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# Synthesis and characterization of new polymethacrylates bearing perfluorocyclobutyl and sulfonyl units

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ABSTRACT

A new methacrylate monomer containing perfluorocyclobutyl and sulfonyl units, *p*-(2-(*p*-(benzenesulfonyl)phenoxy)perfluorocyclobutoxy)phenyl methacrylate, was synthesized from commercially available reagents in good yield and this kind of methacrylate can be homopolymerized by free radical polymerization using 2,2′-azobis(isobutyronitrile) as initiator or atom transfer radical polymerization using methyl 2-bromopropionate as initiator and CuBr/PMDETA as catalytic system. The reactivity ratios for BSPPFCBPMA and MMA were found to be $r_1 = 1.2436$ and $r_2 = 0.8171$ determined by Fineman–Ross method, and $r_1 = 1.2279$ and $r_2 = 0.8023$ by Kelen–Tudos method respectively. The resultant polymethacrylates bearing perfluorocyclobutyl and sulfonyl functionalities exhibit excellent thermal stability as evidenced from thermogravimetric analysis and the decomposition temperature rose dramatically with the increasing of molecular weights. Random copolymers of BSPPFCBPMA and methyl methacrylate were obtained by free radical copolymerization and their thermo-stabilities increase while raising the contents of BSPPFCBPMA.



## 1. Introduction

The chemistry of perfluorocyclobutyl (PFCB) aryl ether polymer has received considerable attention in recent years since its discovery by Babb et al. of Dow Chemical Co. in early 1990s [1,2]. The predominant head-to-head thermal [2π + 2π] cyclopolymerization of aryl trifluorovinyl ethers proceed to form stable diradical intermediate followed by rapid ring closure to provide a mixture of *cis*- and *trans*-1,2-disubstituted perfluorocyclobutanes [3,4]. The stereo-random PFCB rings afforded amorphous polymers with excellent solubility and processability compared to common fluoropolymers. The combination of thermal stability and solution processability makes PFCB aryl ether polymers attractive for a multitude of new applications often inaccessible using commercial fluoropolymer preparative routes as reviewed by Smith et al [5].

Most recent studies of PFCB-based polymers focused on thermal polymerization of different trifluorovinyl ether (TFVE) monomers to synthesize a variety of homopolymers and random copolymers in which PFCB connection also been used as a way to link different functional groups [6–10]. Due to unusual polymerization mechanism ([2π + 2π] cycloaddition) and relative higher polymerization temperature (at least >150 °C), only a few literatures reported the synthesis of copolymers via TFVE and commonly used vinyl monomers via mechanism transformation strategy [11,12]. In addition, Qing et al. [13,14] also applied click chemistry for preparing PFCB-containing copolymers. In these cases, it is difficult to tune the number of PFCB unit in copolymers.

Although those significant efforts towards the design and preparation of copolymers containing PFCB functionality have been done, none has reported the direct chain copolymerization of PFCB-containing monomers with usual vinyl monomers to afford tailor-made homopolymers or copolymers with well-defined architecture and function, which has certainly limited the application of PFCB-based fluoropolymers. In order to break through this restriction, a possible solution is to design new PFCB-containing monomers which combine the high performance of PFCB aryl ether polymer with the versatility of chain polymerization of common vinyl

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monomers. Thus, incorporation of PFCB linkage into (meth)acrylate monomer by a stable covalent connection via commercially available (meth)acryloyl chloride may be a good and convenient choice. Moreover, introduction of thermo-stable groups has been proved to be an efficient way to improve the thermal stability of polymers. For example, adamantyl [15] and sulfonyl [16,17] have been reported to be incorporated into the main chain to enhance the thermal stability. Therefore, PFCB-containing polymethacrylate can be predicted to have better temperature resistance compared to PMMA.

In this work, we report a new kind of polymethacrylate containing PFCB and sulfonyl units with high thermal stability. A new methacrylate monomer bearing PFCB and sulfonyl units, *p*-(2-(*p*-(benzenesulfonyl)phenoxy)perfluorocyclobutoxy)-phenyl methacrylate (BSPPFCBPMA), was first prepared via commercially available reagents as shown in Scheme 1. PFCB and sulfonyl functionalities are incorporated into methacrylate monomer as side groups. Its radical homopolymerization and copolymerization with methyl methacrylate can be easily initiated by 2,2′-azobis(isobutyronitrile). Well-defined homopolymers of BSPPFCBPMA with narrow molecular weight distributions were obtained by atom transfer radical polymerization (ATRP) catalyzed by CuBr/PMDETA system. Thermal stability of homopolymers and copolymers were investigated by TGA in detail and it was found that the thermal stability was influenced by the molecular weight of homopolymer and the content of BSPPFCBPMA in copolymer.

## 2. Experimental section

### 2.1. Materials

2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from anhydrous ethanol and stored at −25 °C prior to use. Granular zinc was activated by washing in 0.1 M 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 according previous literature [18]. Methyl methacrylate (MMA, Aldrich, 99%) was washed with 5% aqueous NaOH solution to remove the inhibitor, then washed with water, dried over $CaCl_2$ and distilled twice over $CaH_2$ under reduced pressure prior to use. Copper(I) bromide (CuBr, Aldrich, 98%) was purified by stirring overnight over $CH_3CO_2H$ at room temperature, followed by washing the solid with ethanol, diethyl ether and acetone prior to drying at 40 °C *in vacuo* for 1 day. 4-Methoxyphenol (Aldrich, 99%), sodium benzenesulfinate (Alfa Aesar, 98%), 4-iodophenol (Alfa Aesar, 98%), L-proline (Aldrich, 99%), cuprous iodide (CuI, Aldrich, 98%), methacryloyl chloride (Alfa Aesar, 97%), methyl 2-bromopropionate (2-MBP, Aldrich, 99%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), 4-methylphenol (Aldrich, 99%) and boron tribromide ($BBr_3$, Alfa Aesar, 99%) were used as received. All solvents were purified by standard methods prior to use.

