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Synthesis and characterization of novel fluoropolymers containing sulfonyl and perfluorocyclobutyl units

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Abstract

A novel sulfonyl-containing monomer, 4,4′-sulfonyl-bis(trifluorovinyloxy)biphenyl, and the resulting fluoropolymers with good thermal stability have been prepared. The monomer was synthesized by two steps using 4,4′-sulfonyldiphenol as starting material and characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and element analysis in detail. Fluoropolymers containing sulfonyl and perfluorocyclobutyl units were prepared by different polymerization methods. A series of fluoropolymers with higher molecular weights were obtained by solution polymerization in diphenyl ether. The molecular weight is dependent on the polymerization time, polymerization temperature and the concentration of the monomer. The resulting polymers show excellent solubility in conventional solvents and good thermal stability with a high decomposition temperature about 500 °C measured by TGA.

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Keywords: Fluoropolymer; Perfluorocyclobutane; Step-growth addition polymerization

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1. Introduction

Fluoropolymers designed for applications of high performance have taken on great significance in recent years, as the benefits of working with fluoropolymers obtained by the incorporation of fluorocarbon functionality including increased thermal/oxidative stability, optical transparency, solvent compatibility, and environmental stability [1]. However, the low processability limited the use of the fluoropolymers [2]. One recent advance in the incorporation of fluorine into polymers with high performance involved the cyclopolymerization of aryl trifluorovinyl ether monomers to give the fluoropolymers containing perfluorocyclobutane (PFCB) linkage which were first synthesized by Dow Chemical [3].

PFCB aromatic ether polymers are a unique class of fluorinated polymer and they are generally synthesized by step-growth addition polymerization in bulk or solution above 150 °C without initiator. Compared with the usual perfluoropolymers, PFCB polymers have the conventional properties such as low dielectric constant, low moisture absorption, low surface energy, high thermal/oxidative stability and chemical resistance, and they also possess many other advantages including optical transparency, improved processability and thermal mechanical properties [4–6].

Recently, many efforts focused on the development of a series of fluorinated polymers which utilize the thermal cyclopolymerization of aryl trifluorovinyl ether (TFVE) to give a variety of polymers containing PFCB aromatic ether linkage [7–9]. From commercially available raw materials such as 1,3-dihydroxybenzene, 4,4′-biphenol, 2,2-bis(*p*-hydroxyphenyl)perfluoropropane, monomers containing two trifluorovinyl groups were synthesized and polymerized by heating to form different PFCB thermoplastic polymers. Furthermore, thermoset PFCB polymers were prepared from the monomers containing three trifluorovinyl groups which were also synthesized from 1,3,5-trihydroxybenzene and 1,1,1-tri(4-hydroxyphenyl)ethane. PFCB strategy combined the flexible, yet thermally robust, aromatic ethers with

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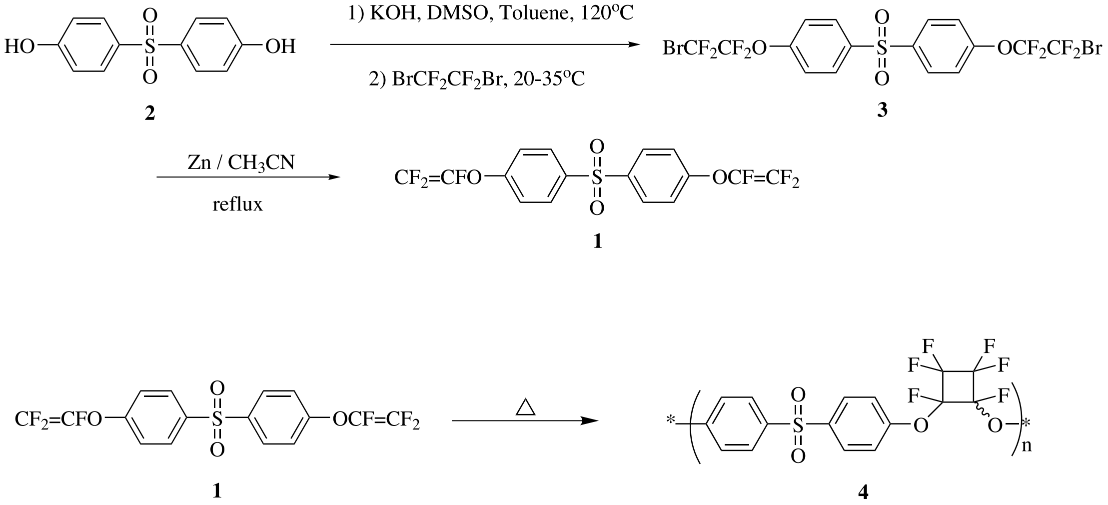


