Journal of Fluorine Chemistry 130 (2009) 354–360

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Perfluorocyclobutyl-based methacrylate monomers: Synthesis and radical polymerization

Yongjun Li [a,b,c], Sen Zhang [b], Liang Tong [b], Qingnuan Li [a,*], Wenxin Li [a], Guolin Lu [b], Hao Liu [b], Xiaoyu Huang [b,*]

[a] Laboratory of Nano-Biology and Medicine, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 2019 Jialuo Road, Shanghai 201800, PR China
[b] Key Laboratory of Organofluorine Chemistry and Laboratory of Polymer Materials, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, PR China
[c] Graduate University of Chinese Academy of Sciences, Beijing 100080, PR China

ARTICLE INFO

Article history:
Received 26 September 2008
Received in revised form 30 December 2008
Accepted 30 December 2008
Available online 9 January 2009

Keywords:
Perfluorocyclobutyl (PFCB)
Methacrylate
Crossing-dimerization

ABSTRACT

A new class of methacrylate monomers containing perfluorocyclobutyl unit was synthesized in multi-steps including crossing-dimerization, demethylation and esterification using commercially available *p*-substituted phenol, tetrafluoroethylene and methacryloyl chloride as starting materials. These monomers can be polymerized in solution to provide perfluorocyclobutyl-based polymethacrylate, a kind of potential transparent material.

1. Introduction

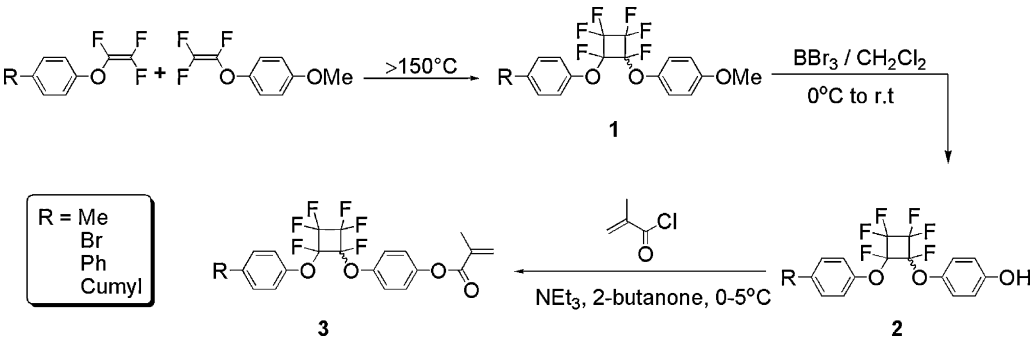
Perfluorocyclobutyl (PFCB) aryl ether polymers are a relatively new class of fluoropolymers developed by the researchers of Dow Chemical Co. in 1993 [1]. This kind of fluoropolymers is generally synthesized by thermal [$2\pi + 2\pi$] step-growth cyclopolymerization of trifluorovinyl aryl ethers at a high temperature between 150 °C and 250 °C in bulk or solution without any initiator or catalyst. As an emerging class of semi-fluorinated polymers, PFCB-based polymers provide the conventional properties of fluoropolymer such as low surface energy, high thermal/oxidative stability and high chemical resistance, also possessing many other advantages including optical transparency and improved processability [2–5].

Most recent studies of PFCB-based polymers focused on thermal polymerization of different fluorinated trifluorovinyl aryl ether monomers to obtain a variety of homopolymers and random copolymers containing PFCB linkages [6–9]. Monomers containing two or three trifluorovinyl ethers were synthesized from different commercially available polyphenols and were polymerized to afford different thermoplastic or thermoset PFCB aryl ether polymers. However, only few literatures reported the synthesis of copolymers via trifluorovinyl aryl ether monomers and other commonly used monomers due to the normal high polymerization temperature (>150 °C) and unusual polymerization mechanism without any initiator [10–13]. The number of PFCB linkage in copolymers was very difficult to be tuned. In addition, none has reported the introduction of PFCB aryl ether unit into commonly used monomer, which has certainly limited the application of PFCB-based fluoropolymers.

In order to enlarge its application range, it is necessary to combine the high performance of PFCB aryl ether polymer with other commercial polymers. To realize this, incorporation of PFCB linkage into acrylate/methacrylate monomer via a stable covalent bond using commercially available (meth)acryloyl chloride is a good and convenient choice. Thus, well-defined polymethacrylates bearing pendant PFCB linkages can be prepared by "living" polymerization of PFCB-based methacrylate monomers and the number of PFCB linkage can be controlled by the feed ratio of the monomer to the initiator. In addition, it is feasible to synthesize well-defined block or graft copolymers containing PFCB linkages via "living" polymerization, which may find potential applications in information storage, photonic material and stimuli-responsive nanostructure [14]. Furthermore, as a new method of modifying methacrylate monomer, the introduction of PFCB linkage may increase the thermal stability and glass transition temperature (T_g) of the obtained polymers [15].

* Corresponding authors. Tel.: +86 21 54925310; fax: +86 21 64166128.
E-mail address: xyhuang@mail.sioc.ac.cn (X. Huang).

0022-1139/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2008.12.012



Scheme 1. Synthesis of PFCB-containing methacrylate monomer.

In this work, we presented the synthesis of a new class of PFCB-containing methacrylate monomers via commercially available reagents (Scheme 1). PFCB linkage was incorporated into methacrylate monomer as a side group. Radical polymerizations of these methacrylate monomers can be easily initiated by 2,2′-azobis(isobutyronitrile) to give PFCB-based polymers.

