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Synthesis of small-molecule initiators derived from fluorinated acrylates and their application in atom transfer radical polymerization (ATRP)

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Abstract The bromo-terminated small-molecule initiator was prepared by the direct addition reaction of 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFMA) or dodecafluoroheptyl methacrylate (DFMA) with hydrobromic acid in acetic acid under mild conditions. This greatly widened the initiators used for atom transfer radical polymerization (ATRP). The successful polymerization of isobutyl methacrylate (IBMA) or methyl methacrylate (MMA) derived from HFMA-Br or DFMA-Br indicated that fluorinated acrylates could be used as initiators for ATRP. The data of GPC showed the well controlling of the initiator system. FTIR and ^{1}H NMR characterized the structures of the initiators and their polymers. Contact angle measurement indicated that although only one molecule of fluorinated acrylate was introduced, the surface properties of polymers were improved greatly.

Keywords Fluorinated acrylates · Initiator · ATRP · Surface properties

Introduction

The synthesis of materials with controlled compositions and architectures continues to be a focus of current polymer research [1]. The “living” radical polymerization methods can well achieve the control. Among varies “living” radical methods, the

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transition-metal mediated atom transfer radical polymerization (ATRP) received great attention in the recent years because of its versatility of monomer types, tolerance of impurities, mild reaction conditions, and excellent control over molecular weight and polydispersity [2, 3].

Atom transfer radical polymerization is usually composed of the monomer, a transferable alkyl halide as initiator, a catalyst with transition metal species, and the suitable ligand [4]. The initiator is very important because it has to form an initiating radical species via homolytic cleavage of its labile bond such as C-halogen by the catalyst [5]. Since 1995, Wang et al. used an alkyl chloride (1-phenylethyl chloride, 1-PECl) as the initiator for ATRP [6]. Many organic halides, such as haloketones, haloesters, haloamides, halonitriles, and sulfonyl halides, have been successfully employed in ATRP [7]. Some novel initiators have also been prepared of late years in the laboratory. Broyer et al. converted amino acids into initiator by reacting with hydrochloric acid in four steps for the ATRP of styrenes and methacrylates [8]. Liu et al. synthesized the ATRP macroinitiator by the reaction between epoxy groups of poly (glycidyl methacrylate) (PGMA) and carboxy functionality of bromoacetic acid (BAA) [9]. Especially, 2-bromoisobutyryl bromide or similar compounds were used as reagents to react with substrates having a hydroxyl group under straightforward reaction conditions, which greatly widens the initiators used for ATRP [10–12].

Fluorinated polymers are very interesting by the imparting of fluorine due to a number of unique properties that include hydrophobicity and low surface energy, as well as high chemical and thermal resistance [13, 14]. They have been broadly applied to high-performance paint and varnish in the textile, paper, leather, construction, automotive and aerospace industries, optics, and microelectronics [15–19]. Fluorinated acrylates are one of the most widely used fluorides. Converting them into initiators will both widen the initiators used for ATRP and introduce the properties of fluorine to the polymers. Xia et al. converted 1,1-dihydroperfluorooctyl methacrylate (FOMA) into macroinitiator via ATRP and then used it to polymerize successfully with methyl methacrylate (MMA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) [20]. Hansen et al. transformed 2,2,2-trifluoroethyl methacrylate (TFEMA) into macroinitiator by ATRP and then initiated the polymerization of 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) to prepare block copolymers [21]. However, the initiators mentioned above are all macroinitiator. To our knowledge, the studies about small-molecule initiators derived from fluorinated acrylates have not been reported.

Consider that the efficiency of fluorine could be maximized by anchoring the fluorinated group at the end of the molecular chain [22–25]. In this article, the bromo-terminated initiators were prepared by the direct addition reaction of 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFMA) or dodecafluoroheptyl methacrylate (DFMA) with hydrobromic acid in acetic acid under mild conditions. Then the series of well-defined polymers with different segments or molecular weights were synthesized via ATRP from the initiators. GPC data obtained verified the synthesis and showed the well controlling of the initiator system. FTIR and ^{1}H NMR measured the structures of the initiators and their polymers. The surface properties of the polymers were also studied by contact angle measurement.