Scheme 1. Synthesis of monomer **1** and PFCB polymers **4**.

fluorocarbon linkage, thereby providing fluoropolymers which are easily processed from solution.

In this paper, we reported the synthesis of a novel sulfonyl-containing trifluorovinyl monomer, 4,4′-sulfonyl-bis(trifluorovinyloxy)biphenyl (**1**) via 4,4′-sulfonyldiphenol (Scheme 1).

A series of PFCB polymers (**4**) were prepared by heating (Scheme 1). All the polymers synthesized from monomer **1** were characterized by FT-IR, GPC, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, DSC and TGA in detail, show better thermal stability compared with PFCB polymers (**8**) which were obtained from the polymerization of monomer **7** just without sulfonyl group.

2. Experimental

2.1. Materials

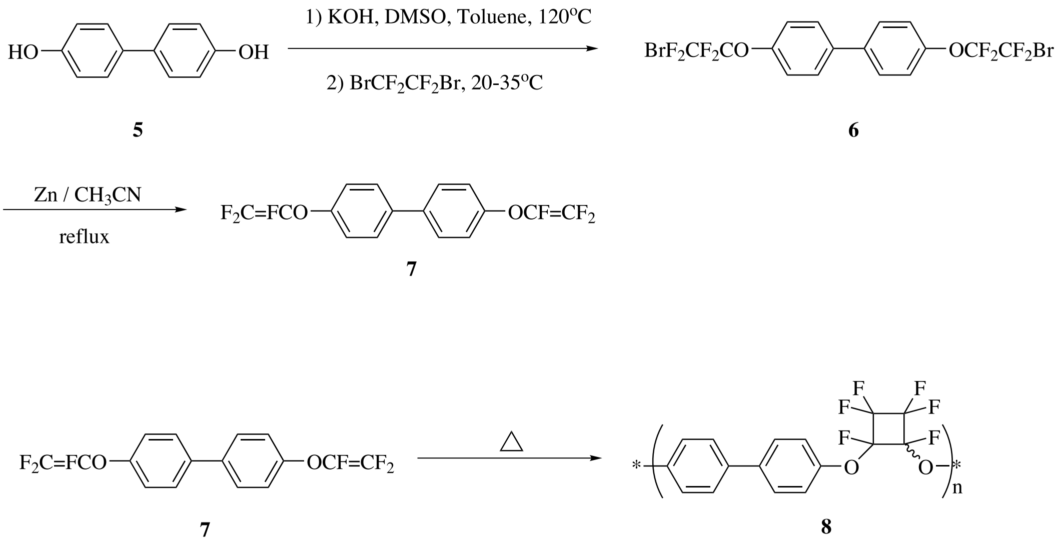
4,4′-Biphenol (97%) and 4,4′-sulfonyldiphenol (98%) were purchased from Aldrich and purified by recrystallization before use. 1,2-Dibromotetrafluoroethane was prepared by condensing equimolar amounts of bromine and tetrafluoroethylene at −195 °C followed by warming up to 22 °C [10]. Granular zinc was activated by washing in 0.1 N hydrochloric acid (HCl) followed by drying in a vacuum oven at 140 °C for 10 h. All other reagents and solvent were used as received.

