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Novel perfluorocyclobutyl (PFCB)-containing polymers formed by click chemistry

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Abstract

The synthesis and characterization of a novel class of linear poly(alkyl aryl) ethers containing 1,2,3-triazolyl and perfluorocyclobutyl units have been described. These polymers were readily prepared from the Huisgen's 1,3-dipolar cycloaddition of poly(ethylene glycol) diazides and 1,2-bis(4-ethynylphenoxy)perfluorocyclobutane that is defined as 'click chemistry' recently. These polymers exhibited relatively small polydispersity, good thermal stability and solubility in common organic solvents.

Keywords: Poly(alkyl aryl) ethers; Perfluorocyclobutane (PFCB); Click chemistry

1. Introduction

Fluoropolymers keep attractive in the development of advanced materials with high thermal and oxidative stability, chemical resistance and superior electrical insulating ability [1,2]. In recent years, partially fluorinated polymers containing perfluorocyclobutane (PFCB) rings have been developed [3–5]. PFCB aromatic ether polymers, combining the engineering thermoplastic nature of polyaryl ethers and the stability of fluorocarbon segments, exhibit excellent processability, optical transparency, high temperature performance and low dielectric constants. These performances make them good candidates for a variety of applications, such as high performance structure coatings, interlayer dielectrics, circuit board laminas, dielectric wave guides and optical cladding layers [6]. PFCB polymers are generally obtained by the thermal $(2\pi + 2\pi)$ cyclopolymerization of aryl trifluorovinyl ethers in bulk or solution. However, this polymerization process generally needs high temperature (>150 °C) and long reaction time [3–5,7].

Recently, click chemistry, the copper (I)-catalyzed Huisgen's azide–alkyne $(3 + 2)$ cycloaddition reaction, has attracted much attention [8]. This type of reaction, characterized by very high yields, mild and simple reaction conditions, oxygen and water tolerance, and simple work-up of products, is highly chemoselective in the formation of the desired 1,4-disubstituted 1,2,3-triazole even in the presence of a large variety of functional groups. This methodology has been applied widely in organic chemistry [9], supramolecular chemistry [10], drug discovery [11], bioconjugations [12] and materials science [13]. The applications in materials science are especially interesting. However, most of them were focused on the preparation of dendronized polymers [13a,b] and conjugated polymers [13c] or incorporation of 1,2,3-triazole ring into polymers by graft [13d–f]. The 1,2,3-triazole ring was seldom incorporated into the backbone of linear polymers [13g–i]. Since the stable 1,4-disubstituted 1,2,3-triazoles could be formed as part of the polymer [9,14], we envisaged that perfluorocyclobutane-containing dialkynes could be used to polymerize with azido-terminated polyethylene glycol via

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a ‘click chemistry’ to give linear poly(alkyl aryl) ethers, which would have good thermal stability, flexibility and solubility. Thus, we describe herein the preparation of novel 1,2-bis(4-ethynylphenoxy)perfluorocyclobutane, its polymerization with polyethylene glycol diazides and the characterization of the resulting polymers.

2. Experimental

2.1. Materials

Triethylamine (TEA), tetrahydrofuran (THF), methanol (MeOH), acetonitrile (MeCN) were distilled over CaH_2. Chlorotrimethylsilane was distilled under nitrogen. 1-Bromobutane was distilled and then purified by rapid passage through basic alumina. Magnesium turnings and zinc granular were treated with 5% aqueous hydrochloric acid for several minutes, and then washed with water, ethanol and ether successively, and dried in vacuum. Other reagents or materials were used as received.

2.2. Measurements

Elemental analysis was carried out on a Carlo-Erba 1106 system. Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. Gas chromatography/mass spectrometry (GC/MS) was recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Bruker AM-400 spectrometer with Me_4Si (^1H NMR) and $CDCl_3$ (^{13}C NMR) as internal standard. ^{19}F NMR (376 MHz) was collected with $CFCl_3$ 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-wavelength 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 THF as eluent with a 1.0 mL/min flow rate. The system was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was conducted on a Perkin–Elmer model DSC Pyris 1 system calibrated with indium and zinc standards. Dynamic thermogravimetric analysis (TGA) was performed on Perkin–Elmer model TGA Pyris 1 system on film or powder samples at a heating rate of 20 °C/min in N_2.

2.3. Synthesis of trimethylsilylacetylene (TMSA)

TMSA was prepared using methods as described in Ref. [15].

2.4. Synthesis of 1,2-bis(4-bromophenoxy)-perfluorocyclobutane **2**

Compound **2** was prepared using methods as described in Refs. [3–5]. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.45–7.48 (m, 4H), 7.07 (d, $J = 9.0$ Hz, 2H), 7.01 (d, $J = 8.9$ Hz, 2H). ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ −126.7, −128.1, −128.7, −129.5, −130.1, −130.3, −130.9, −131.3, −131.4.

2.5. Synthesis of 1,2-bis(4-trimethylsilylphenoxy)-perfluorocyclobutane **3**

To a flame-dried 250 mL three-neck round-bottom flask equipped with a magnetic stirrer, a thermometer, and a condenser with a drying tube were charged compound **2** (20.30 g, 40 mmol), copper (I) iodide (0.76 g, 4 mmol) and bis(triphenylphosphine)palladium dichloride (1.40 g, 2 mmol). TEA/THF (60 mL, 1:1 v/v) was added via syringe under N_2 atmosphere. The solution was stirred for 30 min at room temperature, and then TMSA (17.00 mL, 120 mmol) was added via syringe and the mixture was stirred for another 30 min. The resulting mixture was stirred at 50 °C for further 48 h. TEA and THF were removed under reduced pressure. The resulting dark brown solid was then dissolved in ethyl acetate and water. The organic layer was separated and washed with brine (20 mL × 3), then dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether) to afford the desired product **3** (95%) as a pale yellow solid. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.42–7.46 (m, 4H), 7.10 (d, $J = 8.16$ Hz, 2H), 7.01 (d, $J = 8.6$ Hz, 2H), 0.25 (s, 18H). ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ −126.7, −127.7, −128.1, −128.6, −129.5, −130.1, −130.7, −130.9, −131.3. IR (KBr, cm^{-1}): ν 2960, 2161, 1603, 1504, 1314, 1298, 1251, 1200, 1017, 963, 866, 836, 760. MS (EI): m/z 525, 255, 158, 73. Anal. Calcd for $C_{26}H_{26}O_2F_6Si_2$: C, 57.78%; H, 4.81%. Found: C, 57.62%; H, 4.96%.