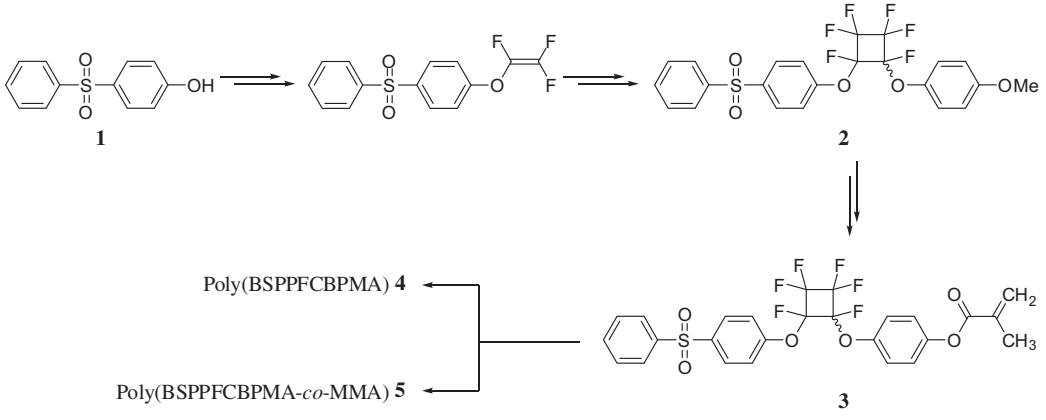
### 2.2. Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 $cm^{-1}$. 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. HRMS and EI-MS were measured by a Waters Micromass GCT instrument and an Agilent 5937N system, respectively. 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 × 300 mm). GPC measurements were carried out at 35 °C using THF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were run on a Perkin-Elmer Pyris 1 system under $N_2$ purge with a heating rate of 10 °C/min. The glass transition temperature ($T_g$) was recorded from the second heating process after a quick cooling from 250 °C and the value was determined form the midpoint of $C_p$ curve. The decomposition temperature ($T_d$) is defined as the temperature with 10% weight loss.

### 2.3. Preparation of crossing-dimer *2*

4-(Benzenesulfonyl)phenol **1** was first prepared via sodium benzenesulfonate and 4-iodophenol with a yield of 78.3% according to previous report [19]. $^1$H NMR: $\delta$ (ppm): 6.31 (br, 1H, –O*H*), 6.88 (d, 2H), 7.46 (m, 3H), 7.77 (d, 2H), 7.87 (d, 2H). EI-MS (*m*/*z*): 234 ($M^+$). Next, **1** was converted to *p*-((benzenesulfonyl)-trifluorovinyloxy)benzene following the established method with a yield of 80.6% [1,2]. $^1$H NMR: $\delta$ (ppm): 7.19 (d, 2H), 7.52 (m, 3H), 7.93 (d, 2H), 7.97 (d, 2H). $^{19}$F NMR: $\delta$ (ppm): −118.4 (dd, 1F), −124.9 (dd, 1F), −135.6 (dd, 1F). EI-MS (*m*/*z*): 314 ($M^+$). HRMS: $C_{14}H_9O_3F_3S$, calcd. 314.0225, found 314.0226.

*p*-(Trifluorovinyloxy)anisole (19.8 g, 0.097 mol) and *p*-((benzenesulfonyl)-trifluorovinyloxy)benzene (20.3 g, 0.065 mol) were added to a pre-dried 50 mL flask and the mixture was heated at




**Scheme 1.** Synthesis of polymethacrylate bearing PFCB and sulfonyl units.

170 °C for 12 h under $N_2$. The desired product, *p*-(2-(*p*-benzenesulfonylphenyloxy)perfluorocyclobutyl)anisole **2** (colorless oil), was obtained by column chromatography (eluent: hexane/ethyl acetate, v:v = 4:1) with a yield of 59.2%. $^1$H NMR: $\delta$ (ppm): 3.79 (s, 3H), 6.79 (d, 2H), 6.98 (d, 1H), 7.04 (d, 1H), 7.23 (d, 2H), 7.56 (m, 3H), 7.93 (d, 4H). $^{19}$F NMR: $\delta$ (ppm): −128.6 to −131.8 (m, cyclobutyl-$F_6$). FT-IR (film): ν ($cm^{-1}$): 3068, 1589, 1506, 1493, 1447, 1322 (S═O), 1249, 1205, 1157 (S═O), 1107, 1072, 962 (PFCB), 834, 732, 687. EI-MS (*m*/*z*): 518 ($M^+$). HRMS: $C_{23}H_{16}O_5F_6S$, calcd. 518.0623, found 518.0624.

### 2.4. Synthesis of BSPPFCBPMA **3**

Demethylation of *p*-(2-(*p*-benzenesulfonylphenyloxy)perfluorocyclobutyl)anisole **2** was carried out treated with $BBr_3$. To a solution of *p*-(2-(*p*-benzenesulfonylphenyloxy)-perfluorocyclobutyl)anisole **2** (42.9 g, 0.083 mol) in $CH_2Cl_2$ (500 mL), $BBr_3$ (1 M in $CH_2Cl_2$, 100 mL, 0.1 mol) was added dropwise at 0 °C for 2 h. The mixture was warmed to room temperature and stirred overnight. Methanol (10 mL) was added to terminate the reaction followed by washing the mixture with brine and drying over $Na_2SO_4$. After concentration, 41.5 g of desired phenol (light brown oil) was obtained by flash column chromatography (eluent: hexane/ethyl acetate, v:v = 10:1) with a quantitative yield. $^1$H NMR: $\delta$ (ppm): 6.76 (d, 2H), 6.95 (d, 2H) 7.23 (d, 2H), 7.53 (m, 3H), 7.92 (dd, 4H). $^{19}$F NMR: $\delta$ (ppm): −128.0 to −133.9 (m, cyclobutyl-$F_6$). EI-MS (*m*/*z*): 504 ($M^+$).

The above-prepared phenol (19.6 g, 0.039 mol) and triethylamine (6.7 mL, 0.047 mol) were dissolved in 200 mL of 2-butanone at 0 °C. Next, methacryloyl chloride (4.6 mL, 0.0476 mol) in 50 mL of 2-butanone was added dropwise for 30 min and the mixture was stirred for another 1 h at 0 °C. 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 anhydrous $Na_2SO_4$ followed by the concentration to remove 2-butanone. A colorless oil, BSPPFCBPMA **3**, was obtained by flash column chromatograph (eluent: hexane/ethyl acetate, v:v = 10:1) with a yield of 88.0%. $^1$H NMR: $\delta$ (ppm): 2.05 (s, 3H), 5.78, 6.35 (s, 2H,═C$H_2$), 7.08 (m, 2H), 7.17 (m, 2H), 7.28 (d, 2H), 7.51 (m, 3H), 7.94 (m, 4H). $^{19}$F NMR: $\delta$ (ppm): −127.8 to −133.7 (m, cyclobutyl-$F_6$). $^{13}$C NMR: $\delta$ (ppm): 18.3 (*C*$H_3$), 118.3–119.5 (4C, PFCB), 122.9, 127.6 (*C*$H_2$═C), 129.4, 130.0, 133.4, 135.5 ($CH_2$═*C*), 138.5, 141.2, 148.3, 149.4, 155.7, 165.6 (*C*═O). FT-IR (film): ν ($cm^{-1}$): 3070, 1737 (C═O), 1635 (C═C), 1589, 1502, 1447, 1320 (S═O), 1264, 1204, 1157 (S═O), 1123, 1014, 962 (PFCB), 837, 733, 687. EI-MS (*m*/*z*): 572 ($M^+$). HRMS: $C_{26}H_{18}O_6F_6S$, calcd. 572.0728, found 572.0726.