2.2. Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with 4 cm^{-1} resolution. All ^{1}H NMR and ^{13}C NMR were performed on a Varian Mercury 300 spectrometer (300 MHz) with TMS (^{1}H NMR) and $CDCl_3$ (^{13}C NMR) as internal standard. ^{19}F NMR was collected on a Bruker AM-300 spectrometer using trifluoroacetic acid as external standard. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual λ absorbance detector and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8×300 mm). GPC measurements were carried out at 35 °C using tetrahydrofuran (THF) as eluent with a 1.0 mL/min flow rate. The system was calibrated with polystyrene standards. Elemental analysis was carried out on a Carlo-Erba1106 system. DSC and TGA measurements were run with a Perkin–Elmer Pyris 1 system with a heating rate of 10 °C/min under N_2 atmosphere. The glass transition temperature (T_g) was recorded from the second heating process after a quick cooling. The value was determined form the midpoint of the C_p curve.

2.3. Synthesis of 4,4′-sulfonyl-bis(2-bromotetrafluoroethoxy)biphenyl 3

To a 500 mL dried three-neck round-bottom flask fitted with a condenser, a thermometer and a water separator, 4,4′-sulfonyldiphenol **2** (25.03 g, 0.1 mol), potassium hydroxide (KOH) (11.22 g, 0.2 mol), dimethyl sulfoxide (DMSO) (180 mL) and toluene (45 mL) were added under N_2 atmosphere. The solution was heated to 120 °C to remove water until no water existed in the separator, then the flask was cooled to 20 °C and 1,2-dibromotetrafluoroethene (57.16 g, 0.22 mol) was added. The solution was stirred at the temperature between 20–25 °C for 8 h and then 35 °C for 8 h. Finally, 100 mL water was added to terminate the reaction. The organic layer was separated and extracted by dichloromethane (100 mL×3), washed by water and brine, and then dried over magnesium sulfate ($MgSO_4$). 4,4′-Sulfonyl-bis(2-bromotetrafluoroethoxy)biphenyl **3** (24.91 g, 41.0%) was obtained by silica column chromatography using petroleum ether (60–90 °C) and ethyl acetate



Scheme 2. Synthesis of monomer **7** and PFCB polymers **8**.

(v:v = 12:1) as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.38 (4H, d, J = 8.7 Hz), 8.01 (4H, d, J = 8.7 Hz). ^{19}F NMR (282 Hz, $CDCl_3$): δ (ppm): −68.3 (2F, s), −86.1 (2F, s). FT-IR (KBr): ν (cm^{-1}) 3110, 1590, 1494, 1336, 1217, 1157, 936, 843. Anal. Calcd for $C_{16}H_8F_8Br_2SO_4$: C, 31.60%; H, 1.33%. Found: C, 31.63%; H, 1.31%. ESI-MS (m/z): calcd 608.1; found 608.2.

2.4. Synthesis of 4,4′-sulfonyl-bis(trifluorovinyloxy) biphenyl *1*

Dry acetonitrile (160 mL), newly activated zinc (4.84 g, 0.074 mol) and **3** (22.50 g, 0.037 mol) were added to a 250 mL three-neck round-bottom flask under N_2 atmosphere. The reaction mixture was stirred for 12 h under reflux. After the flask was cooled to room temperature, acetonitrile was filtered and the salt was washed by dichloromethane (150 mL × 3) to extract the product. The final product we desired, monomer **1**, 4,4′-sulfonyl-bis(trifluorovinyloxy)biphenyl (12.14 g, 80.0%) was obtained by silica column chromatography using petroleum ether (60–90 °C) and ethyl acetate (v:v = 12:1) as eluent. The monomer **1** was purified by recrystallization in petroleum ether. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.21 (4H, d, J = 8.8 Hz), 7.98 (4H, d, J = 8.8 Hz). FT-IR (KBr): ν (cm^{-1}) 3104, 1834 (–OCF=CF$_2$–), 1591, 1492, 1325, 1274, 1142, 837. Anal. Calcd for $C_{16}H_8F_6SO_4$: C, 46.84%; H, 1.97%. Found: C, 46.88%; H, 1.95%. ESI-MS (m/z): calcd 410.3; found 410.2.