2.6. Synthesis of 1,2-bis(4-ethynylphenoxy)-perfluorocyclobutane **4**

To a flame-dried 250 mL three-neck round-bottom flask were charged compound **3** (27.00 g, 0.05 mol) and anhydrous potassium carbonate (20.70 g, 0.15 mol). The flask was flushed with nitrogen and then methanol (60 mL) and THF (60 mL) were added via syringe. The mixture was stirred at room temperature for 3 h. The resulting solution was poured into dichloromethane (50 mL) and water (100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic phases were washed with brine (30 mL × 3), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give compound **4** (19.80 g, 100%) as a pale yellow oil. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.45–7.51 (m, 4H), 7.13 (d, $J = 8.09$ Hz, 2H), 7.04 (d, $J = 8.59$ Hz, 2H), 3.08 (s, 2H), ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ −126.6, −127.8, −128.1, −128.7, −129.5, −130.1, −130.7, −131.2, −131.5. IR (neat, cm^{-1}): ν 3300, 2928, 2112, 1605, 1504, 1315, 1303, 1262, 1202, 1017, 962, 835. MS (EI): m/z 198, 151, 101, 75. Anal. Calcd for $C_{20}H_{10}O_2F_6$: C, 60.61%; H, 2.53%. Found: C, 61.05%; H, 2.80%.

2.7. General procedure for the preparation of polyethylene glycol dinitrates ***5a–d***

To a 250 mL three-neck round-bottom flask equipped with a magnetic stirrer, a thermometer, and a condenser with a drying tube were charged 98% nitric acid (20 mL), 98% sulfuric acid (20 mL) and CH_2Cl_2 (80 mL). The mixture was cooled to ~5 °C, and a solution of polyethylene glycol (PEG) (0.05 mol) in CH_2Cl_2 (20 mL) was added dropwise while the temperature was kept below 10 °C. Then the reaction mixture was poured into stirring cold water (500 mL). The organic layer was separated and washed successively with water (100 mL), 5% aqueous sodium bicarbonate (20 mL), and water (30 mL) and then dried over $MgSO_4$. The solvent was removed and the residue was purified by flash chromatography over neutral alumina with chloroform as eluent to give **5a–d** as colorless oils.

Compound **5a**: 72.7% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.66 (s, 4H), 3.79–3.83 (m, 4H), 4.62–4.64 (m, 4H). IR (neat, cm^{-1}): ν 2896, 1629, 1453, 1365, 1280, 1128, 1029, 907, 859.

Compound **5b**: 71.8% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.66 (s, 8H), 3.78–3.80 (m, 4H), 4.61–4.64 (m, 4H). IR (neat, cm^{-1}): ν 2875, 1630, 1452, 1353, 1280, 1131, 1027, 907, 858.

Compound **5c**: 70.9% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.63 (t, $J = 1.56$ Hz, 24H), 3.77–3.82 (m, 4H), 4.59–4.62 (m, 4H). IR (neat, cm^{-1}): ν 2873, 1629, 1454, 1351, 1280, 1110, 1030, 907, 859.

Compound **5d**: 70.4% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.65 (t, $J = 1.58$ Hz, 44H), 3.75–3.80 (m, 4H), 4.58–4.61 (m, 4H). IR (neat, cm^{-1}): ν 2866, 1629, 1454, 1376, 1280, 1126, 1029, 907, 858.

2.8. General procedure for the preparation of polyethylene glycol diazides ***6a–d***

To a 250 mL three-neck round-bottom flask equipped with a magnetic stirrer, a thermometer and a condenser were charged compounds **5a–d** (10 mmol), sodium azide (40 mmol), DMF (40 mL) and water (10 mL). The mixture was stirred vigorously at 90 °C for 24 h. The reaction mixture was cooled to room temperature and was diluted with water (100 mL) and CH_2Cl_2 (100 mL). The organic phase was separated and washed with water (30 mL × 3), and dried over $MgSO_4$. The solvent was removed and the residue was purified by flash chromatography over neutral alumina with chloroform as eluent to give **6a–d** as colorless oils.

Compound **6a**: 84.0% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.68–3.71 (m, 8H), 3.39 (t, $J = 5.04$ Hz, 4H). IR (neat, cm^{-1}): ν 2869, 2111, 1442, 1345, 1286, 1124, 1029, 853.

Compound **6b**: 82.5% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.67–3.70 (m, 12H), 3.39 (t, $J = 5.02$ Hz, 4H). IR (neat, cm^{-1}): ν 2869, 2109, 1442, 1345, 1286, 1124, 1033, 854.

Compound **6c**: 79.5% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.65–3.69 (m, 28H), 3.39 (t, $J = 5.0$ Hz, 4H). IR (neat, cm^{-1}): ν 2869, 2106, 1448, 1350, 1301, 1119, 1038, 852.

Compound **6d**: 76.8% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.64–3.70 (m, 48H), 3.39 (t, $J = 5.08$ Hz, 4H). IR (neat, cm^{-1}): ν 2869, 2104, 1454, 1350, 1299, 1113, 1050, 852.