Experimental

Materials

2,2,3,4,4,4-Hexafluorobutyl methacrylate (HFMA) and dodecafluoroheptyl methacrylate (DFMA) were purchased from Xeogia Fluorine-Silicon Chemical Co. Ltd. (Harbin, China). Isobutyl methacrylate (IBMA), methyl methacrylate (MMA), and butanone were obtained from Kemiou Chemical Co. (Tianjin, China). Hydrobromic acid in acetic acid (44 wt%) was supplied by King Success fine Chemical Co. Ltd. (Hubei, China). 2,2′-Bipyridine(Bpy) and copper(0) powder were from Alfa Aesar Chemical Co. Copper(II) bromide was purchased from Zhenxin Chemical Co. (Shanghai, China).

All chemicals used were without further purification. All solvents were reagent grade.

Sample preparation

Preparation of the initiator of bromo-terminated HFMA or DFMA

HFMA (20.00 g) or DFMA (31.99 g) and hydrobromic acid in acetic acid (300 mL) were put into a 500-mL three-necked flask, which was fitted with a mechanical stirrer, a thermometer, and an apparatus for dealing with tail gas (HBr). Then, the reaction mixture was stirred at 0 °C. After 12 h, the products were extracted by water until the pH of the oil liquid was 7.0. Because that the HFMA and DFMA have strong electron-drawing substitutes, the main products were those according to anti-Markovnikov's rule. However, it was reported that the activity of alkyl group for ATRP initiators followed the order of $3° > 2° > 1°$ [26]. Therefore, the products according to Markovnikov's rule were used as the ATRP initiators in this article. The isomers were separated by column chromatographic (ordinary column; stationary phase: silica gel for column chromatography; mobile phase: petroleum ether) [27]. Finally, excess solvent was thoroughly removed by a rotary evaporator under vacuum. The structure of the initiator was measured by FTIR and ^{1}H NMR.

Synthesis of HFMA-PIBMA or HFMA-PMMA by ATRP

The initiator of HFMA-Br 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 molar ratio monomers (IBMA or MMA)/$CuBr_2$/bpy = 100/0.1/0.2 was injected into the reaction flask. The relative weight for the initiator and IBMA or MMA was 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 or 85 °C. Finally, Cu(0) powder (with a molar ratio $CuBr_2$/Cu(0) = 0.1/0.2) was added to initiate the polymerization, 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 HFMA-PIBMA

Table 1 The condition of the polymerization, conversion, molecular weight, polydispersity index, and the relative weight for the initiator and monomer

Polymer	T, °C	Time, h	Conv[a], %	$M^{b}_{n,theo}$	$M_{n,GPC}$	PDI[c]	Initiator:monomer[d]	
							Before the reaction	Obtained in the polymer[e]
HFMA-PIBMA(1)	90	8	95	6315	6415	1.20	5:95	5.2:94.9
HFMA-PIBMA(2)	90	8	96	3198	3356	1.21	10:90	10.2:89.8
HFMA-PMMA(1)	85	8	96	6378	6422	1.22	5:95	5.1:94.9
HFMA-PMMA(2)	85	8	97	3225	3337	1.21	10:90	10.1:89.9
DFMA-PIBMA(1)	95	9	95	9180	9247	1.22	5:95	5.2:95.1
DFMA-PIBMA(2)	95	9	96	4644	4809	1.22	10:90	10.1:89.9
DFMA-PMMA(1)	90	9	94	9083	9275	1.21	5:95	5.1:94.9
DFMA-PMMA(2)	90	9	95	4599	4680	1.21	10:90	9.9:90.1

[a] The monomer conversion was determined gravimetrically

[b] The theoretical molecular weights were predicted from the equation, $M_{n,theo} = M_{n(HFMA\text{-}Br)} + M_{n(MMA)} \times ([MMA]_0/[HFMA\text{-}Br]_0) \times$ conversion

[c] PDI: the polydispersity index, determined by GPC

[d] The data were the relative weight ratios

[e] The data determined by ^{1}H NMR

or HFMA-PMMA was obtained after precipitation in water, filtration, washing with methanol, and drying under high vacuum to constant weight.

Synthesis of DFMA-PIBMA or DFM-PMMA by ATRP

The DFMA initiator (DFMA-Br) was 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 molar ratio monomers (IBMA or MMA)/$CuBr_2$/bpy = 100/0.1/0.2 was injected into the flask. The relative weight for the initiator and IBMA or MMA was shown in Table 1, too. After the reaction mixture was thoroughly purged by vacuum and flushed with nitrogen three times, the flask was immersed in an oil bath at 95 or 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 or MMA, and the reaction was conducted under nitrogen atmosphere all the time. After 9 h, the reaction was stopped and quickly cooled down to room temperature. The product was obtained according to the same procedure for HFMA-PIBMA or HFMA-PMMA.