### 2.5. Free radical polymerization of BSPPFCBPMA **3** initiated by AIBN

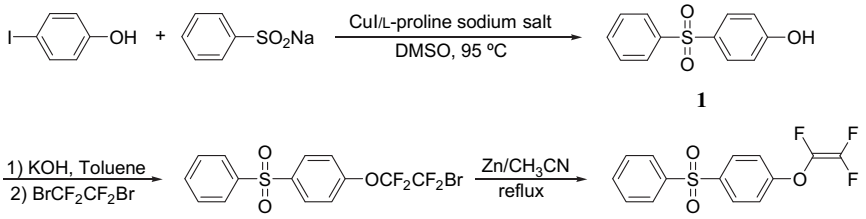
In a typical procedure, a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum was charged with AIBN (3.0 mg, 0.018 mmol) for degassing. Next, BSPPFCBPMA **3** (0.52 mg, 0.91 mmol) and 2-butanone (1 mL) were introduced via a gastight syringe. The solution was degassed by three cycles of freezing–pumping–thawing followed by immersing the flask into an oil bath preset at 60 °C to start the polymerization. The polymerization was terminated by putting the flask into liquid nitrogen after 7 h. After repeated purification by dissolving in THF and precipitating in methanol for three times, 0.4214 g of PBSPPFCBPMA **4b** was obtained after drying *in vacuo* at 40 °C. GPC: $M_n$ = 98,700, $M_w/M_n$ = 2.19. $T_g$: 122.8 °C; $T_d$: 306 °C. $^1$H NMR: $\delta$ (ppm): 1.39, 1.50 (CC$H_3$), 2.27 (C$H_2$), 6.96, 7.19, 7.43, 7.88 (phenyl). $^{19}$F NMR: $\delta$ (ppm): −128.2 to −133.9 (m, cyclobutyl-$F_6$). FT-IR (KBr): ν ($cm^{-1}$): 3070, 1752 (C═O), 1589, 1502, 1447, 1322 (S═O), 1264, 1205, 1157 (S═O), 1107, 1014, 963 (PFCB), 837, 733, 687.

### 2.6. ATRP of BSPPFCBPMA **3**

ATRP of BSPPFCBPMA **3** was initiated by 2-MBP using PMDETA/CuBr as catalytic system in 2-butanone to obtain the corresponding homopolymer with narrow molecular weight distribution. In a typical procedure, CuBr (5.2 mg, 0.036 mmol) was added to a 10 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under $N_2$. Next, BSPPFCBPMA **3** (1.037 g, 1.81 mmol), PMDETA (15.0 μL, 0.072 mmol), 2-MBP (4.0 μL, 0.036 mmol) and 2-butanone (1.5 mL) were introduced via a gastight syringe. The solution was degassed by three cycles of freezing–pumping–thawing and then the flask was immersed into an oil bath thermostated at 70 °C to start the polymerization. The polymerization was terminated by immersing the flask into liquid nitrogen after 2 h. After repeated purification by dissolving in THF and precipitating in methanol for three times, narrow-dispersed PBSPPFCBPMA **4e** (0.2443 g) was obtained after drying *in vacuo* at 40 °C. GPC: $M_n$ = 9,600, $M_w/M_n$ = 1.31. $^1$H NMR: $\delta$ (ppm): 1.39, 1.50 (CC$H_3$), 2.27 (C$H_2$), 3.59 ($CO_2CH_3$), 6.96, 7.19, 7.43, 7.88 (phenyl).

### 2.7. Copolymerization of BSPPFCBPMA **3** and MMA

In a typical procedure, MMA (2.6 g, 26 mmol), BSPPFCBPMA **3** (0.52 g, 0.9 mmol), AIBN (25 mg, 0.15 mmol) and 2-butanone (2.8 mL) were added to a 10 mL pre-dried Schlenk flask and the solution was degassed by three cycles of freezing–pumping–thawing followed by immersing the flask into an oil bath preset at 60 °C to start the polymerization. The polymerization lasted 3 h and terminated by putting the flask into liquid nitrogen. Purified random copolymer **5a** (2.46 g) was obtained by repeated precipitation into a 10-fold excess of methanol and drying *in vacuo* at 40 °C. GPC: $M_n$ = 74,500, $M_w/M_n$ = 1.74. $^1$H NMR: $\delta$ (ppm): 0.86, 1.04 (C$H_3$ of PMMA), 1.24, 1.53 (C$H_3$ of PBSPPFCBPMA), 1.87, 1.94 (C$H_2$ of PMMA), 2.27 (C$H_2$ of PBSPPFCBPMA), 3.62 (COOC$H_3$ of PMMA), 6.96, 7.19, 7.43, 7.88 (phenyl). FT-IR (KBr): ν ($cm^{-1}$): 2995, 2951, 1731 (C═O), 1589, 1487, 1448, 1242, 1194, 1150 (S═O), 963 (PFCB).




**Scheme 2.** Preparation of *p*-((Benzenesulfonyl)trifluorovinyloxy)benzene.

## 3. Results and discussion

### 3.1. Design and synthesis of BSPPFCBPMA monomer

Sulfonyl-containing phenol, 4-(benzenesulfonyl)phenol, was first prepared *via* L-proline-promoted coupling of 4-iodophenol with sodium benzenesulfinate catalyzed by CuI according to the procedure developed by Ma et al. [19] as shown in Scheme 2. Next, *p*-benzenesulfonyl (trifluorovinyloxy)benzene was prepared by fluoroalkylation of 4-(benzenesulfonyl)phenol with $BrCF_2CF_2Br$ followed by Zn-mediated elimination with a high yield of 80.6% [1,2].

The obtained TFVE precursor was then cross-coupled with *p*-(trifluorovinyloxy)-anisole via a thermal $[2\pi + 2\pi]$ cycloaddition to afford cross-product **2**, *p*-(2-(*p*-benzenesulfonylphenyloxy)perfluorocyclobutyl)anisole (Scheme 3), which can be easily separated from the mixture of two homo-dimers and one cross-dimer by flash column chromatography [20].