2.9. General procedure for polymerization

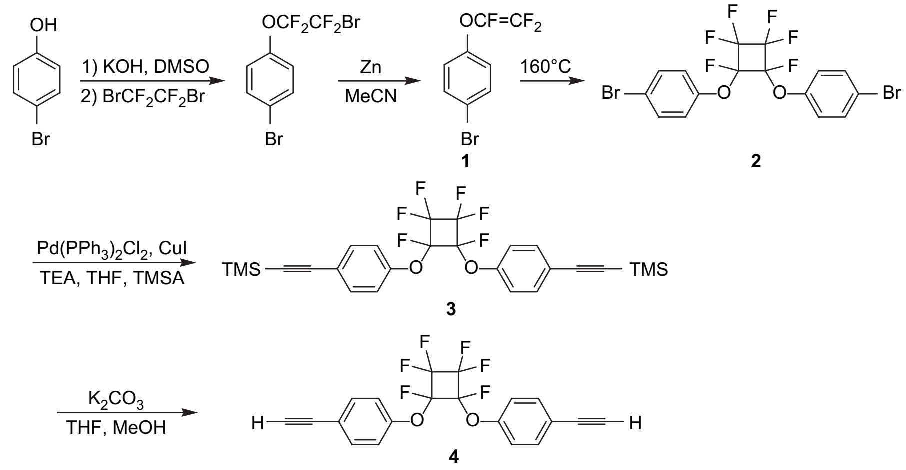
To a 50 mL three-neck round-bottom flask equipped with a magnetic stirrer, a thermometer, and a condenser were charged compound **4** (0.32 g, 0.8 mmol), compounds **6a–d** (0.8 mmol), *t*-BuOH (8 mL) and TEA (0.2 mL). Then a solution of sodium ascorbate (0.02 g, 0.08 mmol) and $CuSO_4 \cdot 5H_2O$ (0.01 g, 0.04 mmol) in water (8 mL) was added. The resulting mixture was degassed and stirred at 80 °C for 10–12 h. The solvent was decanted to leave a gum residue in the flask. The residue was then stirred with H_2O (10 mL) and concentrated ammonia (2 mL) for 20 min. The mixture was filtered and the resulting filter cake was washed with H_2O (3 × 20 mL). The filter cake was then dissolved in THF and a yellow precipitate was formed by addition of hexane. After filtration, the desired fluoropolymers **7a–d** were obtained as yellow solids, respectively.

Compound **7a**: 74.9% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.83 (s, 2H), 7.75 (d, 4H), 7.18 (q, 4H), 4.47 (s, 4H), 3.81 (s, 4H), 3.53 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 50.4, 69.4, 70.6, 118.5, 118.9, 120.8, 120.9, 127.0, 127.1, 127.9, 128.2, 146.5, 152.1, 152.3. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ −126.6, −127.9, −128.7, −129.5, −130.3, −130.7, −131.1. IR ($CHCl_3$, cm^{-1}): ν 3137, 2873, 2104, 1609, 1560, 1496, 1460, 1356, 1318, 1263, 1201, 1115, 1016, 961, 841, 805.

Compound **7b**: 70.8% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.83 (s, 2H), 7.75 (d, 4H), 7.18 (q, 4H), 4.48 (s, 4H), 3.81 (s, 4H), 3.53 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 50.3, 69.3, 70.5, 118.0, 118.5, 118.9, 120.9, 127.0, 127.1, 127.9, 128.2, 146.5, 152.1, 152.3. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ −126.6, −127.9, −128.7, −129.5, −130.3, −130.7, −131.1. IR ($CHCl_3$, cm^{-1}): ν 3136, 2870, 2104, 1615, 1560, 1496, 1461, 1361, 1316, 1263, 1202, 1118, 1017, 962, 841, 807.

Compound **7c**: 72.1% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.98 (s, 2H), 7.80 (d, 4H), 7.20 (q, 4H), 4.56 (s, 4H), 3.87 (s, 4H), 3.53 (br, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 50.1, 69.1, 70.2, 118.5, 118.9, 120.8, 120.9, 127.0, 127.1, 127.4, 129.1, 145.5, 151.8, 152.0. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ −126.6, −127.9, −128.6, −129.5, −130.2, −130.7, −131.1. IR ($CHCl_3$, cm^{-1}): ν 3134, 2870, 2104, 1615, 1558, 1496, 1461, 1350, 1314, 1262, 1201, 1112, 1017, 962, 842, 805.

Compound **7d**: 64.9% yield; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.00 (s, 2H), 7.82 (d, 4H), 7.22 (q, 4H), 4.58 (s, 4H), 3.90 (s, 4H), 3.53 (br, 44H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 50.1, 69.1, 70.2, 118.5, 118.9, 120.8, 120.9, 127.0, 127.1, 127.6, 129.6, 145.5, 151.9, 152.1. ^{19}F NMR ($CDCl_3$, 376 MHz, ppm): δ −126.6, −127.9, −128.6, −129.5, −130.2, −130.7, −131.1. IR ($CHCl_3$, cm^{-1}): ν 3135,



Scheme 1. Synthesis of 1,2-bis(4-ethynylphenoxy)perfluorocyclobutane **4**.

2870, 2103, 1610, 1556, 1496, 1461, 1362, 1300, 1258, 1203, 1109, 1016, 961, 842, 805.

3. Result and discussion

3.1. Synthesis and characterization of 1,2-bis(4-ethynylphenoxy)perfluorocyclobutane *4*

The synthesis of compound **4** was outlined in Scheme 1 as similar to Ref. [16a–d]. Compound **2** was prepared from 4-bromophenol as described in Refs. [3–5]. The next step involved a Sonogashira coupling [16e] between **2** and trimethylsilylacetylene (TMSA). Typically, $Pd(PPh_3)_2Cl_2$ was used as a palladium catalyst (5 mol%), CuI (10 mol%) as a cocatalyst and triethylamine as a base and co-solvent. The desired product **3** was obtained in 95% yield. Treatment of **3** with K_2CO_3 in THF and MeOH gave **4** in quantitative yield [17].