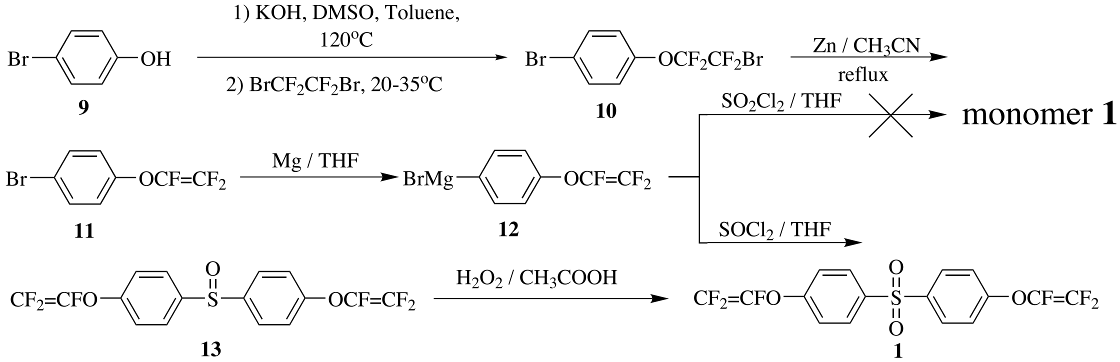
2.5. Synthesis of 4,4′-bis(trifluorovinyloxy)biphenyl *7*

Monomer **7** was synthesized according to Scheme 2. The procedure was similar to those of previous literature [11]. The yield is 42.8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.19 (d, J = 9.0 Hz, 4H), 7.55 (d, J = 8.7 Hz, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −119.8 (dd, 2F), −126.8 (dd, 2F), −134.3 (dd, 2F). Anal. Calcd for $C_{16}H_8F_6O_2$: C, 55.50%; H, 2.33%. Found: C, 55.47%; H, 2.30%. ESI-MS (m/z): calcd 346.2; found 346.3.

2.6. Synthesis of thionyl compound *13* and following oxidation to form sulfonyl monomer *1*

A 100 mL THF solution of 16.64 g Grignard's reagent **12** (0.06 mol), which was synthesized according to previous literature [7], was added to a 250 mL three-neck round-bottom flask containing 3.56 g anhydrous $SOCl_2$ (0.03 mol) in 25 mL THF under N_2 atmosphere. The reaction lasted for 10 h under reflux and 50 mL water was added to quench the reaction. The organic layer was separated and extracted by dichloromethane (50 mL × 3), followed by drying over magnesium sulfate ($MgSO_4$). 4,4′-Thionyl-bis(trifluorovinyloxy)biphenyl **13** (4.37 g, 36.9%) was obtained by silica column chromatography using petroleum ether (60–90 °C) and ethyl acetate (v:v = 8:1) as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.19 (d, J = 8.7 Hz, 4H), 7.67 (d, J = 8.7 Hz, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm): −118.4 (dd, 2F), −125.0 (dd, 2F), −133.8 (dd, 2F). Anal. Calcd for $C_{16}H_8F_6SO_3$: C, 48.74%; H, 2.05%. Found: C, 48.77%; H, 2.07%. ESI-MS (m/z): calcd 394.3; found 394.2.

4,4′-Thionyl-bis(trifluorovinyloxy)biphenyl **13** (3.94 g, 0.01 mol) was added to a 100 mL dried three-neck round-bottom flask containing 1.20 g 30% H_2O_2 in 40 mL acetic acid. The reaction lasted for 10 h under reflux. After cooling, 40 mL water was added for dilution. The organic layer was separated and extracted by dichloromethane (30 mL × 3), followed by drying over magnesium sulfate ($MgSO_4$). Monomer **1** (3.65 g, 89.0%) was obtained by



Scheme 3. Synthesis of monomer **1** using *p*-bromophenol as starting material.

silica column chromatography using petroleum ether (60–90 °C) and ethyl acetate (v:v = 12:1) as eluent.