This PFCB and sulfonyl-containing anisole was well characterized by $^1$H NMR and $^{19}$F NMR. Fig. 1A shows $^1$H NMR spectrum of cross-dimer **2**. The peak at 3.79 ppm was attributed to 3 protons of $-OCH_3$ and the signal of 4 protons of benzene ring adjacent to sulfonyl was found to locate at 7.93 ppm. The signals at 6.79 and 7.23 ppm belonged to 4 protons of benzene ring adjacent to PFCB unit. Typical multiplets of PFCB unit ranging from −128 to −134 ppm appeared in $^{19}$F NMR spectrum as shown in Fig. 1B. The existence of PFCB (962 $cm^{-1}$) and sulfonyl (1322 and 1157 $cm^{-1}$) units was also confirmed by FT-IR.

The demethylation of cross-dimer **2** was carried out by reacting with $BBr_3$ to give the corresponding phenol a quantitative yield. Finally, this phenol was esterified by methacryloyl chloride in dichloromethane to provide the targeted methacrylate monomer, BSPPFCBPMA **3**, with a high yield of 88.0%. The chemical structure of **3** was examined by FT-IR, $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR. The peaks at 962, 1447, 1502 and 1589 $cm^{-1}$ showed the successful incorporation of PFCB linkage. The presence of sulfonyl was verified by the sharp bands at 1157 and 1320 $cm^{-1}$. Characteristic signals of carbonyl and double bond appeared at 1737 and 1635 $cm^{-1}$, respectively. Typical resonance signals of double bond located at 5.78 and 6.35 ppm in $^1$H NMR spectrum of **3** (Fig. 2A). The peaks at 7.08, 7.17, 7.28, 7.51 and 7.94 ppm are attributed to 13 protons of benzene ring in PFCB aryl ether and sulfonyl units. The resonance signals at 127.6 and 135.5 ppm in $^{13}$C NMR spectrum of **3** (Fig. 2B) belonged to 2 carbons of double bond. The peak at 165.6 ppm corresponded to the carbon of carbonyl and multiple peaks ranging from 118.3 to 119.5 ppm came from 4 carbons of PFCB connection.

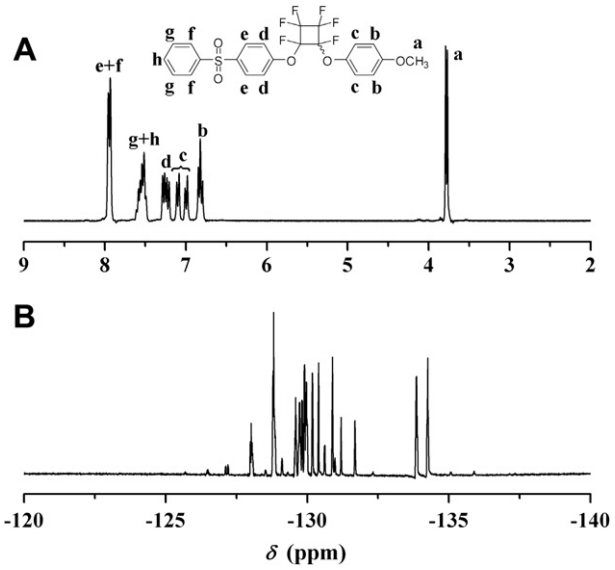


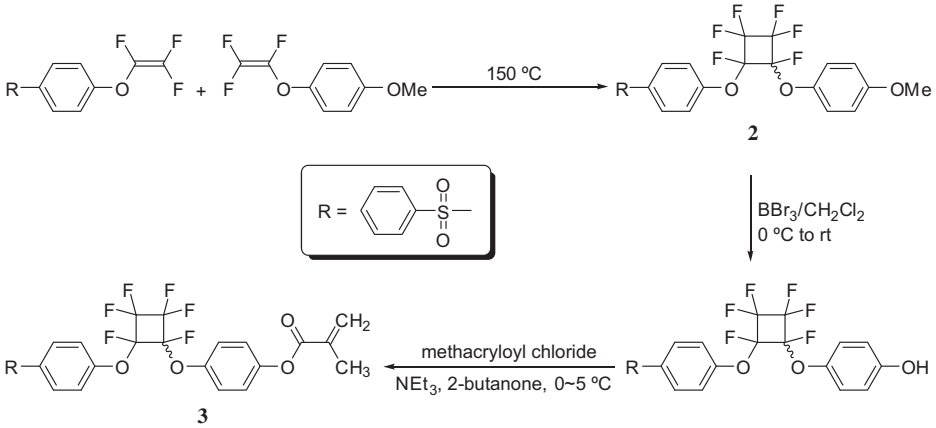

**Fig. 1.** $^1$H NMR (A) and $^{19}$F NMR (B) spectra of cross-dimer **2**.

Furthermore, a series of peaks between −127.8 and −133.7 ppm in $^{19}$F NMR spectrum of **3** also testified the existence of PFCB linkage. All these evidences confirmed the successful synthesis of BSPPFCBPMA **3**.

### 3.2. Homopolymerization of BSPPFCBPMA

Free radical homopolymerization of BSPPFCBPMA **3** was initiated by AIBN at 60 °C using 2-butanone as solvent [21,22] to give PBSPPFCBPMA **4** homopolymers with broad molecular weight distributions and the results are listed in Table 1.

These homopolymers were characterized by FT-IR, $^1$H NMR and $^{19}$F NMR. Fig. 3A shows FT-IR spectrum of PBSPPFCBPMA **4**. We can not find any trace of the signal of C=C stretching vibration at 1637 $cm^{-1}$ after homopolymerization compared to that of the monomer as shown in Fig. 3B. Moreover, the sharp peak of C=O stretching vibration shifted from 1737 $cm^{-1}$ to 1752 $cm^{-1}$ due to the disappearance of double bond. The signals at 962, 1157, 1322, 1447, 1502 and 1589 $cm^{-1}$ indicated the existence of PFCB linkage and sulfonyl. $^1$H NMR spectrum after homopolymerization demonstrated the disappearance of the signals of double bond (Fig. 4A). The peaks at 1.39, 1.50 and 2.27 ppm were attributed to 3




**Scheme 3.** Synthesis of **3** via cross-coupling, demethylation and esterification.

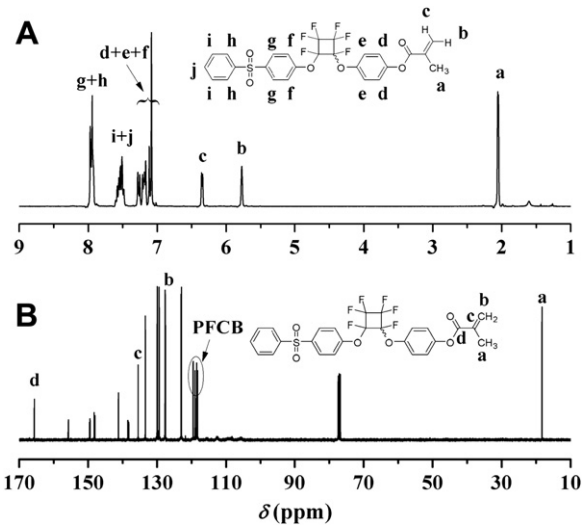



**Fig. 2.** $^{1}$H NMR (A) and $^{13}$C NMR (B) spectra of BSPPFCBPMA **3**.

protons of CC$H_3$ group and 2 protons of C$H_2$ group, respectively, which is similar to previous reports [23,24]. In addition, the presence of PFCB connection in homopolymer was also illustrated by the multiplets ranging from −128.2 to −133.9 ppm in $^{19}$F NMR spectrum.