The conversion of **2** to **3** was confirmed by FT-IR (Fig. 1). The IR spectrum of **3** exhibited the C≡C stretch at 2161 cm^{-1}. The formation of **3** was further confirmed by the signal of Me_3Si group at 0.24 ppm in the ^1H NMR spectrum. The conversion of **3** to monomer **4** was also identified not only by the FT-IR spectrum of **4** which exhibited the ≡C–H stretch at 3300 cm^{-1} (Fig. 1) but also by the disappearance of the signals corresponding to Me_3Si group and the presence of the signal at 3.07 ppm corresponding to ≡C–H in the ^1H NMR spectrum (Fig. 2A). ^{19}F NMR of compound **4** displayed a series of peaks between −126.6 and −131.5 ppm which were assigned as the perfluorocyclobutyl fluorine signals (Fig. 2B). The structures of **3** and **4** were characterized by ^1H NMR, ^{19}F NMR, IR and elemental analysis.

3.2. General preparation of polyethylene glycol diazides *6a–d*

Azides can be prepared from halides, alcohols, amines or hydrazines [18]. In our work, diazides **6a–d** were prepared in two steps from alcohols as similar to Ref. [19], as shown

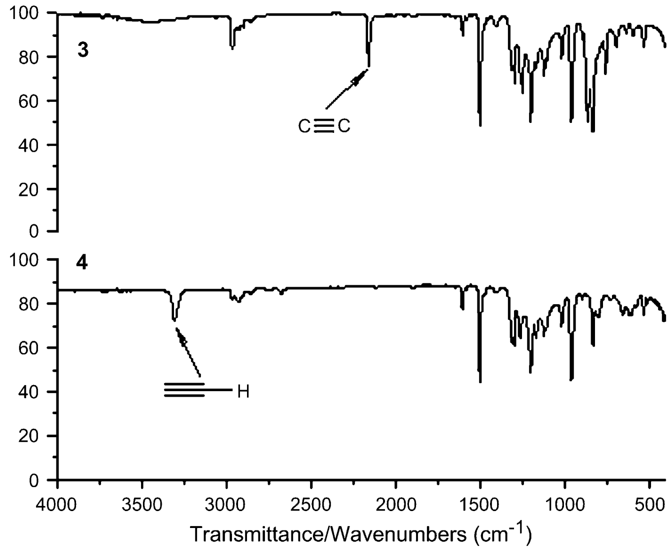


Fig. 1. FT-IR spectra of compounds **3** and **4**.

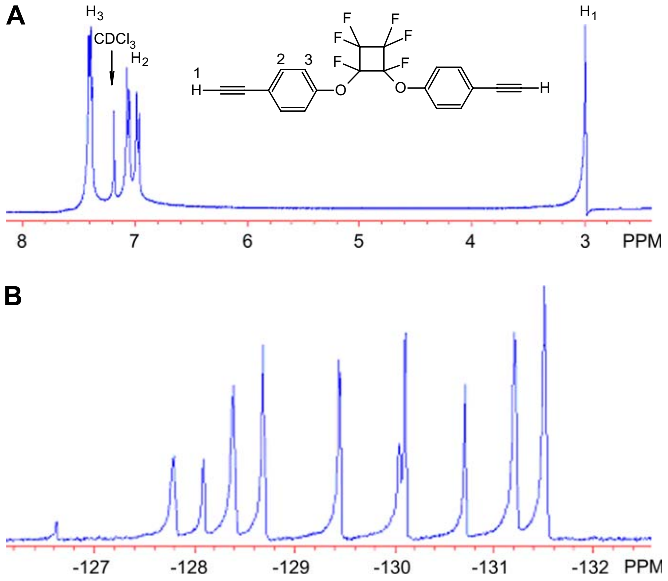
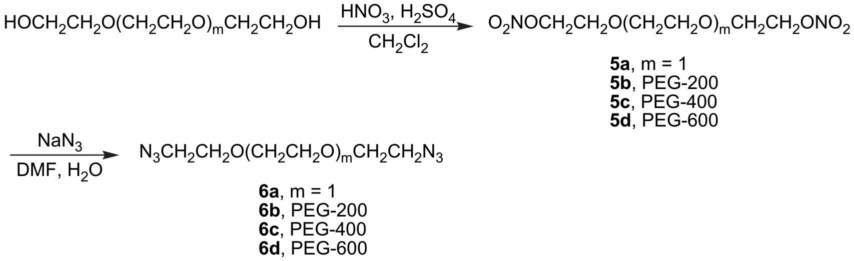


Fig. 2. ^1H NMR (A) and ^{19}F NMR (B) spectra of compound **4**.



Scheme 2. Synthesis of polyethylene glycol diazides **6a–d**.

in Scheme 2. The classical approach through the intermediate tosylate derivative of polyethylene glycol was firstly considered. However, the use of the tosylate moiety as a leaving group for such large molecular weight materials has the disadvantages of lower yields and higher costs. Therefore, we chose nitryl as a leaving group. The polyethylene glycol dinitrates were readily prepared from the glycols and nitric acid, and then converted to the corresponding diazides. Thus, triethylene glycol and a series of commercially available polyethylene glycols (PEG) with molecular weights ranging from 200 to 600 (PEG-200, PEG-400, and PEG-600) were converted to the corresponding diazides. Their structures were characterized by ^{1}H NMR and FT-IR.