Synthesis of homopolymer

The homopolymer were synthesized via conventional-free radical polymerization (CFRP). The appropriate amounts of IBMA or MMA were placed in a flask. AIBN in ethanol (20 mL) was added to the mixture. The final concentrations of the monomers and the initiator were 4.2 and 0.1 mmol, respectively. The polymerization was carried out at 75 °C for 5 h.

Characterization

The gel permeation chromatography (GPC) measurements were carried out on a Waters 515-410 instrument at 35° 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.

^{1}H NMR was performed on a 400-MHz Brüker NMR spectrometer (Model DRX-400) 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° for 3 h and 60° for 3 h under vacuum. More than 10 readings were averaged to get a reliable value for each sample.

Results and discussion

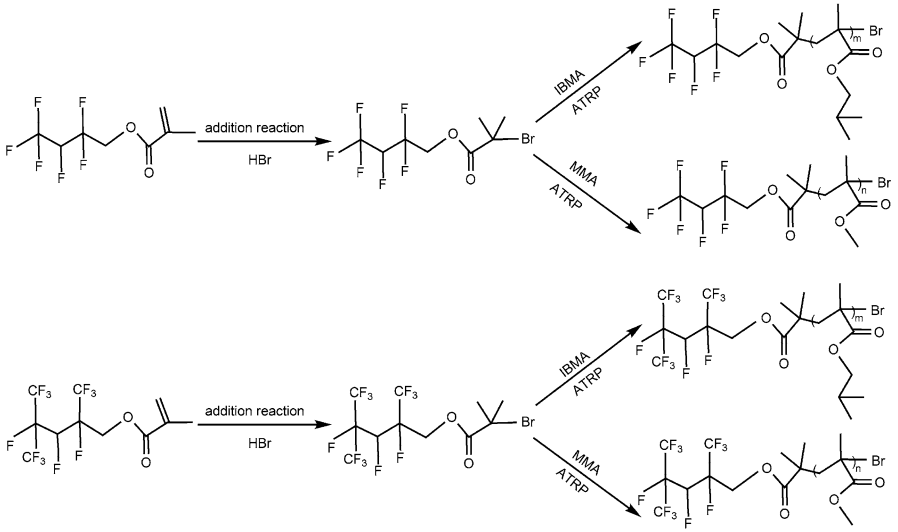
The synthesis of initiators and the polymers

In this article, HFMA and DFMA transformed into initiators by direct addition reaction with hydrobromic acid in acetic acid, and then the initiators polymerized with IBMA or MMA to get a series of polymers, as shown in Scheme 1.

The condition of the polymerization, conversion, molecular weights, polydispersity index (PDI), and the relative weight for the initiator and monomer before or after the reaction were shown in Table 1. According to the mechanism of direct addition reaction, the molecular weights of HFMA-Br and DFMA-Br were about 331.06 and 481.08 g/mol, respectively. As can be seen, the molecular weights of all the polymers were much larger than that of their initiators, the PDI of all polymers were narrow, and the value of the relative weight for the initiator and monomers before or after the reaction was very close. From the results of Table 1, a conclusion may be drawn that the initiator prepared could be successfully employed for ATRP and the initiator system had good controlling on the polymerization.

Characterization of HFMA initiator and the polymers

The FT-IR spectra of HFMA monomer (a), HFMA initiator (b), and the polymers (c and d) were shown in Fig. 1. The peak of Fig. 1a was very similar to that of Fig. 1b, they both exhibited the characteristic peaks at 1190 and 690 cm^{-1}, which are caused by the typical stretching vibration and wagging vibrations of C–F



Scheme 1 The synthesis of initiators and their polymers

[28, 29]. Comparing Fig. 1a with Fig. 1b, unambiguous disappearance of the characteristic peak of C=C at 1640 cm^{-1} (Fig. 1a) and the appearance of the characteristic peak of C–Br at 523 cm^{-1} (Fig. 1b) were observed, this indicated the completion of the addition reaction and the successful preparation of HFMA initiator. Figure 1c showed the spectrum of the HFMA-PIBMA. The characteristic peaks of C–F mentioned above became faintness, two double peaks range from 1100 to 1270 cm^{-1} and characteristic absorbance at 988 cm^{-1} can be seen, which were ascribed to the variation absorbance of C–C–O–C and $–CH(CH_3)_2$ in IBMA, respectively. The spectrum of the HFMA-PMMA was shown in Fig. 1d, it was similar to Fig. 1c except the characteristic absorbance at 988 cm^{-1} of $–CH(CH_3)_2$ in IBMA [30, 31].