ATRP of BSPPFCBPMA **3** was performed in solution [25–27] to provide well-defined PBSPPFCBPMA **4** homopolymers with narrow molecular weight distributions ($M_w/M_n < 1.40$). ATRP mechanism was confirmed by a minor peak at 3.59 ppm, which corresponded to 3 protons of COOC$H_3$ in ATRP initiation group. Furthermore, all PBSPPFCBPMA **4** homopolymers obtained by ATRP showed unimodal and symmetrical GPC curves (Fig. 5) with narrow molecular weight distributions ($M_w/M_n < 1.40$), which are characteristic of ATRP [28].

On the basis of the results of the molecular weights and the conversions of BSPPTCBPMA measured by $^{1}$H NMR, ATRP kinetics of BSPPFCBPMA was investigated (Fig. 6). Fig. 6A shows the conversion of BSPPFCBPMA increases with the time and a linear dependence of $\ln([M]_0/[M])$ on the time. The apparent polymerization rate is first order with respect to the concentration of BSPPFCBPMA, this indicating a constant number of propagating species during the polymerization of BSPPFCBPMA. This phenomenon accorded with the characteristic of ATRP [28]. The evolutions of the molecular weights and the molecular weight distributions of the homopolymers with the conversions of BSPPFCBPMA are shown in Fig. 6B. The molecular weights increased linearly with the conversions of BSPPFCBPMA and the molecular weight distributions kept narrow during the polymerization ($M_w/M_n < 1.40$). Thus, it is clear that BSPPFCBPMA **3** can be easily homopolymerized via ATRP and AIBN-initiated free radical polymerization to afford narrow- and broad-dispersed PBSPPFCBPMA **4** homopolymers, respectively.

**Table 1**
Free radical homopolymerization of BSPPFCBPMA **3**.[a]

| Sample | [**3**]: [AIBN] | Yield (%) | $M_n$[b] (KDa) | $M_w/M_n$[a] | $T_d$[c] (°C) |
|---|---|---|---|---|---|
| **4a** | 60:1 | 20.3 | 98.7 | 2.19 | 306 |
| **4b** | 50:1 | 81.3 | 150.4 | 2.13 | 327 |
| **4c** | 100:1 | 78.5 | 251.4 | 1.91 | 329 |
| **4d** | 150:1 | 75.1 | 260.0 | 1.98 | 357 |

[a] Initiated by AIBN at 60 °C in 2-butanone.
[b] Measured by GPC in THF at 35 °C.
[c] Measured by TGA in $N_2$ (heating rate: 10 °C/min).

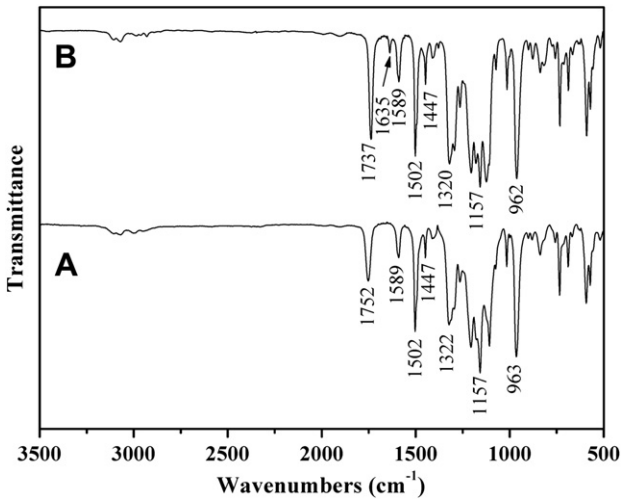



**Fig. 3.** FT-IR spectra of PBSPPFCBPMA **4** (A) and BSPPFCBPMA **3** (B).

### 3.3. Free radical copolymerization of BSPPFCBPMA with MMA

Random copolymerizations of BSPPFCBPMA **3** and MMA with different feed ratios were carried out in 2-butanone via AIBN-initiated free radical polymerization. The mole ratios of **3** in P(BSPPFCBPMA-*co*-MMA) **5** copolymers were calculated from the area ratios of the peaks of 13 aromatic protons of PBSPPFCBPMA between 6.90 ppm and 7.90 ppm to the peak of 3 protons of COOC$H_3$ of PMMA at 3.62 ppm in $^{1}$H NMR and the results are summarized in Table 2.

As we can see from Table 2, the mole ratios of BSPPFCBPMA **3** in P(BSPPFCBPMA-*co*-MMA) **5** copolymers raised with the increasing of the fractions of **3** in the feeding. FT-IR spectra of the copolymers (Fig. 7) also demonstrated this result, the intensity ratio of the peak of PFCB at 963 cm$^{-1}$ to the peak of carbonyl at 1731 cm$^{-1}$ increased in order of **5a**, **5b**, **5c** and **5d**, which is same as the sequence of heightening the fractions of **3** in the feeding. Moreover, the compositions of BSPPFCBPMA **3** in copolymers were all higher than its fractions in the feeding, indicating the higher copolymerization reactivity of **3** compared to that of MMA in the current copolymerization system.