2.7. Bulk polymerization

A series of bulk polymerization of monomer **1** were performed to synthesize PFCB polymers **4**. A typical procedure of bulk polymerization is listed as follows: Monomer **1** (0.50 g) was added to a pre-dried 10 mL Schlenk flask. The flask was pumped and filled back with N_2 for 3 times. Then the flask was placed into an oil bath set at 250 °C. The polymerization lasted for 24 h. The flask was cooled by liquid nitrogen to terminate the polymerization and 5 mL chloroform was added to dissolve the polymer. PFCB polymer **4** was precipitated by acidic methanol. After filtration, the solid was dried overnight to give 0.45 g polymer **4** (yield: 90.1%), $M_n = 25{,}300$, $M_w/M_n = 2.45$.

2.8. Solution polymerization

A series of solution polymerization of monomer **1** and **7** were performed to synthesize PFCB polymers **4** and **8** using diphenyl ether as solvent. A typical procedure of solution polymerization is listed as follows: Monomer **1** (0.50 g) and diphenyl ether (2.00 mL) were added to a pre-dried 10 mL Schlenk flask. The flask was stirred until all solids dissolved. The flask was degassed for three cycles of freezing-pumping-thawing at −196 °C (77 K). Then the flask was placed into an oil bath set at 250 °C. The polymerization lasted for 24 h. The flask was cooled by liquid nitrogen to terminate the polymerization and 5 mL chloroform was added for dilution. PFCB polymer **4** was precipitated by methanol. After filtration, the solid was dried overnight to give 0.38 g polymer **4** (yield: 76.1%), $M_n = 48{,}500$, $M_w/M_n = 2.27$.

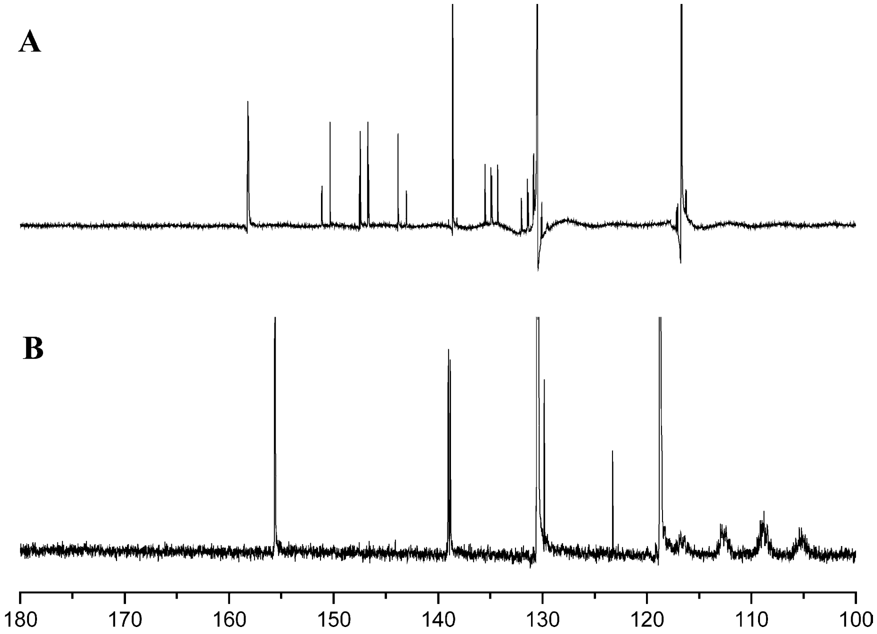


Fig. 1. ^{13}C NMR of Monomer **1** (A) and polymer **4** (B) in $CDCl_3$.