The conversion of **PEG-200** to **5b** was confirmed by the disappearance of –OH stretching at 3500–3100 cm^{-1} of **PEG-200** in the IR spectrum, and the presence of $-ONO_2$ group stretching at 1630 cm^{-1} (s) and 1280 cm^{-1} of **5b** (Fig. 3). The conversion of **5b** to **6b** was also confirmed by the FT-IR spectrum of **6b** (Fig. 3). The strong absorbance of $-ONO_2$ group at 1630 cm^{-1} disappeared and a new strong band at 2110 cm^{-1} appeared for the $-N_3$ group.

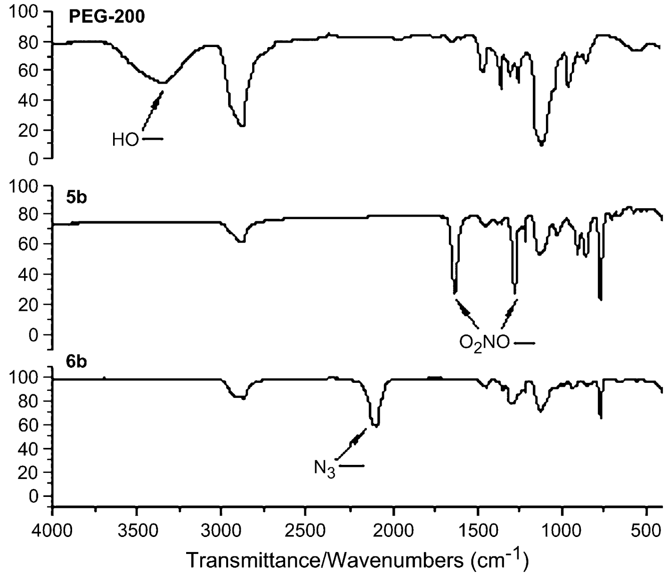
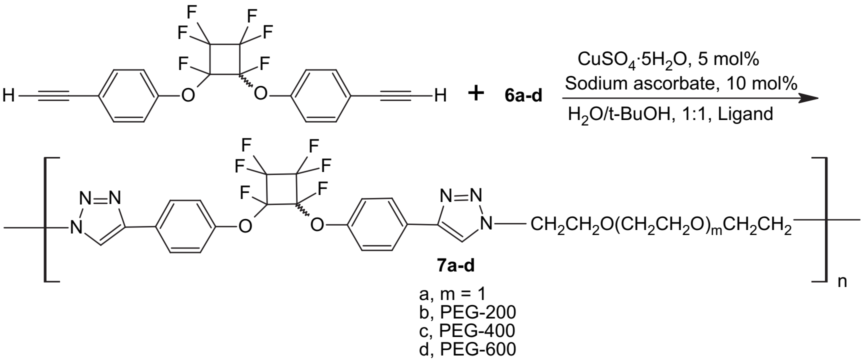


Fig. 3. FT-IR spectra of compounds **PEG-200**, **5b** and **6b**.

3.3. Polymer synthesis

Polymers containing 1,2,3-triazole rings and perfluorocyclobutyl groups were prepared from **4** and polyethylene glycol diazides **6a–d** by click chemistry as shown in Scheme 3.

When we used similar reaction conditions as described by Sharpless et al. [8], i.e. 5 mol% copper (II) sulfate and 10 mol% sodium ascorbate in isobutanol and water (1:1, v/v) and stirred for 24 h at room temperature, the isolated yield of polymers was very poor. Substitution of isobutanol with THF or acetonitrile gave almost the same result. It might be that the reactivity of diazides containing long CH_2CH_2O chain was low. As a result, CuI was used as a catalyst, acetonitrile and water (1:2, v/v) were used as co-solvents, the reaction rate was improved markedly, however, what we obtained was an emulsion after removal of acetonitrile, and it was difficult to extract the emulsion with dichloromethane, diethyl ether or ethyl acetate. When the emulsion was concentrated to dryness, the resulting residue was dissolved in THF and the polymeric compound was precipitated by adding hexane. The yield was very poor. When copper (II) sulfate and sodium ascorbate



Scheme 3. Preparation of fluoropolymers by click chemistry.