2. Results and discussion

2.1. Design and synthesis of monomers

Substituted *p*-(trifluorovinyloxy)benzene compounds were firstly prepared by established method in good yield from commercially available raw materials including 4-bromophenol, *p*-cresol, 4-phenylphenol, 4-cumylphenol and 4-methoxyl phenol [1]. Second, a series of anisoles containing PFCB linkage was obtained by the cross-coupling reaction between substituted *p*-(trifluorovinyloxy)benzene and *p*-(trifluorovinyloxy)anisole with reasonable yields. The anisoles were demethylated by BBr_3 to give the corresponding phenols containing PFCB unit. Finally, methacryloyl chloride was used to esterify the phenols to provide the targeted PFCB-containing methacrylate monomers.

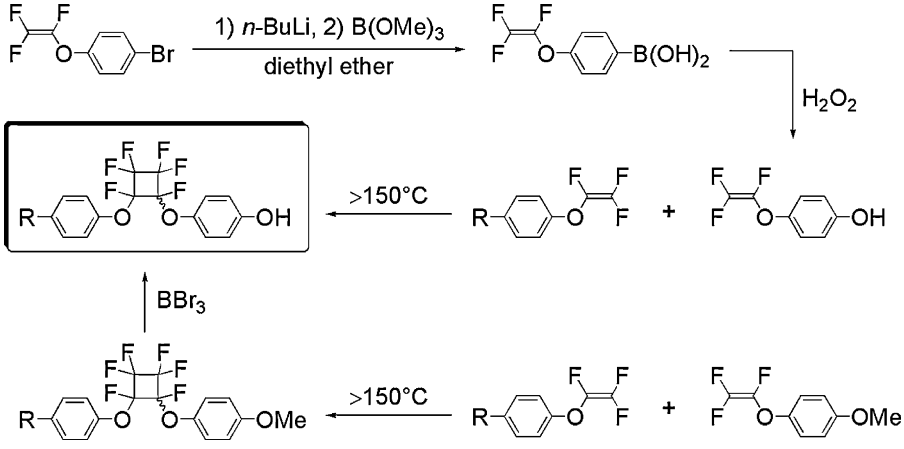
The key step of the synthesis is the preparation of important intermediate, *p*-(2-aryloxyperfluorocyclobutoxy)phenol. This kind of intermediates can be prepared via a cross-coupling reaction using different starting materials as shown in Scheme 2, *p*-(trifluorovinyloxy)phenol or *p*-(trifluorovinyloxy)anisole. The synthesis of *p*-(trifluorovinyloxy)phenol has been reported via a boronic acid intermediate from *p*-bromo(trifluorovinyloxy)benzene [16]. However, the relative severe reaction condition confined the preparation in a large scale. Thus, *p*-(trifluorovinyloxy)anisole was selected as starting material since that it can be easily prepared from commercially available 4-methoxyphenol. After cross-coupling, the transformation of methoxyl into phenolic hydroxyl was readily carried out by treating with boron tribromide [17,18].

It is well-known that thermal $[2\pi + 2\pi]$ cyclodimerization of fluorinated olefins proceed via a biradical mechanism, the single requirement being the presence of a terminal difluoromethylene group in the olefin [1,19]. Therefore, three types of crossing-dimer products would be obtained after the cross-coupling reaction between *p*-(trifluorovinyloxy)anisole and substituted *p*-(trifluorovinyloxy)benzene (Scheme 3).

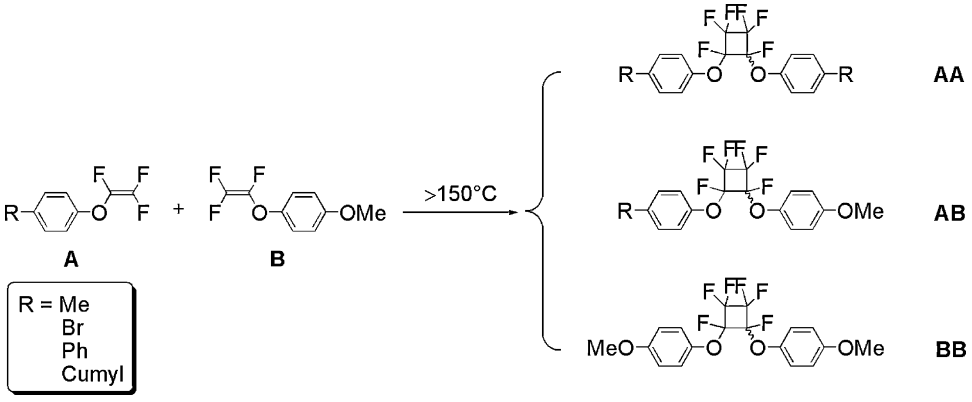
While the reactivity of trifluorovinyl was influenced by electronic effect of the *p*-substitution group of the benzene ring [16], the consumption rate of different TFVE monomers may be different. *p*-Bromo(trifluorovinyloxy)benzene (A) and *p*-(trifluorovinyloxy)anisole (B) were heated neat in NMR tubes and the area ratio of *trans* (to O) fluorine signal of A (peak b) to B (peak b′) was measured as a function of time by ^{19}F NMR (Fig. 1). It was found that *p*-(trifluorovinyloxy)anisole (B) had a higher consumption rate due to the strong electron-donating character of OCH_3 group.

The distribution percentages of three different dimers with various feed ratios were determined by HPLC. Pure homo-dimers of *p*-bromo(trifluorovinyloxy)benzene and *p*-(trifluorovinyloxy)anisole were prepared firstly via thermo-cyclodimerization and used as calibrations (Fig. 2A and C). The mixtures of cross-dimerization reaction were analyzed by HPLC under the same condition (Fig. 2B) and the signal of cross-coupling product located between those of homo-dimers. Relative contents of three dimers were calculated from the area ratios as summarized in Table 1.

