolecules 40 (2007) 6557–6563.
[14] S. Bencherif, N. Washburn, K. Matyjaszewski, Biomacromolecules 10 (2009) 2499–2507.
[15] M. Khan, Z. Xue, D. He, S. Noh, W. Lyoo, Polymer 51 (2010) 69–74.
[16] H. Qian, L. He, Anal. Chem. 81 (2009) 4536–4542.
[17] H. Ni, X. Wang, W. Zhang, X. Wang, Z. Shen, Surf. Sci. 601 (2007) 3632–3639.
[18] E. Möller, U. Schreiber, S. Beuermann, Macromol. Symp. 289 (2010) 52–63.
[19] M. Destarac, K. Matyjaszewski, E. Silverman, B. Ameduri, B. Boutevin, Macromolecules 33 (2000) 4613–4615.
[20] G. Lu, S. Zhang, X. Huang, J. Polym. Sci. A: Polym. Chem. 44 (2006) 5438–5444.
[21] J. Xia, T. Johnson, S. Gaynor, K. Matyjaszewski, J. Simone, Macromolecules 32 (1999) 4802–4805.
[22] F. Wang, H. Li, Z. Zhang, C. Hu, S. Wu, J. Polym. Sci. A: Polym. Chem. 42 (2004) 4809–4819.
[23] N. Hansen, M. Gerstenberg, D. Haddleton, S. Hvilsted, J. Polym. Sci. A: Polym. Chem. 46 (2008) 8097–8111.
[24] M. Bcrker, E. Remsen, K. Wooley, J. Polym. Sci. A: Polym. Chem. 39 (2001) 4152–4166.
[25] X.S. Li, L.H. Gan, Y.Y. Gan, Polymer 49 (2008) 1879–1884.
[26] Y. Chen, C. Zhang, X. Chen, Eur. Polym. J. 42 (2006) 694–701.
[27] L. Chen, H. Shi, H. Wu, J. Xiang, J. Fluorine Chem. 131 (2010) 731–737.
[28] X. Cui, S. Zhong, H. Wang, Colloids Surf. A 303 (2007) 173–178.
[29] Z. Wei, W. Liu, D. Tian, C. Xiao, X. Wang, Appl. Surf. Sci. 256 (2010) 3972–3976.
[30] Y.S. Lipatov, G.M. Semenovich, Polymer 40 (1999) 6485–6492.
[31] Z. Luo, T. He, H. Yu, L. Dai, Macromol. React. Eng. 2 (2008) 398–406.
[32] D. Li, A.W. Neumann, J. Colloid Interface Sci. 137 (1990) 304–307.
[33] S. Xiong, L. Li, S. Wu, Z. Xu, P. Chu, J. Polym. Sci. A: Polym. Chem. 47 (2009) 4895–4907.
[34] Y. Kitayama, M. Yorizane, Y. Kagawa, H. Minami, P.B. Zetterlund, M.O. Kubo, Polymer 50 (2009) 3182–3187.