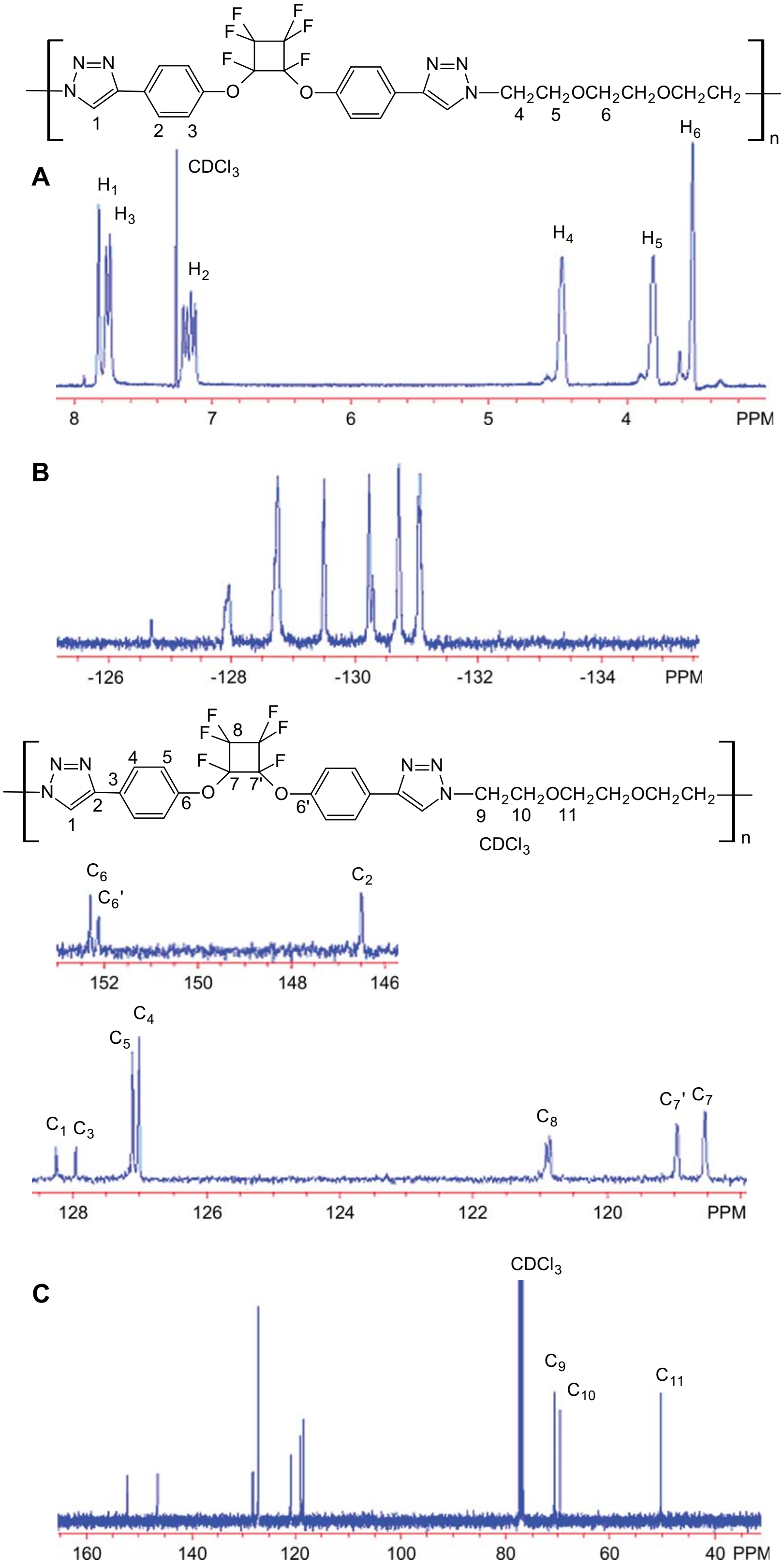


Fig. 4. ^{1}H NMR (A), ^{19}F NMR (B) and ^{13}C NMR (C) spectra of polymer **7a**.

were used in isobutanol and water in the same manner, but the reaction temperature was raised to 80 °C, a polymer was obtained with low molecular weight, a large polydispersity and several overlapping distributions. The problem was solved when triethylamine was used as a ligand for Cu (I). Thus, compounds **4** and **6a–d** were polymerized in the presence of copper (II) sulfate, sodium ascorbate and triethylamine at 80 °C, the desired fluoropolymers **7a–d** were obtained in 65–75%

yields, respectively with reasonable molecular weight. This result was complied with the findings reported by Lewis et al. [20] and Rodionov et al. [21] that ligands could improve the azide–alkyne cycloaddition process.

The 1,2,3-triazole rings of the polymer were characterized by signals near 7.9 ppm of the triazole protons in the ^{1}H NMR spectrum (Fig. 4A), and signals at 146.5 and 128.2 ppm of triazole carbons in the ^{13}C NMR spectrum (Fig. 4C). The triazole ring was confirmed further by the presence of =C–H of 1,2,3-triazole ring stretch near 3135 cm^{-1} in the FT-IR spectrum (Fig. 5).

A particularly useful method of characterization available for PFCB polymers is FT-IR spectrum. A strong sharp band near 960 cm^{-1} is diagnostic for the presence of hexafluorocyclobutyl group. This easily resolved absorption has proven to be a useful analytical tool since this region in the IR is rarely occupied by other functionalities [3a]. The hexafluorocyclobutyl groups in PFCB polymers were characterized further by ^{19}F NMR (Fig. 4B), in which fluorine signals of these groups were presented from −126.6 to −131.1 ppm.

The 1,2-disubstituted perfluorocyclobutyl group was further identified in the ^{13}C NMR spectrum of polymers **7a–d** by the presence of four separated multiplets from 118 to 121 ppm. These unresolved cyclobutyl carbon signals showed that both cis and trans geometric isomers were all coupled to each nonequivalent fluorine atom attached to the cyclobutyl ring. The aromatic carbons of polymer **7a–d** adjacent (*ipso*) and *ortho* to the perfluorocyclobutyl ether linkage did give separate signals dictated by the 1,2-disubstituted cis/trans (*Z*/*E*) configuration of the ring: the *ipso* carbon signals near 152.1 (presumably trans) and 152.3 ppm (cis) (Fig. 4C).

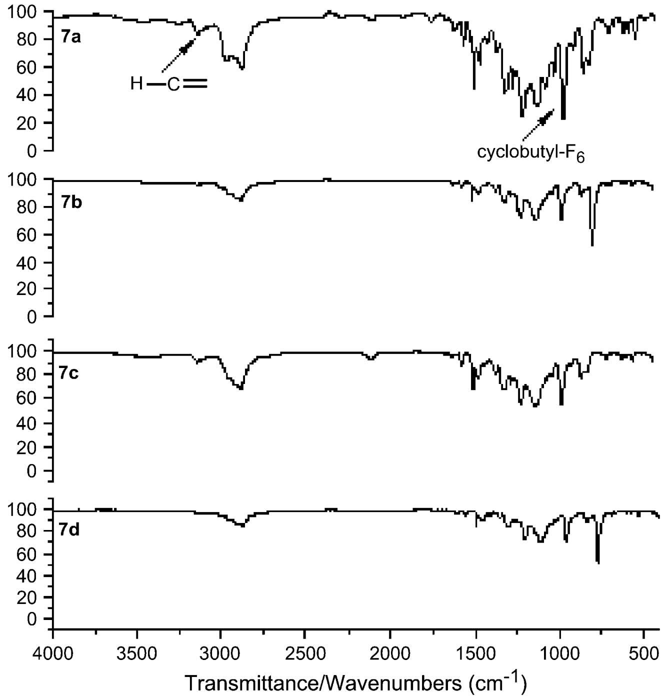


Fig. 5. FT-IR spectra of polymer **7a–d**.