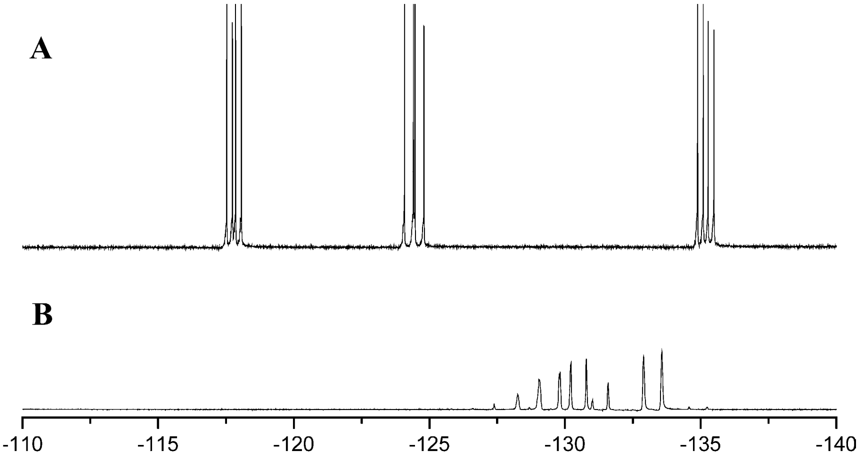


Fig. 2. ^{19}F NMR of monomer **1** (A) and polymer **4** (B) in $CDCl_3$.

3. Results and discussion

3.1. Synthesis and characterization of monomer *1* and PFCB polymer *4*

Traditional TFVE monomers were prepared in two steps from commercially available phenolic precursors via fluoroalkylation with $BrCF_2CF_2Br$ followed by Zn mediated elimination [12,13]. At first, we tried another route to synthesize monomer **1** (Scheme 3).

We used *p*-bromophenol as starting material and –OH group was transformed into $–OCF{=}CF_2$ group after 2 steps [7]. Next, we tried to synthesize monomer **1** by reacting Grignard's reagent **12** with SO_2Cl_2 according to previous literature [14], but we did not get monomer **1**. So we run the reaction of Grignard's reagent **12** with $SOCl_2$ to obtain compound **13** with 37% yield [15]. Then, compound **13** was oxidized by H_2O_2 in acetic acid to give monomer **1** with 89% yield [16]. By this way, we can synthesize monomer **1** we desired. But we took 5 steps to get the monomer with the disadvantage of the low yield of the reaction of Grignard's reagent **12** with $SOCl_2$.

So we performed the synthesis of monomer **1** by the conventional way and after 2 steps we obtained the new monomer with 32.8% total yield. As shown in Fig. 1(A), we can find the typical ^{13}C NMR signals of monomer **1**. The signals between 134.0 and 135.5 ppm attributed to the unit of $–OCF{=}$ and the signals between 143.0 and 151.5 ppm attributed to the unit of $=CF_2$. Fig. 2(A) depicts its ^{19}F NMR spectrum in $CDCl_3$, the resonance signals of $–OCF{=}CF_2$

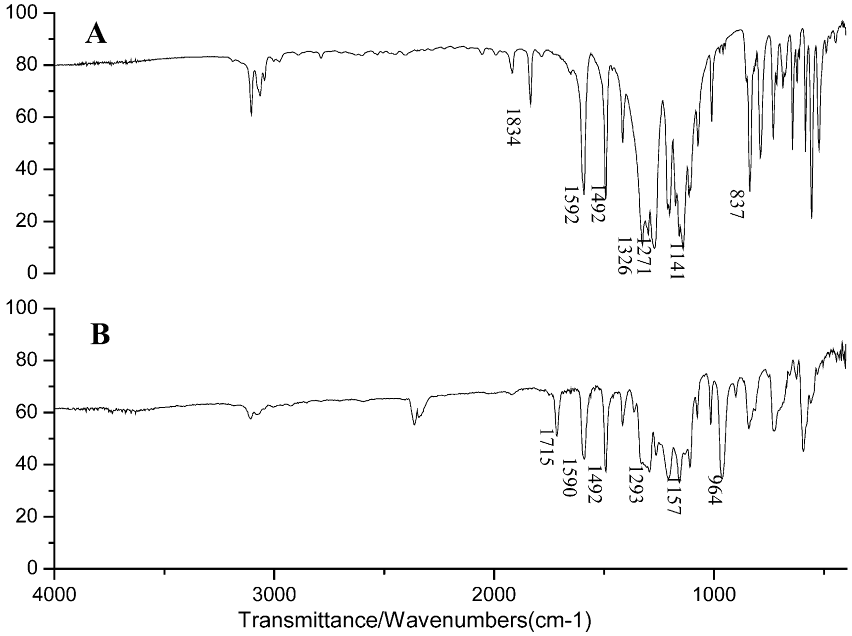


Fig. 3. FT-IR of monomer **1** (A) and polymer **4** (B).