It was found that the crossing-dimer (AB) accounted for at least 42% of the dimers under various feed ratios. When the feed ratio of A to B was 1:1, the percentage of AB crossing-dimer was higher than others. Due to the higher consumption rate of *p*-(trifluor-



Scheme 2. Two different strategies to synthesize the intermediate.



Scheme 3. Crossing-dimerization of *p*-(trifluorovinyloxy)anisole and substituted *p*-(trifluorovinyloxy)benzene.

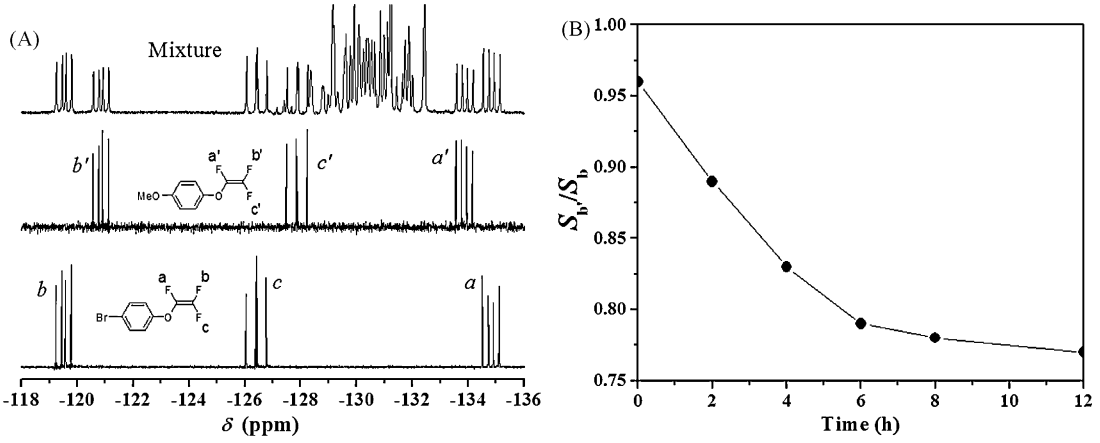


Fig. 1. (A) ^{19}F NMR spectra of *p*-bromo(trifluorovinyloxy)benzene, *p*-(trifluorovinyloxy)anisole and their cross-dimerization mixture. (B) Relative consumption rate of *p*-bromo(trifluorovinyloxy)benzene to *p*-(trifluorovinyloxy)-anisole determined by ^{19}F NMR.

ovinyloxy)anisole evidenced by ^{19}F NMR, the feed ratio of A to B was selected to be 1:1.2 with a slight excess of *p*-(trifluorovinyloxy)anisole in order to raise the yield of crossing-dimer or to reduce the self-coupling products of substituted *p*-(trifluorovinyloxy)benzene. The mixture of three different dimers was readily separated by column chromatograph and the isolated yield of crossing-dimer was higher than 50%.

The structures of desired crossing-dimers were characterized by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and EI-MS. Fig. 3A shows ^{1}H NMR spectrum of crossing-dimer **1b**. The signals of the protons of benzene ring adjacent to $-OCH_3$ and PFCB were found to locate at 6.83 ppm and 7.05 ppm, respectively. The peak of two protons of benzene ring adjacent to Br appeared at 7.43 ppm. In particular, the peak at 3.79 ppm was attributed to three protons of $-OCH_3$ and its

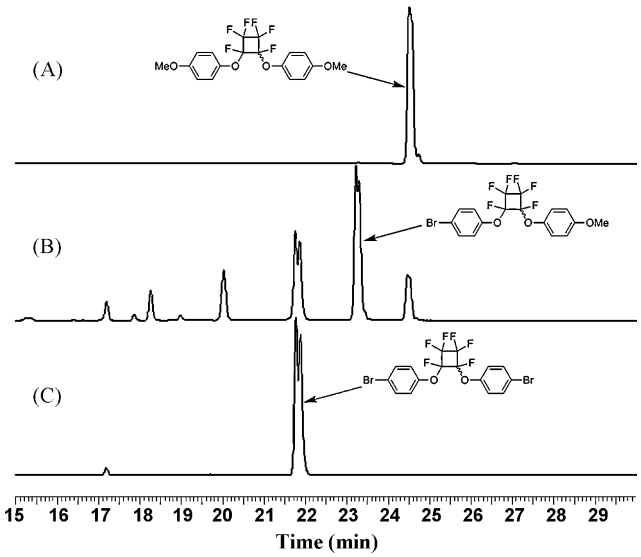


Fig. 2. HPLC traces of homo-dimers and cross-dimerization mixture of *p*-bromo-(trifluorovinyloxy)benzene and *p*-(trifluorovinyloxy)anisole.

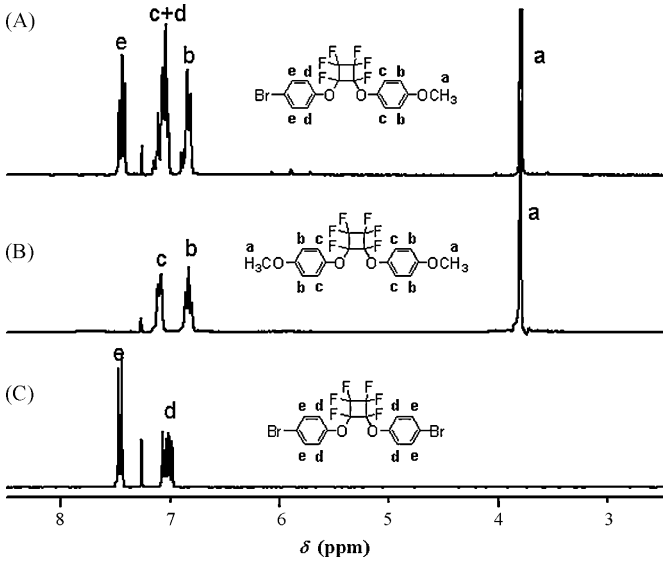


Fig. 3. ^{1}H NMR spectra of the dimers from the cross-coupling reaction between *p*-(trifluorovinyloxy)anisole and *p*-bromo(trifluorovinyloxy)benzene in $CDCl_3$.