Table 1
Characteristics of the perfluorocyclobutane-containing polymers

Polymers	M_n [a]	M_w [a]	(M_w/M_n) [a]	T_d (°C) [b]
7a	20,780	25,560	1.2	427
7b	14,480	25,570	1.7	425
7c	15,950	20,790	1.3	417
7d	7520	9960	1.3	412

[a] GPC in THF vs. polystyrene at 35 °C.
[b] TGA at 20 °C/min in N_2.

The corresponding data of GPC analysis in THF for **7a–d** were listed in Table 1. The molecular weights reduced from **7a** to **7d.** The shorter the polyethylene glycol chain was, the higher the molecular weight obtained. Compared to the high M_n and M_w of polymers **7a–c**, the M_n and M_w of **7d** were much lower. It may be due to the open-chain crown ether action of long CH_2CH_2O chain [19]. The action can encircle Cu (II) that prevents the reduction reaction from Cu (II) to Cu (I). For the count of repeating unit of CH_2CH_2O for **6a–c** was less than seven, the crown ether action was inconspicuous, however, the crown ether action of **6d** became relatively evident. The polydispersities of fluoropolymers **7a–d** were low which indicated that the click chemistry was efficient.

3.4. Thermal properties of polymers

The DSC and TGA curves of the resulting polymers were presented in Figs. 6 and 7, and the corresponding data of thermal analysis were listed in Table 1. The DSC curves showed that no crystalline transitions and glass transitions were observed. The TGA curves and data in Table 1 showed that the decomposition temperature T_d was higher than 410 °C. The results of thermal analysis demonstrated that the resulting poly(alkyl aryl) ethers had good thermal stability and melting fluidity; this would be suitable for application and processing.

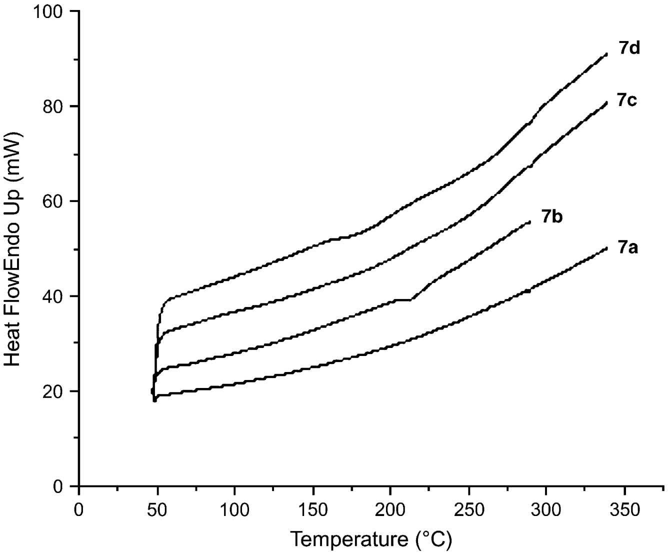


Fig. 6. DSC analysis of polymer **7a–d** at 20 °C/min.

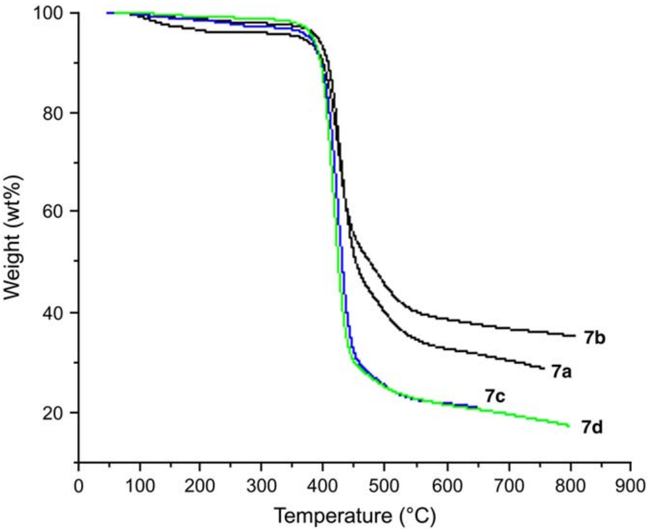


Fig. 7. TGA analysis of polymer **7a–d** at 20 °C/min.

3.5. Solubility tests

Polymers **7a–d** were performed with solubility tests in four common solvents including chloroform, acetone, tetrahydrofuran and *N*,*N*-dimethylformamide at room temperature. The results indicated that polymers **7a–d** containing 1,2,3-triazole rings and perfluorocyclobutyl groups exhibited excellent solubility in all solvents mentioned above.

4. Conclusion

A novel dialkyne, 1,2-bis(4-ethynylphenoxy)perfluorocyclobutane **4,** was prepared by the Sonogashira coupling reaction between 1,2-bis(4-bromophenoxy)perfluorocyclobutane and trimethylsilylacetylene. A series of diazide monomers **6a–d** were prepared from polyethylene glycol dinitrates. The click chemistry between **4** and diazides **6a–d** provided novel polymers containing 1,2,3-triazole rings and perfluorocyclobutyl groups. These polymers exhibited good solubility and had reasonable molecular weight. TGA results showed that they possessed good thermal stability. These properties can make them the candidates for good thermal-stable and soluble linear polymers.