The ^{1}H NMR spectra of HFMA-Br and the polymers were shown in Fig. 2. Trace I showed the spectra of HFMA-Br. Peaks at 1.84 ppm were assigned as $–CH_3$ (a), while peaks at 4.4–4.5 and 4.8–5.0 ppm were corresponding to $–OCH_2$ (b) and –CHF (c). Peaks at ~4.8 ppm were designated to the splitting of –CHF (d), which may result from the coupling of proton with nuclei of fluorine atoms [32]. Olefinic proton signals derived from unreacted HFMA could not be detected in trace I. For HFMA-PIBMA (as shown in trace II), some new peaks compared with trace I appeared. Peaks at 3.6–3.8, 1.7–1.9, and 1.4–1.6 ppm are assigned as $–COOCH_2$ (f), $–CH_2$ (e), and –CH (g) in the PIBMA segments, respectively. The heterotactic (mr), isotactic (mm), and syndiotactic (rr) triad peaks of $–CH_3$ (d) in IBMA segments can also be seen at 0.7–1.0 ppm [33]. Among these, $–CH_3$ (h), $–CH_3$ (d_{mm}) of IBMA segments overlapped with $–CH_3$ (a) of HFMA segments at 0.83 ppm. Trace III showed the spectra of HFMA-PMMA. Except the peaks of HFMA mentioned above, peaks at 3.5–3.6 and 1.7–1.9 ppm were assigned as $–OCH_3$ (f) and $–CH_2$ (e) in the PMMA segments, respectively, while peaks at 1.50, 0.93, and 0.79 ppm were corresponding to mm, mr, and rr triad resonances of $–CH_3$ (d) in MMA segments [34].

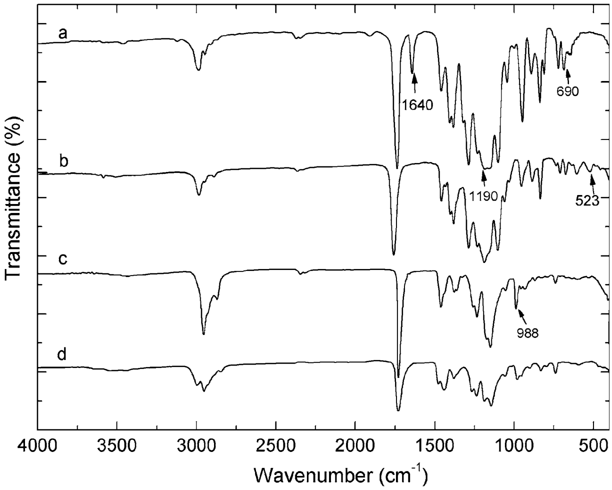


Fig. 1 The FT-IR spectra of HFMA monomer (*a*), HFMA initiator (*b*), HFMA-PIBMA (*c*), and HFMAPMMA (*d*)

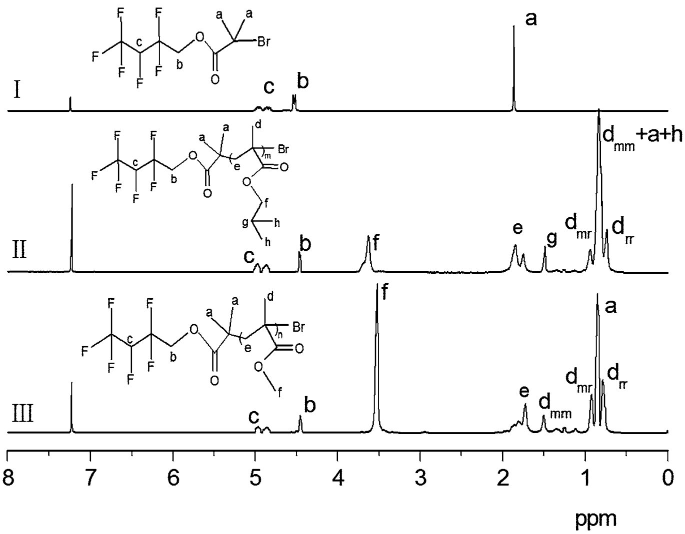


Fig. 2 The ^{1}H NMR spectra of HFMA-Br and its polymers

From the FTIR and ^{1}H NMR spectra, structures of HFMA initiator and the polymers were verified.