Table 1
Synthesis of polymers **4** by bulk polymerization

Run	Time (h)	Temperature (°C)	M_n (g/mol)[a]	M_w/M_n[a]	Yield (%)
1	12	150	5400	2.33	73.3
2	12	200	11,700	2.42	79.4
3	12	250	17,600	2.39	83.2
4	24	150	10,800	2.41	80.6
5	24	200	18,900	2.47	85.2
6	24	250	25,300	2.45	90.1

[a] Measured by GPC under 35 °C.

group appeared at −117.6 ppm (dd, 2F), −124.3 ppm (dd, 2F) and −134.3 ppm (dd, 2F).

Fig. 3(A) displays the FT-IR spectrum of monomer **1**. The sharp band at 1834 cm^{-1} is the typical signal of trifluorovinyl ether group, also the strong bands at 1141 and 1271 cm^{-1} attributed to sulfonyl group.

PFCB polymer **4** synthesized from monomer **1** is also characterized by ^{13}C NMR, ^{19}F NMR and FT-IR. In Fig. 1(B), we cannot find any trace of trifluorovinyl ether group of monomer **1** in ^{13}C NMR spectrum in $CDCl_3$, instead of 4 weak broad peaks between 105.0 and 117.0 ppm which are the typical signals of perfluorocyclobutyl. Fig. 2(B) shows ^{19}F NMR spectrum of PFCB polymer **4** in $CDCl_3$, the resonance signals of $-OCF{=}CF_2$ group disappeared, a series of new peaks between −128.3 and −133.7 ppm appeared which denoted perfluorocyclobutyl unit in polymer. Fig. 3(B) displays the FT-IR spectrum of PFCB polymer **4**. The sharp band at 1834 cm^{-1} disappeared and a new strong band at 964 cm^{-1} appeared which represented perfluorocyclobutyl unit in polymer.

All these evidence confirmed the structure of monomer **1** and PFCB polymer **4**. Therefore, PFCB polymer **4** was successfully prepared by the polymerization of monomer **1**.

3.2. Effect of polymerization conditions on molecular weight

We first performed a series of bulk polymerization of monomer **1**. The data of yield, molecular weight and molecular weight distribution are presented in Table 1. It is obvious that the yield and molecular weight increase with lifting of polymerization time and temperature. This phenomenon can be explained by the polymerization mechanism: The polymerization of monomer **1** followed by stepwise polymerization mechanism to obtain PFCB polymer **4** through intra-molecular [2+2] cycloaddition of trifluorovinyl ether group [17] one by one. So when the polymerization time extended, more and more monomer molecules took part in the polymerization to result in the increasing of the yield and molecular weight; when the polymerization temperature is lifted, the reaction of cycloaddition was accelerated to increase the yield and molecular weight. But even with a high yield (90.1%), the molecular weight of polymer **4** is only 25,300 due to the high viscosity of bulk polymerization to prevent from the diffusing of polymers with low molecular weight to react into polymers with higher molecular weight.

To get polymer **4** with higher molecular weight for better application, a series of solution polymerization of monomer **1** were run using diphenyl ether as solvent due to its high boiling point and good solubility of monomer **1** and polymer **4**. Table 2 listed the data of yield, molecular weight and molecular weight distribution. It is evident that the molecular weight increases with the lifting of the concentration of monomer. Also the yield increases with the lifting of monomer concentration because the reaction of cycloaddition was accelerated by the higher monomer concentration. The molecular weights of polymer **4** synthesized by solution polymerization are much higher than those synthesized by bulk polymerization. It can be explained that the good solubility of diphenyl ether makes the diffusion of polymers with low molecular weight easy to react into polymers with higher molecular weight. The

Table 2
Synthesis of polymers **4** by solution polymerization

Run	Monomer **1** (g)	Solvent (mL)	M_n (g/mol)[a]	M_w/M_n[a]	Yield (%)
7	0.50	0.30	164,200	2.51	91.5
8	0.50	0.50	132,200	2.39	87.6
9	0.50	0.70	114,400	2.20	82.5
10	0.50	1.00	85,300	2.35	79.9
11	0.50	2.00	48,500	2.27	76.1
12	0.50	4.00	24,600	2.19	72.4
13	0.50	10.00	6300	2.32	68.9

Polymerization time, 24 h; polymerization temperature, 250 °C.