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References

[1] Labadie JW, Hedrick JL. Macromolecules 1990;23:5371.
[2] Mercer F, Goodman T, Wojtowciz J, Duff D. J Polym Sci Part A Polym Chem 1993;30:1767.
[3] (a) Smith Jr DW, Babb DA, Shah HV. Macromolecules 1996;29:852;
(b) Smith Jr DW, Babb DA, Shah HV, Hoeglund A, Traiphol R, Perahia D, et al. J Fluorine Chem 2000;104:109.
[4] Babb DA, Ezzell BR, Clement KS, Richey WF, Kennedy AP. J Polym Sci Part A Polym Chem 1993;31:3465.
[5] (a) Ma H, Wong S, Luo JD, Kang SH, Jen AK-Y, Barto R, et al. Polym Prepr (Am Chem Soc Div Polym Chem) 2002;43:493;
(b) Lee SE, Lee DS, Kim CE, Yi DK, Shin BG, Kang JW. Polym Prepr (Am Chem Soc Div Polym Chem) 2002;43:625.
[6] (a) Fishbeck G, Moosburger R, Kostrzewa C, Aehen A, Peterman K. Electron Lett 1997;33:518;
(b) Moosburger R, Petermann K. IEEE Photon Technol Lett 1998;10:684;
(c) Tumolillo Jr TA, Thomas A, Ashley PR. Appl Phys Lett 1993;82:3068;
(d) Choi W-S, Harris FW. Polymer 2000;41:6213.
[7] (a) Jin JY, Topping CM, Suresh S, Foulger SH, Rice N, Mojazza BH, et al. Polymer 2005;46:6923;
(b) Huang XY, Wang RW, Zhao PQ, Lu GL, Zhang S, Qing FL. Polymer 2005;46:7590;
(c) Jin JY, Topping CM, Chen SG, Ballato J, Foulger SH, Smith Jr DW. J Polym Sci Part A Polym Chem 2004;42:5292.
[8] Kolb HC, Finn MG, Sharpless KB. Angew Chem Int Ed 2001;40:2004.
[9] (a) Wang ZX, Qin HL. Chem Commun 2003;19:2450;
(b) Rostovtsev VV, Green LG, Fokin VV, Sharpless KB. Angew Chem Int Ed 2002;41:2596.
[10] Badjic JD, Balzani V, Credi A, Lowe JN, Silvi S, Stoddart JF. Chem Eur J 2004;10:1926.
[11] (a) Lenda F, Guenoun F, Tazi B, Larbi NB. Tetrahedron Lett 2004;45:8905;
(b) Manetsch R, Krasinski A, Radic Z, Raushel J, Taylor P, Sharpless KB, et al. J Am Chem Soc 2004;126:12809;
(c) Wu YM, Deng J, Fang X, Chen QY. J Fluorine Chem 2004;125:1415.
[12] (a) Wang Q, Chan TR, Hilgraf R, Fokin VV, Sharpless KB, Finn MG. J Am Chem Soc 2003;125:3192;
(b) Meng JC, Siuzdak G, Finn MG. Chem Commun 2004;18:2108;
(c) Link AJ, Vink MKS, Tirrell DA. J Am Chem Soc 2004;126:10598.
[13] (a) Scheel AJ, Komber H, Viot BI. Macromol Rapid Commun 2004;25:1175;
(b) Wu P, Feldman AK, Nugent AK, Hawker CJ, Scheel A, Voit B, et al. Angew Chem Int Ed 2004;43:3928;
(c) Van Steenis DJVC, David ORP, Van Strijdonck GPF, Van Maarseveen JH, Reek JNH. Chem Commun 2005;34:4333;
(d) Helms B, Mynar JL, Hawker CJ, Fréchet JMJ. J Am Chem Soc 2004;126:15020;
(e) Parrish B, Breitenkamp RB, Emrick T. J Am Chem Soc 2005;127:7404;
(f) Carroll JB, Jordan BJ, Xu H, Erdogan B, Lee L, Cheng L, et al. Org Lett 2005;7:2551;
(g) Opsteen JA, Van Hest JCM. Chem Commun 2005;1:57;
(h) Díaz DD, Punna S, Holzer P, McPherson AK, Sharpless KB, Fokin VV, et al. J Polym Sci Part A Polym Chem 2004;42:4392;
(i) Ossipov DA, Hilborn J. Macromolecules 2006;39:1709.
[14] Tornoe CW, Christensen C, Meldal M. J Org Chem 2002;67:3057.
[15] Holmes AB, Sporikou CN. Org Synth 1987;65:61.
[16] (a) Tour JM, Rawlett AM, Kozaki M, Yao YX, Jagessar RC, Dirk SM, et al. Chem Eur J 2001;7:5118;
(b) McIlroy SP, Clo E, Nikolajsen L, Frederiksen PK, Nielsen CB, Mikkelsen KV, et al. J Org Chem 2005;70:1134;
(c) Khan MS, Ahrens B, Male L, Raithby PR. Acta Crystallogr 2004;E60:O915;
(d) Khan MS, Ahrens B, Mahon MF, Male L, Raithby PR. Acta Crystallogr 2002;E58:O1202;
(e) Sonogashira K, Tohda Y, Hagihara N. Tetrahedron Lett 1975;16:4467.
[17] Jones TV, Blatchly RA, Tew GN. Org Lett 2003;5:3297.
[18] Scriven EFV, Turnbull K. Chem Rev 1988;88:297.
[19] (a) Wilson ER, Frankel MB. J Chem Eng Data 1982;27:472;
(b) Wang XH, Feng ZG. Acta Polym Sin 2000;3:350.
[20] Lewis WG, Magallon FG, Fokin VV, Finn MG. J Am Chem Soc 2004;126:9152.
[21] Rodionov VO, Fokin VV, Finn MG. Angew Chem Int Ed 2005;44:2210.