### 3.4. Determination of monomer reactivity ratios

The monomer reactivity ratios of BSPPFCBPMA and MMA were determined by linear least-squares regression analysis according to

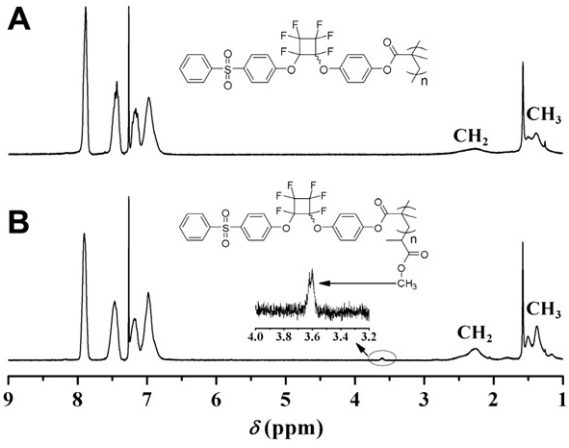



**Fig. 4.** $^{1}$H NMR spectra of PBSPPFCBPMA **4** via AIBN (A) and 2-MBP (B).

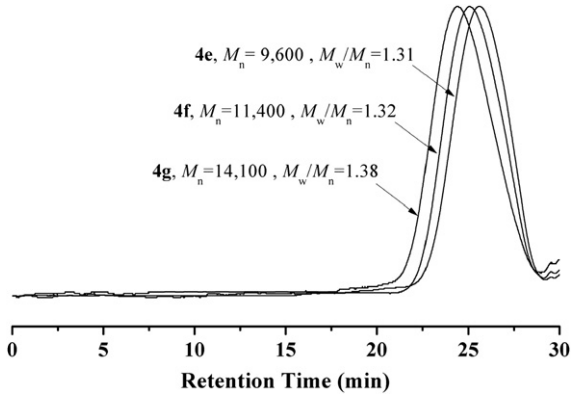



**Fig. 5.** GPC traces of PBSPPFCBPMA **4** obtained by ATRP.

Fineman–Ross (FR) [29] and Kelen–Tudos (FT) [30] equations via the data listed in Table 3. The FR equation is given as below:

$$G = r_1 H - r_2 (\mathrm{FR})$$

where $r_1$ and $r_2$ correspond to the monomer reactivity ratios of BSPPFCBPMA and MMA, respectively. The parameters $G$ and $H$ are defined as follows:

$$G = F(f-1)/f \text{ and } H = F^2/f$$

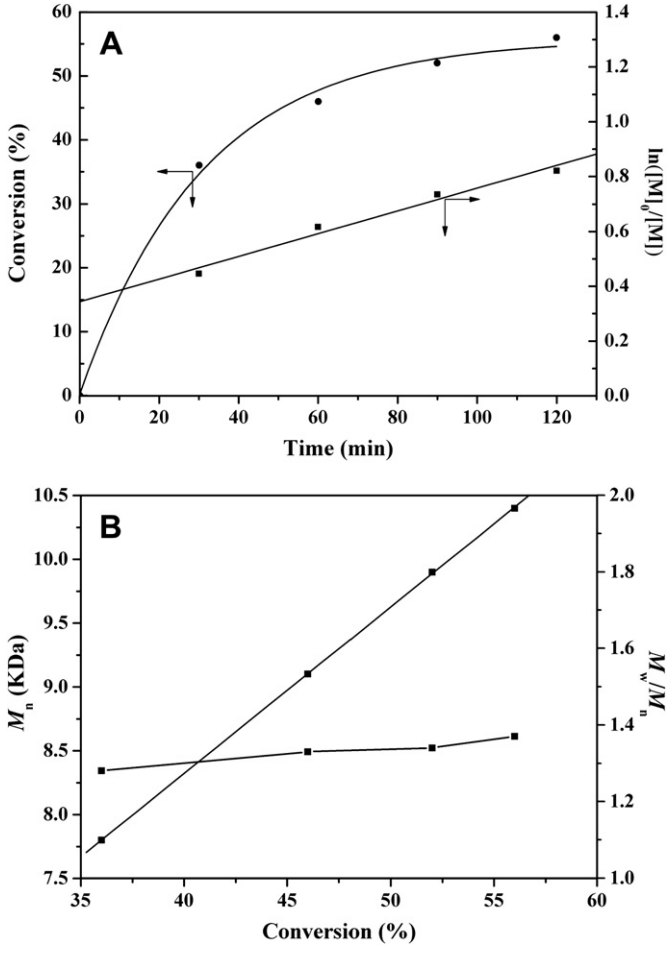



**Fig. 6.** Kinetic plot (A) and the dependence of $M_n$ and $M_w/M_n$ on the conversion of the monomer for solution ATRP of BSPPFCBPMA **3** initiated by 2-MBP.

**Table 2**
Copolymerization of BSPPFCBPMA **3** and MMA.[a]

| Sample | [**3**]:[MMA] (w/w) | Mole ratio of **3** | | $M_n$ (KDa)[c] | $M_w/M_n$[c] | $T_d$[d] (°C) |
|---|---|---|---|---|---|---|
| | | Feed | Found[b] | | | |
| **5a** | 1:5 | 3.4 | 3.8 | 74.5 | 1.74 | 298 |
| **5b** | 2:5 | 6.5 | 8.8 | 74.6 | 1.76 | 307 |
| **5c** | 3:5 | 9.5 | 11.1 | 81.6 | 1.78 | 314 |
| **5d** | 4:5 | 12.2 | 14.3 | 93.2 | 1.77 | 317 |
| **5e**[e] | | 10 | 11.5 | 15.1 | 1.43 | 293 |

[a] Initiated by AIBN at 60 °C in 2-butanone.
[b] Calculated from $^1$H NMR.
[c] Measured by GPC in THF at 35 °C.
[d] Measured by TGA in $N_2$ (heating rate: 10 °C/min).
[e] [**3**]:[MMA] = 1:9, ([**3**] + [MMA]):[2-MBP]:[CuBr]:[PMDETA] = 100:1:2:4.

with $F = M_1/M_2$ and $f = m_1/m_2$, where $M_1$ and $M_2$ are the monomer molar fractions in the feed and $m_1$ and $m_2$ are the copolymer molar compositions.

The reactivity ratio can also be obtained with KT method, which is based on the following equation:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \quad (\mathrm{FT})$$

where $\eta$ and $\xi$ are the functions of the parameters $G$ and $H$, and $\alpha$ is a constant equal to $(H_{max}H_{min})^{1/2}$, $H_{max}$ and $H_{min}$ being the lowest and highest $H$ values, respectively.

$$\eta = G/(\alpha + H) \text{ and } \xi = H/(\alpha + H)$$

The linear extrapolation plots concerning the previous reported methods are depicted in Fig. 8. Both plots afforded the similar values of the reactivity ratios. The reactivity ratios of BSPPFCBPMA ($r_1$) and MMA ($r_2$) are 1.2436 and 0.8171 inferred with FR technique, and 1.2279 and 0.8023 obtained by KT method.

The higher $r_1$ value of BSPPFCBPMA confirmed the higher reactivity of BSPPFCBPMA compared to that of MMA, and the copolymer sequence was statistical in structure with more BSPPFCBPMA units.