[a] Measured by GPC under 35 °C.

Table 3
Synthesis of polymers **4** with different conditions by solution polymerization

Run	Time (h)	Temperature (°C)	M_n (g/mol)[a]	M_w/M_n[a]	Yield (%)
14	12	150	8900	2.33	63.3
15	12	200	16,200	2.42	67.9
16	12	250	21,100	2.40	72.8
17	24	150	15,800	2.41	68.6
18	24	200	26,900	2.47	71.9
19	24	250	48,500	2.27	76.1

Polymerization condition: monomer **1**: 0.50 g; solvent: 2.00 mL.
[a] Measured by GPC under 35 °C.

Table 4
Thermal properties of polymers **4** with different molecular weights

M_n (g/mol)[a]	M_w/M_n[a]	T_g (°C)[b]	T_d (°C)[c]
5400	2.33	150.2	494.0
21,100	2.40	154.6	497.0
48,500	2.27	158.0	501.8
85,300	2.35	159.9	506.7
114,400	2.20	162.2	510.8
132,200	2.39	165.3	515.4
164,200	2.51	166.1	520.0

[a] Measured by GPC under 35 °C.
[b] Measured by DSC at 10 °C/min under N_2.
[c] Measured by TGA at 10 °C/min under N_2.

Table 5
Thermal properties of polymers **8** with different molecular weights

M_n (g/mol)[a]	M_w/M_n[a]	T_g (°C)[b]	T_d (°C)[c]
7800	1.54	155.6	427.6
20,000	1.62	157.0	431.8
54,000	1.95	159.7	435.4
107,000	2.03	162.3	442.8

[a] Measured by GPC under 35 °C.
[b] Measured by DSC at 10 °C/min under N_2.
[c] Measured by TGA at 10 °C/min under N_2.

effects of polymerization time and temperature are same as those of bulk polymerization (Table 3).

3.3. Thermal properties

Thermal stability is one of eminent properties of fluoropolymer. The high decomposition temperature T_d around 500 °C indicates that PFCB polymer **4** containing sulfonyl unit has excellent thermal stability (Table 4). From the data listed in Table 4, we can find that the glass transition temperature T_g and decomposition temperature T_d increase with the increasing of the molecular weight of polymer **4** as usual polymer. Compared with PFCB polymer **8**, the glass transition temperature T_g of PFCB polymer **4** is similar with that of PFCB polymer **8** (Table 5), but the decomposition temperature T_d of PFCB polymer **4** is much higher than that of PFCB polymer **8** (about 430 °C). That means the introduction of the sulfonyl group has greatly increased the thermal stability of PFCB polymer **4** which may be explained by the thermal decomposition mechanism of these types of polymers [18]. This implies that we can introduce sulfonyl group to different polymer for bettering its thermal stability in the future.

3.4. Solubility tests

PFCB polymers **4** with high molecular weights were performed with solubility tests in 4 conventional solvents with low boiling point: Tetrahydrofuran, chloroform, dichloromethane, and acetone. The results indicated that PFCB polymer **4** containing sulfonyl group exhibits excellent solubility in above 4 solvents.

4. Conclusion

A series of sulfonyl-containing PFCB polymers **4** were synthesized by bulk and solution polymerization of a novel monomer, 4,4′-sulfonyl-bis(trifluorovinyloxy)biphenyl. When the polymerization time and temperature increased, polymer yield and molecular weight also increased. Polymers with higher molecular weights can only be synthesized by solution polymerization due to the easier diffusion of monomer. The resulting PFCB polymer **4** showed good solubility and excellent thermal stability with a much higher decomposition temperature about 500 °C compared with another PFCB polymer **8**. The T_g and T_d temperatures of PFCB polymers **4** increase with the increasing of molecular weights.

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