Characterization of DFMA initiator and the polymers

The structures of the DFMA initiator and the polymers were analyzed by FT-IR and ^{1}H NMR data. Figure 3 showed the FT-IR spectra of DFMA monomer (a), DFMA initiator (b), DFMA-PIBMA (c), and DFMA-PMMA (d). The peaks of Fig. 3a were

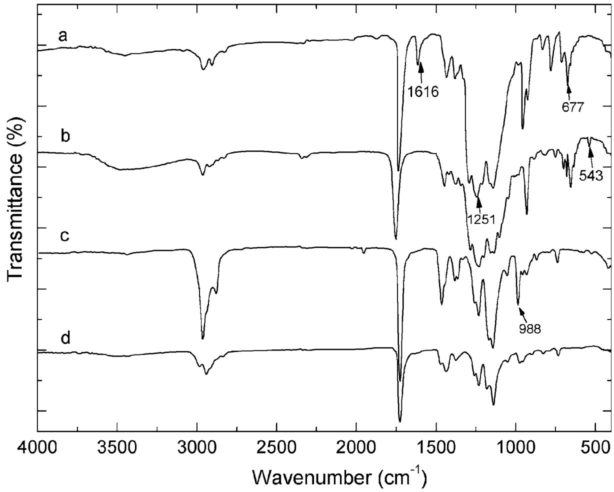


Fig. 3 The FT-IR spectra of DFMA monomer (*a*), DFMA initiator (*b*), DFMA-PIBMA (*c*), and DFMAPMMA (*d*)

very similar to that of Fig. 3b, they both exhibited the characteristic peaks at 1251 and 677 cm^{-1} which are caused by the typical stretching vibration and wagging vibrations of C–F [35, 36]. Comparing Fig. 3a with Fig. 3b, unambiguous disappearance of the characteristic peak of C=C at 1616 cm^{-1} (Fig. 3a) and the appearance of the characteristic peak of C–Br at 543 cm^{-1} (Fig. 3b) were observed, this indicated the completion of the addition reaction and the successful preparation of the DFMA initiator. Figure 3c showed the spectrum of DFMA-PIBMA. The characteristic peaks of C–F mentioned above became faintness, two double peaks range from 1100 to 1270 cm^{-1} and characteristic absorbance at 988 cm^{-1} can be seen, which were ascribed to the variation absorbance of C–C–O–C and $–CH(CH_3)_2$ in IBMA, respectively. The spectrum of the DFMA-PMMA was shown in Fig. 3d, it was similar to Fig. 3c except the characteristic absorbance at 988 cm^{-1} of $–CH(CH_3)_2$ in IBMA.

The ^{1}H NMR spectra of DFMA-Br and its polymers were shown in Fig. 4. Trace I showed the spectra of DFMA-Br. Peaks at 1.85 ppm was assigned as $–CH_3$ (a), while peaks at 4.4–4.8 and 5.3–5.6 ppm are corresponding to $–OCH_2$ (b) and –CHF (c). The fluoroacrylate monomer DFMA have two isomers, and so the peaks of the band of the CH_2 group in fluorinated side chain spread in 4.4–4.8 ppm range [37]. Olefinic proton signals derived from unreacted DFMA were not detected in trace I. For DFMA-PIBMA (as shown in trace II), some new peaks compared with trace I appeared. Peaks at 3.5–3.8, 1.6–2.0, and 1.5–1.6 ppm were assigned as $–COOCH_2$ (f), $–CH_2$ (e), and –CH (g) in the PIBMA segments, respectively. The heterotactic (mr), isotactic (mm), and syndiotactic (rr) triad peaks of $–CH_3$ (d) in IBMA segments could also be seen at 0.7–1.0 ppm. Among these, $–CH_3$ (h), $–CH_3$ (d_{mm}) of IBMA segments overlapped with $–CH_3$ (a) of DFMA segments [33]. Trace III showed the spectra of DFMA-PMMA. Except the peaks of DFMA mentioned above, peaks at 3.50 and 1.6–1.9 ppm were assigned as $–OCH_3$ (f) and $–CH_2$ (e) in