### 3.5. Thermal properties

One eminent property of PFCB-based polymer is its high thermal resistance. Taking advantage of this thermo-stability, some

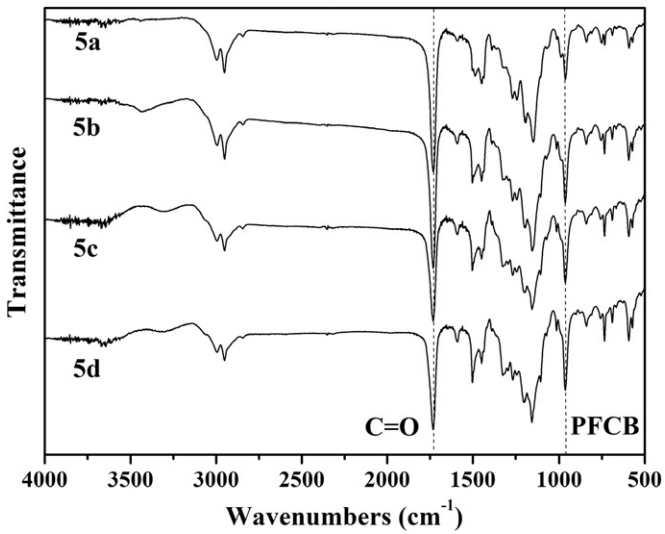



**Fig. 7.** FT-IR spectra of P(BSPPFCBPMA-*co*-MMA) **5**.

**Table 3**
FR and KT parameters of BSPPFCBPMA-MMA system.[a]

| $[M_1]$:$[M_2]$ | $F$ | $f$ | $G$ | $H$ | $\eta$ | $\xi$ |
|---|---|---|---|---|---|---|
| 1:9 | 0.111 | 0.134 | −0.720 | 0.092 | −0.791 | 0.101 |
| 2:8 | 0.250 | 0.335 | −0.496 | 0.186 | −0.493 | 0.1860 |
| 3:7 | 0.428 | 0.525 | −0.388 | 0.350 | −0.332 | 0.29971 |
| 5:5 | 1.000 | 1.176 | 0.150 | 0.850 | 0.090 | 0.510 |
| 6:4 | 1.500 | 1.850 | 0.689 | 1.216 | 0.340 | 0.5980 |
| 7:3 | 2.333 | 2.920 | 1.533 | 1.866 | 0.571 | 0.695 |
| 9:1 | 9.000 | 11.180 | 8.195 | 7.245 | 1.016 | 0.899 |

[a] Reaction conditions: ([**3**] + [MMA]):[AIBN] = 50:1; solvent: 2-butanone; $[M_1]$ and $[M_2]$ represent the concentrations of BSPPFCBPMA and MMA, respectively; conversion <10%; $\alpha = 0.814$ for poly(BSPPFCBPMA-*co*-MMA) system.

attempts were devoted to prepare new functional materials with PFCB group to improve the thermal stability [31,32]. Therefore, the above-synthesized polymethacrylate homo and copolymers containing PFCB and sulfonyl groups can be expected to show good thermal resistance.

Thermal decompositions of PBSPPFCBPMA **4** and P(BSPPFCBPMA-*co*-MMA) **5** were investigated by TGA in $N_2$ with a heating rate of 10 °C/min and typical TG (thermogravimetry) and DTG (derivative thermogravimetry) curves are shown in Figs. 9 and 10 respectively. The decomposition temperature ($T_d$) of PBSPPFCBPMA **4** homopolymers ranged from 306 °C to 357 °C as listed in Table 1 and the values of $T_d$ raised remarkably with the increasing of the molecular weights of the homopolymers (Fig. 7) as usual polymers. In general, the thermal degradation of radically prepared polymethacrylate undergoes three steps including the scission of head-to-head linkages (around 165 °C), the chain-end

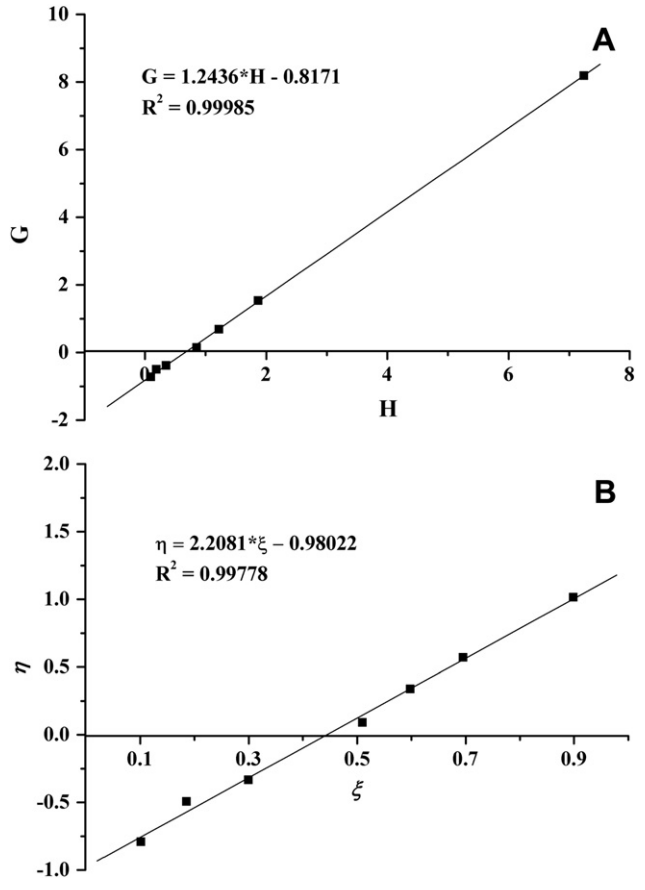



**Fig. 8.** FR (A) and KT (B) plots for determining the reactivity ratios in the copolymerization of BSPPFCBPMA ($M_1$) and MMA ($M_2$).