Table 1
Distribution percentage of dimers with different feed ratios.

Entry	A:B (mole ratio)	Distribution percentage (%)[a]		
		AA	AB	BB
1	1:1	14.1	52.6	33.3
2	1:2	6.3	42.7	51.0
3	2:1	31.9	52.2	15.9

[a] Determined by HPLC in CH_3CN/H_2O at 25 °C.

presence can be confirmed from ^{1}H NMR spectra of homo-dimers derived from *p*-(trifluorovinyloxy)anisole (Fig. 3B) and *p*-bromo(-trifluorovinyloxy)benzene (Fig. 3C).

The demethylation of crossing-dimers firstly proceeded according to the method introduced by Morita et al. [20]. However, that system did not fit our substrates and we did not find any trace of anticipated product. Therefore, another approach of demethylation using BBr_3 was employed in CH_2Cl_2 at room temperature [17,18], which gave PFCB-containing phenols with almost quantitative yields. The esterification of PFCB-containing phenols and methacryloyl chloride was carried out following previously reported procedure [21] with a yield about 70%. Chemical structure of PFCB-containing methacrylate monomers was confirmed by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, FT-IR and HRMS.

2.2. Radical homopolymerization of PFCB-containing methacrylate monomer

PFCB-containing methacrylate monomers could be easily homopolymerized by free radical solution polymerization in toluene or 2-butanone using some traditional free radical initiators such as 2,2′-azobis(isobutyronitrile) (AIBN) or benzoyl peroxide (BPO). The details of polymerization conditions, molecular weights and molecular weight distributions were listed in Table 2.

Fig. 4B shows FT-IR spectrum of polymerized product of **3a**, the signal of C=C stretching vibration at 1638 cm^{-1} disappeared compared to that of **3a** (Fig. 4A). The sharp peak of C=O stretching vibration shifted from 1740 cm^{-1} to 1752 cm^{-1} after the polymerization due to the disappearance of double bond. A strong sharp band at 962 cm^{-1} evidenced the presence of PFCB linkage,

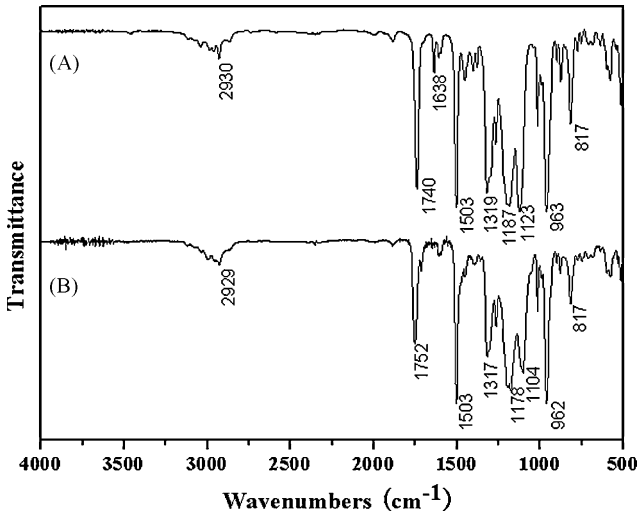


Fig. 4. FT-IR spectra of **3a** (A) and PMePFCBMA (B).

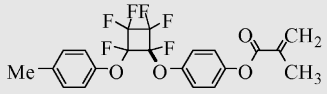
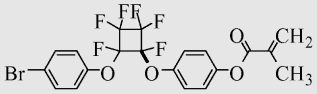
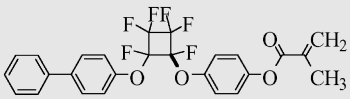
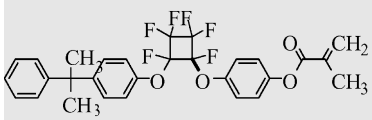
which has been proven to be a useful analytical tool since that this region is rarely occupied by other functionalities [22].

^{1}H NMR spectrum of polymerized product of **3a** clearly showed the disappearance of vinylidene signals at 5.78 ppm and 6.35 ppm and the signals of the backbone appeared at 1.37 (CCH_3) ppm and 1.47 (CH_2) ppm (Fig. 5A). In addition, the existence of PFCB linkage was also illustrated by the typical multiplets ranging from −128.1 ppm to −133.0 ppm in ^{19}F NMR spectrum (Fig. 5B) of polymerized product of **3a**.

Thermal properties of these homopolymers were measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) as listed in Table 2. The initial decomposition temperatures (T_d) are all higher than 250 °C and the glass transition temperatures (T_g) are all above 160 °C. These results demonstrated that the incorporation of PFCB unit indeed increased the thermal stability and glass transition temperature (T_g) of the resulting polymers.

Solubility tests were performed for PFCB-based polymethacrylate in a majority of commonly used organic solvents. This kind of

Table 2
Homopolymerization of PFCB-containing methacrylate monomer **3**.

Monomer structure	[M]:[I]	M_n[a] (Da)	M_w/M_n[a]	N[b]	T_d[c] (°C)	T_g[d] (°C)
	55:1	53,200	1.81	119	234	160
	55:1	62,200	1.87	121	259	193
	49:1	72,700	1.91	143	242	166
	42:1	77,900	2.16	141	266	213

[a] Measured by GPC in THF at 35 °C.
[b] Degree of polymerization.
[c] Measured by TGA (10 °C/min) in N_2.
[d] Measured by DSC (10 °C/min) in N_2.