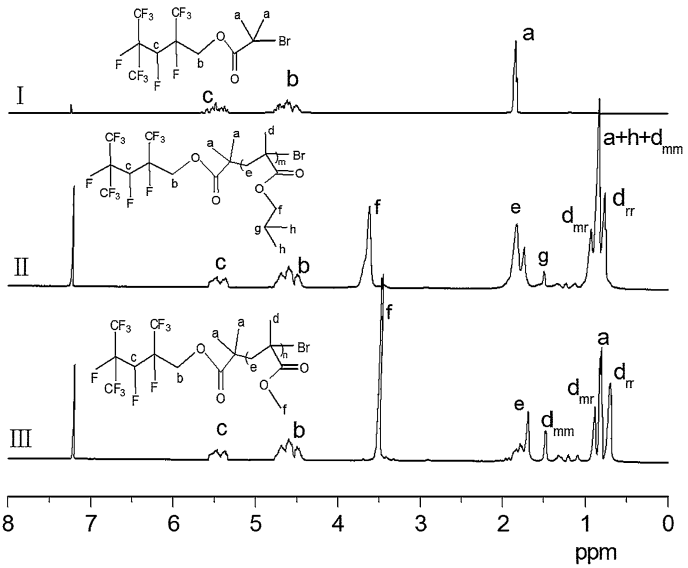


Fig. 4 The ^{1}H NMR spectra of DFMA-Br and its polymers

the PMMA segments, respectively, while peaks at 1.48, 0.89, and 0.70 ppm were corresponding to mm, mr, and rr triad resonances of –CH_3 (d) in MMA segments [34].

From the FTIR and ^{1}H NMR spectra, structures of DFMA initiator and the polymers were verified.

The surface properties of the polymers

Low-surface energy of fluorinated polymers was well known. The series of polymers were designed to see the affecting of fluorinated units on the surface energy. The contact angles of the water and dodecane on the polymer films were shown in Table 2. As expected, although only one molecule of fluorinated acrylate (HFMA or DFMA) was introduced, the contact angles of water on the polymers increased greatly comparing with the homopolymers of IBMA or MMA, and they increased with the gradual increase of fluorine content in polymers. The contact angle value for dodecane on the polymers film also exhibited the same phenomenon. This may result from the push-me/pull-you architectures of fluorinated block polymers, which indicated that the polymers have an ordered and close-packed structure on the surface [22].

We obtained indirectly surface energy from the water contact angle. An equation, $1 + \cos\theta = 2(\gamma_S/\gamma_L)^{1/2} \exp[-\beta(\gamma_L - \gamma_S)^2]$ [38, 39], was applied to calculate the surface energy. β was a constant with a value of 0.0001247 $(m^2/mJ)^2$ [36]; θ, γ_S, and γ_L were the contact angle, the surface energy of the solid, and the surface energy of the tested liquid, respectively. The results in Table 2 showed that the surface energies of polymers decreased rapidly with a slight increase of the fluorine content.

Table 2 The fluorine content, contact angle, and the surface energy of the series of polymers

Sample	Copolymer	Content of fluorine[a], %	Contact angle (°)[b]		γ_S^c, mN/m
			$C_{12}H_{26}$	H_2O	
1	PIBMA	–	16.1	84.0	33.0
2	HFMA-PIBMA(1)	2.4	20.2	89.5	29.6
3	HFMA-PIBMA(2)	4.6	24.4	93.1	27.3
4	DFMA-PIBMA(1)	3.0	22.3	91.3	28.4
5	DFMA-PIBMA(2)	5.8	27.9	96.8	25.0
6	PMMA	–	12.2	79.6	35.8
7	HFMA-PMMA(1)	2.3	19.2	88.0	30.5
8	HFMA-PMMA(2)	4.6	23.3	92.6	27.6
9	DFMA-PMMA(1)	2.9	21.6	90.2	29.1
10	DFMA-PMMA(2)	5.6	26.5	94.6	26.4

[a] The data determined by ^{1}H NMR

[b] The contact angle on the air-side surface of the copolymers films

[c] Surface energy obtained indirectly from the water contact angle

Especially, when the fluorine content was 5.8% (sample 5 of Table 2), the surface energy of the polymer dropped to 25.0 mN/m, which was much lower than that of MMA homopolymers (35.8 mN/m). This was presumably associated with the better chain alignment and packing of the fluorinated units in HFMA [22]. All the results of surface energy were agreeable with the contact angle measurements.

Conclusion

The new small-molecule fluorinated initiators were prepared by direct addition reaction of HFMA or DFMA with hydrobromic acid in acetic acid under mild conditions. This greatly widened the initiators used for ATRP. The successful polymerization of IBMA or MMA derived from HFMA-Br or DFMA-Br indicated that fluorinated acrylates could be used as initiators for ATRP. The data of GPC showed the well controlling of the initiator system. FTIR and ^{1}H NMR characterized the structures of the initiators and their polymers. Contact angle measurement indicated that although only one molecule of fluorinated acrylate was introduced the surface properties of polymers were improved greatly.

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