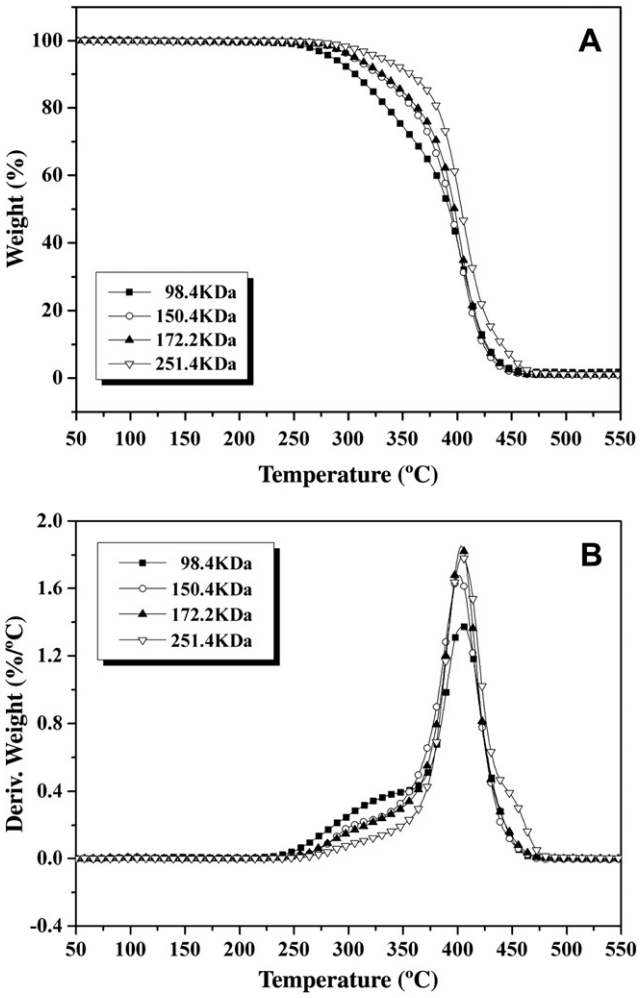



**Fig. 9.** TG (A) and DTG (B) curves of PBSPPFCBPMA **4** with different $M_n$s.

initiation from the vinylidene ends (around 270 °C) and random scission within the chain (around 360 °C) [13,33]. As shown in Fig. 9B, the pyrolysis of PBSPPFCBPMA **4** homopolymer prepared by AIBN-initiated radical polymerization processed a two-stage degradation pattern occurred around 308 °C–404 °C, which may originate from the end-initiated degradation and random scission [34,35].

This result can be explained that incorporation of bulky pendent group containing PFCB and sulfonyl greatly inhibited the coupling reaction of propagating radicals which resulted in a head-to-head linkage within the chain [36–38]. Moreover, it is notable that with the increasing of the molecular weights of the homopolymers, the weight loss percentage of PBSPFCBPMAs at the first decomposition stage decreased compare to the increasing at the second stage, which may be attributed to the $T_d$s increased with increasing $M_n$ of the homopolymers.

The incorporation of PBSPPFCBPMA segment into PMMA domain shows a significant effect on elevating the decomposition temperature of the copolymers (Table 2). The thermolysis of radical-polymerized P(BSPPFCBPMA-*co*-MMA) **5** copolymers also shows a two-step degradation process around about 305 °C–392 °C similar to the homopolymer (Fig. 10B), which corresponding respectively to the end-initiated degradation and random scission [34,35]. The absence of head-to-head linkages could be as a result of the incorporation of bulky PBSPPFCBPMA segment which greatly inhibited the coupling reaction of propagating radicals and thereby

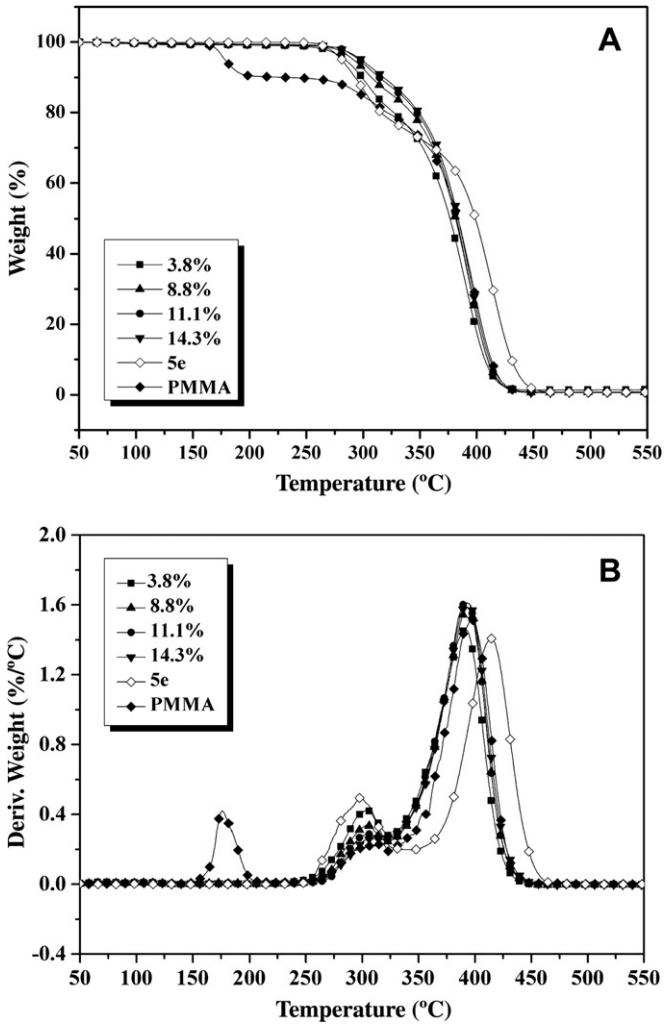



**Fig. 10.** TG (A) and DTG (B) curves of P(BSPPFCBPMA-*co*-MMA) **5** with different compositions and PMMA ($M_n = 35{,}000$, $M_w/M_n = 1.64$).

reduced the least stable step to stabilize PMMA [36–39]. The copolymer **5e** synthesized by ATRP shows a higher temperature of the second major weight loss, this indicating the higher 'tacticity' along the main chain [40,41]. The thermal stability of the copolymers is also greatly improved upon increasing the content of BSPPFCBPMA unit. While raising the mole ratio of BSPPFCBPMA from 3.8% to 14.3%, the values of $T_d$ increased from 298 °C to 317 °C; such an improved stability is likely to be associated with a decreasing fraction of end-initiated degradation. This implies that we can introduce this type of monomer to different vinyl polymer for bettering its thermal stability in the future.

## 4. Conclusion

The present study provides a specific case of preparing PFCB-based polymers via usual free radical polymerization. Compared to traditional PFCB aryl ether polymers, this kind of PFCB-containing polymethacrylate can be prepared by AIBN-initiated free radical polymerization or ATRP under mild conditions. These homopolymers exhibited excellent thermal stability and the decomposition temperature rose with the increasing of molecular weights. Incorporation of BSPPFCBPMA unit into PMMA domain shows a significant effect on the elevation of the decomposition temperature of the copolymers and their thermo-stabilities increase while raising the contents of BSPPFCBPMA. This is the first example of direct copolymerization of PFCB units with usual vinyl monomers.

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