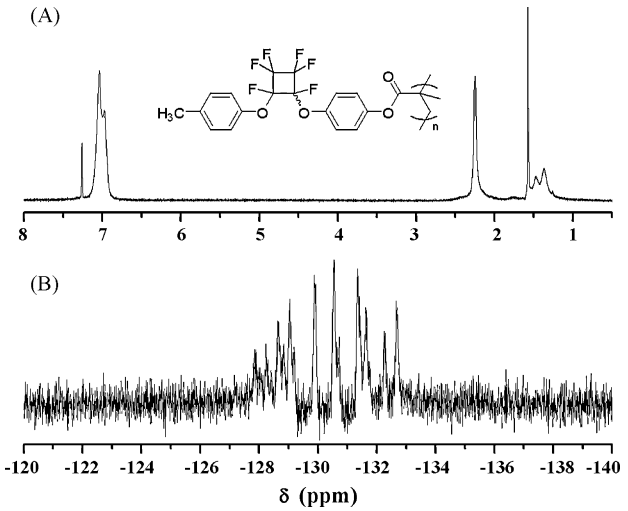


Fig. 5. ^{1}H NMR and ^{19}F NMR spectra of PMePFCBMA.

polymethacrylate is soluble in acetone, dichloromethane, acetonitrile, *N,N*-dimethylformamide, ethyl acetate, tetrahydrofuran, and toluene; insoluble in dimethyl sulfoxide and hexane. The results implied these PFCB-based homopolymers have good processability.

3. Conclusion

In summary, we have developed an efficient strategy for synthesis of a new family of PFCB-containing methacrylate monomers from commercially available phenols and tetrafluoroethylene. *p*-(2-Aryloxyperfluorocyclobutoxy)anisole was prepared by the cross-coupling reaction between *p*-(trifluorovinyloxy)anisole and substituted *p*-(trifluorovinyloxy)benzene followed by the almost quantitative removing of methyl. PFCB-containing methacrylate monomers were synthesized by the esterification of *p*-(2-aryloxyperfluorocyclobutoxy)phenol with methacryloyl chloride. They can be readily polymerized using common AIBN or BPO as free radical initiators. The excellent solubility of the homopolymers in conventional solvents indicated improved processability.

4. Experimental

4.1. Materials

2,2′-Azobis(isobutyronitrile) (Aldrich, 98%) was recrystallized from anhydrous ethanol. Granular zinc was activated by washing in 0.1 N HCl followed by drying at 140 °C *in vacuo* for 10 h. 1,2-Dibromotetrafluoroethane was prepared by condensing equimolar amounts of Br_2 and tetrafluoroethylene at −195 °C followed by warming up to 22 °C [23]. All solvents were purified by standard methods prior to use. 4-Methoxyphenol (Aldrich, 99%), *p*-cresol (Aldrich, 98%), 4-bromophenol (Aldrich, 99%), 4-cumylphenol (Aldrich, 99%), 4-phenylphenol (Aldrich, 97%), methacryloyl chloride (Alfa Aesar, 97%) and boron tribromide (BBr_3, Alfa Aesar, 99%) were used as received

4.2. Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. EI-MS was measured by an Agilent 5937N system. HRMS was recorded on a Waters Micromass GCT instrument. All NMR analyses were performed on a Bruker Avance 500 spectrometer (500 MHz) in $CDCl_3$, TMS (^{1}H NMR) and $CDCl_3$ (^{13}C NMR) were used as internal standards and CF_3CO_2H was used as external standard for ^{19}F NMR. HPLC measurements were carried out on a PerkinElmer LC200 instrument equipped with a Kromasil C18 column and a PerkinElmer 785A UV/vis detector (λ = 254 nm) at 25 °C using CH_3CN/H_2O as eluent with a flow rate of 1.0 mL/min. Relative molecular weights and molecular weight distributions were measured by a Waters gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI) and a set of Waters Styragel columns (HR3, HR4, and HR5, 7.8 mm × 300 mm). GPC measurements were carried out at 35 °C using tetrahydrofuran (THF) as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Differential scanning calorimetry and thermogravimetric analysis measurements were run on a PerkinElmer Pyris 1 system under N_2 purge with a heating rate of 10 °C/min.

4.3. Preparation of crossing-dimers (**1a–d**)

4.3.1. 4-(2-(p-Tolyloxy)perfluorocyclobutoxy)anisole (**1a**)

p-(Trifluorovinyloxy)toluene (20 mL, 0.13 mol) and *p*-(trifluorovinyloxy)anisole (25 mL, 0.15 mol) were added to a pre-dried flask and the mixture was heated at 170 °C for 12 h under N_2. The desired product **1a** of a colorless oil was obtained by column chromatography (hexane: ethyl acetate = 100:1) with a yield of 51.6%. ^{1}H NMR: δ (ppm): 2.32 (s, 3H), 3.78 (d, 3H), 6.86 (dd, 2H), 7.10 (m, 6H). ^{19}F NMR: δ (ppm): −128.6 to −131.81 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 20.5, 20.6, 55.4, 55.5, 114.5, 114.6, 118.0, 118.4, 119.8, 120.1, 122.9, 130.0, 130.1, 134.7, 135.0, 145.9, 146.2, 150.3, 150.5, 156.9, 157.1, 157.9. FT-IR (KBr): ν (cm^{-1}): 2956, 2860, 1507, 1193, 962 (PFCB). EI-MS: *m*/*z* 392. HRMS: $C_{18}H_{14}O_3F_6$, calcd. 392.0847, found 392.0865.

4.3.2. 4-(2-(p-Bromophenoxy)perfluorocyclobutoxy)anisole (**1b**)

The product is a colorless oil with a yield of 54.4%. ^{1}H NMR: δ (ppm): 3.79 (d, 3H), 6.83 (dd, 2H), 7.05 (m, 4H), 7.43 (dd, 2H). ^{19}F NMR: δ (ppm): −129.2 to −132.5 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 55.3, 114.5, 119.6, 119.8, 119.9, 120.3, 120.4, 122.9, 132.6, 132.7, 145.7, 146.0, 151.5, 151.7, 157.1, 157.3. FT-IR (KBr): ν (cm^{-1}): 2956, 2839, 1506, 1486, 1197, 962 (PFCB). EI-MS: *m*/*z* 456. HRMS: $C_{17}H_{11}O_3F_6Br$, calcd. 455.9796, found 455.9786.

4.3.3. 4-(2-(p-Phenylphenoxy)perfluorocyclobutoxy)anisole (**1c**)

The product is a white crystal with a yield of 56.5%. ^{1}H NMR: δ (ppm) 3.76 (d, 3H), 6.84 (q, 2H), 7.12 (t, 2H), 7.25 (q, 2H), 7.36 (d, 1H), 7.42 (t, 2H), 7.53 (m, 4H). ^{19}F NMR: δ (ppm): −128.6 to −132.1 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 55.5, 114.5, 114.6, 118.4, 118.7, 119.7, 120.2, 126.9, 127.4, 128.2, 128.3, 128.8, 138.4, 139.9, 145.9, 151.8, 157.1. FT-IR (KBr): ν (cm^{-1}): 2961, 2838, 1605, 1506, 1481, 1184, 961 (PFCB), 763. EI-MS: *m*/*z* 454. HRMS: $C_{23}H_{16}O_3F_6$, calcd. 454.1004, found 454.1001.

4.3.4. 4-(2-(p-Cumylphenoxy)perfluorocyclobutoxy)anisole (**1d**)

The product is a colorless oil with a yield of 67.9%. ^{1}H NMR: δ (ppm): 1.75 (s, 6H), 3.83 (s, 3H), 6.93 (d, 2H), 7.29 (m, 11H). ^{19}F NMR: δ (ppm): −128.3 to −132.2 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 30.7, 42.5, 42.6, 55.5, 114.5, 114.6, 117.5, 117.6, 119.8, 120.0, 125.8, 126.7, 128.0, 128.1, 145.9, 146.2, 147.5, 147.8, 150.2, 150.4, 156.8, 157.0. FT-IR (KBr): ν (cm^{-1}): 2970, 2839, 1602, 1506, 1202, 1184, 962 (PFCB), 763. EI-MS: *m*/*z* 496. HRMS: $C_{26}H_{22}O_3F_6$, calcd. 496.1473, found 496.1468.

4.4. Demethylation of crossing-dimers by BBr_3

4.4.1. 4-(2-(p-Tolyloxy)perfluorocyclobutoxy)phenol (**2a**)

To a solution of **1a** (13.67 g, 0.035 mol) in CH_2Cl_2 (240 mL), BBr_3 (1 M in CH_2Cl_2, 70 mL, 0.07 mol) was added dropwise at 0 °C for 1 h.

The mixture was warmed to room temperature and stirred overnight. Water (50 mL) was added to terminate the reaction followed by adding 1 N NaOH (100 mL). The mixture was extracted with ethyl acetate and the extracts were washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4. After concentration, the desired product **2a** of a light brown oil was obtained by flash chromatography (hexane: ethyl acetate = 10:1) with a quantitative yield. ^{1}H NMR: δ (ppm): 2.32 (s, 3H), 5.30 (s, 1H), 6.79 (dd, 2H), 7.08 (m, 6H). ^{19}F NMR: δ (ppm): −128.6 to −131.8 (m, cyclobutyl-F_6). EI-MS: *m/z* 378.

4.4.2. 4-(2-(p-Bromophenoxy)perfluorocyclobutoxy)phenol (2b)

The product is a light brown oil with a quantitative yield. ^{1}H NMR: δ (ppm): 5.30 (s, 1H), 6.79 (dd, 2H), 7.02 (m, 4H), 7.42 (dd, 2H). ^{19}F NMR: δ (ppm): −128.3 to −132.5 (m, cyclobutyl-F_6). EI-MS: *m/z* 442.

4.4.3. 4-(2-(p-Phenylphenoxy)perfluorocyclobutoxy)phenol (2c)

The product is a light brown crystal with a quantitative yield. ^{1}H NMR: δ (ppm): 5.30 (s, 1H), 6.77 (dd, 2H), 7.06 (t, 2H), 7.20 (t, 2H), 7.35 (t, 1H), 7.44 (t, 2H), 7.54 (m, 4H). ^{19}F NMR: δ (ppm): −128.6 to −132.0 (m, cyclobutyl-F_6). EI-MS: *m/z* 440.

4.4.4. 4-(2-(p-Cumylphenoxy)perfluorocyclobutoxy)phenol (2d)

The product is a light brown oil with a quantitative yield. ^{1}H NMR: δ (ppm): 1.72 (s, 6H), 5.30 (s, 1H), 6.80 (dd, 2H), 7.09 (m, 4H), 7.23 (m, 7H),. ^{19}F NMR: δ (ppm): −128.5 to −132.1 (m, cyclobutyl-F_6). EI-MS: *m/z* 482.

4.5. Synthesis of PFCB-containing methacrylate monomers (3a–d)

4.5.1. 4-(2-(p-Tolyloxy)perfluorocyclobutoxy)phenyl methacrylate (3a)

2a (3.0 g, 0.008 mol) and triethylamine (0.93 mL, 0.0096 mol) were dissolved in 25 mL of 2-butanone and the mixture was stirred at 0–5 °C. Methacryloyl chloride (1.4 mL, 0.0096 mol) in 10 mL of 2-butanone was added dropwise for 30 min and the mixture was stirred for another 1 h. Finally, the mixture was stirred at room temperature for 1 h. The precipitated triethylammonium chloride was filtered and the filtrate was washed twice with water. The solution was dried over Na_2SO_4 followed by the concentration to remove 2-butanone. The desired product **3a** of a colorless oil was obtained by flash column chromatograph (hexane: ethyl acetate = 100:1) with a yield of 87.0%. ^{1}H NMR: δ (ppm): 2.06 (s, 3H), 2.32 (s, 3H), 5.78 (s, 1H), 6.35 (s, 1H), 7.12 (m, 8H). ^{19}F NMR: δ (ppm): −128.4 to −132.4 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 18.3, 20.6, 117.8, 117.9, 119.2, 119.5, 121.2, 122.7, 122.8, 126.9, 127.4, 129.9, 130.1, 130.2, 134.8, 135.3, 136.0, 147.8, 148.0, 148.7, 149.7, 149.9, 150.2, 165.6. FT-IR (KBr): ν (cm^{-1}): 2930, 1740 (C=O), 1638, 1503, 1319, 1187, 1123, 963 (PFCB), 817. EI-MS: *m/z* 446. HRMS: $C_{21}H_{16}O_4F_6$, calcd. 446.0953, found 446.0964.

4.5.2. 4-(2-(p-Bromophenoxy)perfluorocyclobutoxy)phenyl methacrylate (3b)

The product is a colorless oil with a yield of 75.6%. ^{1}H NMR: δ (ppm): 1.98 (s, 3H), 5.69 (s, 1H), 6.27 (s, 1H), 7.04 (m, 6H), 7.37 (dd, 2H). ^{19}F NMR: δ (ppm): −128.3 to −132.1 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 18.0, 118.9, 119.5, 119.7, 120.2, 122.5, 122.6, 127.3, 132.6, 132.7, 135.5, 147.9, 148.2, 149.4, 149.6, 151.3, 151.4, 165.3, 165.4. FT-IR (KBr): ν (cm^{-1}): 3106, 2963, 2931, 1740 (C=O), 1638, 1503, 1486, 1317, 1202, 1124, 963 (PFCB), 825. EI-MS: *m/z* 510. HRMS: $C_{21}H_{16}O_4F_6$, calcd. 509.9901, found 509.9902.

4.5.3. 4-(2-(p-Phenylphenyloxy)perfluorocyclobutoxy)phenyl methacrylate (3c)

The product is a white crystal with a yield of 68.2%. ^{1}H NMR: δ (ppm): 2.04 (s, 3H), 5.76 (s, 1H), 6.32 (s, 1H), 7.10 (d, 2H), 7.19 (d, 2H) 7.25 (d, 2H), 7.35 (t, 1H), 7.44 (t, 2H), 7.53 (d, 4H).^{19}F NMR: δ (ppm): −128.2 to −132.3 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 18.2, 118.2, 118.7, 119.1, 119.5, 122.7, 126.9, 127.3, 127.4, 128.2, 128.3, 128.7, 135.5, 138.2, 138.5, 139.8, 147.7, 148.0, 149.6, 149.8, 151.7, 151.8, 165.5. FT-IR (KBr): ν (cm^{-1}): 3060, 3035, 2930, 1739 (C=O), 1638, 1503, 1483, 1318, 1202, 1124, 962 (PFCB). EI-MS: *m/z* 508. HRMS: $C_{21}H_{16}O_4F_6$, calcd. 508.1109, found 508.1094.

4.5.4. 4-(2-(p-Cumylphenyloxy)perfluorocyclobutoxy)phenyl methacrylate (3d)

The product is a colorless oil with a yield of 64.3%. ^{1}H NMR: δ (ppm): 1.66 (s, 6H), 2.05 (s, 3H), 5.76 (s, 1H), 6.34 (s, 1H), 7.00 (dd, 2H), 7.07 (m, 4H), 7.19 (m, 7H). ^{19}F NMR: δ (ppm): −128.2 to −132.3 (m, cyclobutyl-F_6). ^{13}C NMR: δ (ppm): 18.2, 30.6, 42.5, 117.4, 117.7, 119.1, 119.4, 122.7, 122.8, 125.7, 126.6, 127.4, 128.0, 128.1, 135.6, 147.6, 147.8, 147.9, 148.0, 149.7, 150.1, 150.3, 165.5. FT-IR (KBr): ν (cm^{-1}): 3059, 3024, 2970, 1740 (C=O), 1638, 1503, 1318, 1202, 1124, 963 (PFCB). EI-MS: *m/z* 550. HRMS: $C_{21}H_{16}O_4F_6$, calcd. 550.1579, found 550.1580.

4.6. Radical homopolymerization of PFCB-containing methacrylate monomers

4.6.1. General procedure

To a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum, certain amounts of PFCB-containing methacrylate monomer **3**, AIBN and 2-butanone (1 mL) were charged followed by three cycles of freeze-pump-thaw. The flask was immersed into an oil bath preset at 70 °C. The homopolymerization lasted for 8 h and the homopolymer was precipitated into excess methanol. The raw product was purified by dissolving in THF and precipitating into methanol for three times, a white solid was obtained after drying *in vacuo* at 50 °C for 24 h.

Poly(4-(2-(*p*-tolyloxy)perfluorocyclobutoxy)phenyl methacrylate): ^{1}H NMR: δ (ppm): 1.36 (3H, CCH_3), 1.47 (2H, CH_2), 2.25 (3H, $C_6H_4CH_3$), 6.97, 7.04 (8H, phenyl). ^{19}F NMR: δ (ppm): −128.1 to −133.0 (m, cyclobutyl-F_6). FT-IR (KBr): ν (cm^{-1}): 2929, 1752 (C=O), 1503, 1317, 1178, 1104, 962 (PFCB).

Poly(4-(2-(*p*-bromophenoxy)perfluorocyclobutoxy)phenyl methacrylate): ^{1}H NMR: δ (ppm): 1.38 (3H, CCH_3), 1.48 (2H, CH_2), 7.00, 7.38 (8H, phenyl). ^{19}F NMR: δ (ppm): −128.1 to −132.0 (m, cyclobutyl-F_6). FT-IR (KBr): ν (cm^{-1}): 2956, 1752 (C=O), 1502, 1314, 1200, 1103, 962 (PFCB).

Poly(4-(2-(*p*-phenylphenyloxy)perfluorocyclobutoxy)phenyl methacrylate): ^{1}H NMR: δ (ppm): 1.35 (3H, CCH_3), 1.45 (2H, CH_2), 6.97, 7.09, 7.33, 7.43 (13H, phenyl). ^{19}F NMR: δ (ppm): −127.9 to −132.7 (m, cyclobutyl-F_6). FT-IR (KBr): ν (cm^{-1}): 2930, 1751 (C=O), 1502, 1314, 1201, 1104, 962 (PFCB).

Poly(4-(2-(*p*-cumylphenyloxy)perfluorocyclobutoxy)phenyl methacrylate): ^{1}H NMR: δ (ppm): 1.37 (3H, CCH_3), 1.48 (2H, CH_2), 1.59 (6H, $C_6H_5C(CH_3)_2$), 7.00, 7.13 (13H, phenyl). ^{19}F NMR: δ (ppm): −127.7 to −133.0 (m, cyclobutyl-F_6). FT-IR (KBr): ν (cm^{-1}): 2970, 1752 (C=O), 1502, 1317, 1202, 1105, 963 (PFCB).

Acknowledgements

The authors thank the financial support from National Natural Science Foundation of China (20674094 and 10775169), Ministry of Science and Technology of "National High Technology Research and Development Program" (2006AA03Z541).

References

[1] D.A. Babb, B.R. Ezzell, K.S. Clement, W.F. Richey, A.P. Kennedy, J. Polym. Sci. Polym. Chem. 31 (1993) 3465–3477.

[2] A.E. Feiring, in: R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry: Principle and Commercial Applications, Plenum Press, New York, 1994, pp. 339–371.
[3] M. Yamabe, in: R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry: Principle and Commercial Applications, Plenum Press, New York, 1994, pp. 397–402.
[4] P.R. Resnick, W.H. Buck, in: J. Schirs (Ed.), Modern Fluoropolymers: High Performance Polymers for Diverse Applications, Wiley, New York, 1997, pp. 397–420.
[5] S.T. Iacono, S.M. Budy, J.Y. Jin, D.W. Smith, J. Polym. Sci. Polym. Chem. 45 (2007) 5705–5721, and references therein.
[6] X.Z. Jiang, S. Liu, M.S. Liu, P. Herguth, A.K.Y. Jen, H. Fong, M. Sarikaya, Adv. Funct. Mater. 12 (2002) 745–751.
[7] D.W. Smith, D.A. Babb, H.V. Shah, A. Hoeglund, R. Traiphol, D. Perahia, H.W. Boome, C. Langhoff, M. Radler, J. Fluorine Chem. 104 (2000) 109–117.
[8] S.Y. Cho, H.R. Allcock, Chem. Mater. 19 (2007) 6338–6344.
[9] V.E. Campbell, P. Paoprasert, J.D. Mykietyn, I. In, D.J. McGee, P. Gopalan, J. Polym. Sci. Polym. Chem. 45 (2007) 3166–3177.
[10] R. Souzy, B. Ameduri, B. Boutevin, Prog. Polym. Sci. 29 (2004) 75–106.
[11] X.Y. Huang, G.L. Lu, D. Peng, S. Zhang, F.L. Qing, Macromolecules 38 (2005) 7299–7305.
[12] G.L. Lu, S. Zhang, X.Y. Huang, J. Polym. Sci. Polym. Chem. 44 (2006) 5438–5444.
[13] Y.Q. Zhu, Y.G. Huang, W.D. Meng, H.Q. Li, F.L. Qing, Polymer 47 (2006) 6272–6279.
[14] C. Park, J. Yoon, E.L. Thomas, Polymer 44 (2003) 6725–6760.
[15] A.A. Kavitha, N.K. Singha, J. Polym. Sci. Polym. Chem. 46 (2008) 7101–7113.
[16] B.K. Spraul, S. Suresh, J.Y. Jin, D.W. Smith, J. Am. Chem. Soc. 128 (2006) 7055–7064.
[17] J. Storch, J. Cermak, J. Karban, Tetrahedron Lett. 48 (2007) 6814–6816.
[18] H.Y. Lee, J.Y. Oh, H.Y. Chu, J.I. Lee, S.H. Kim, Y.S. Yang, G.H. Kim, L.M. Do, T. Zyung, J. Lee, Y. Park, Tetrahedron 59 (2003) 2773–2779.
[19] I. Wlassics, J. Fluorine Chem. 125 (2004) 1519–1528.
[20] T. Morita, Y. Okamoto, H. Sakurai, J. Chem. Soc. Chem. Commun. (1978) 874–875.
[21] M.V. Patel, J.N. Patel, A. Ray, R.M. Patel, J. Polym. Sci. Polym. Chem. 43 (2005) 157–167.
[22] D.W. Smith, D.A. Babb, Macromolecules 29 (1996) 852–860.
[23] Y. Kastsuhara, D.D. DesMarteau, J. Am. Chem. Soc. 102 (1980) 2681–2686.