Journal of Fluorine Chemistry 129 (2008) 1003–1010

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Synthesis of novel aromatic ether polymers containing perfluorocyclobutyl and triazole units via click chemistry

Rong-Xing Yao [a,b], Lei Kong [a,b], Zeng-Shen Yin [a,b], Feng-Ling Qing [a,c,*]

[a] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China
[b] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China
[c] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

ARTICLE INFO

Article history:
Received 24 March 2008
Received in revised form 23 April 2008
Accepted 23 April 2008
Available online 4 May 2008

Keywords:
Click chemistry
Perfluorocyclobutane (PFCB)
Fluorinated polymer

ABSTRACT

The synthesis and characterization of a novel class of linear aromatic ether polymers containing perfluorocyclobutyl and triazole unites is described. These polymers were prepared from the click chemistry (the copper-catalyzed Huisgen's 1,3-dipolar cycloaddition) of new monomer 1,2-bis(4-azidomethylphenoxy) perfluorocyclobutane and bisethynyl compounds.

1. Introduction

The Huisgen 1,3-dipolar cycloadditions of azides and terminal alkynes were shown to be the most effective and versatile and thus became the prime example of click chemistry that was introduced by Sharpless and co-workers in 2001 [1]. Because of their high selectivity, near-perfect reliability, high yields, and exceptional tolerance towards a wide range of functional groups and reaction conditions, click chemistry have recently attracted increased attention in organic synthesis and, in particular, have gained popularity in material synthesis. Click chemistry is widely used in polymer synthesis as well as in the modification of surfaces nanometer- and mesoscale structures [2]. Fluoropolymers keep attractive in the development of advanced materials with high thermal and oxidative stability, chemical resistance and superior electrical insulating ability [3]. In recent years, partially fluorinated polymers containing perfluorocyclobutane (PFCB) rings have been developed [4]. 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. 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 [4]. Recently, our group has applied click chemistry for the synthesis of fluorinated polymer containing perfluorocyclobutane (PFCB) rings. The Huisgen 1,3-dipolar cycloaddition of poly(ethylene glycol) diazides and 1,2-bis(4-ethynylphenoxy)perfluorocyclobutane in the presence of copper(I) at 80 °C provided alternating copolymers in high yields (Scheme 1). These novel polymers showed good thermal stability and solubility in common organic solvents [5]. Here we describe the synthesis of a novel class of linear aromatic ether polymers containing perfluorocyclobutyl and triazole unites from the click chemistry of 1,2-bis(4-azidomethylphenoxy) perfluorocyclobutane and bisethynyl compounds.

2. Experimental

2.1. Materials

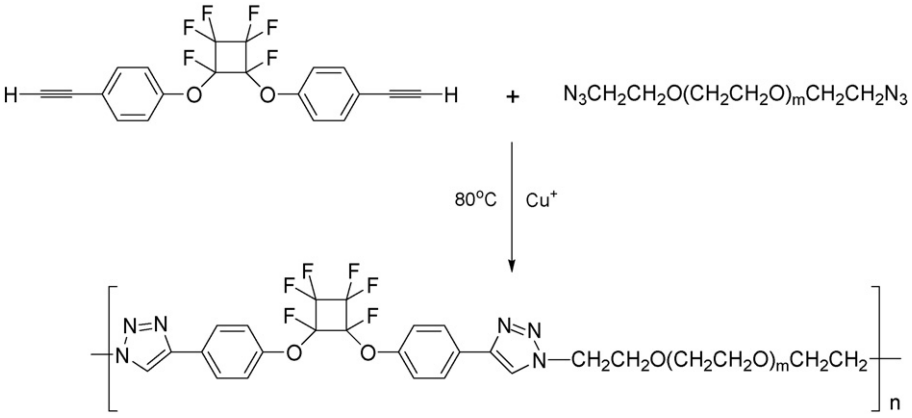
THF was distilled under nitrogen over sodium. DMSO, acetonitrile, and acetone were dried over calcium hydride, and distillated before use. Granular zincs were activated with 0.1 M hydrochloric acid, washed with ethanol and ether, and dried at 120 °C under vacuum for 4 h. Other reagents or materials were used as received.

2.2. Measurements

Melting point ranges were determined on a WRS-2A capillary melting point apparatus (uncorrected). Elemental analysis was carried out on a Carlo-Erba 1106 system. Infrared spectra were

* Corresponding author. Tel.: +86 21 54925187; fax: +86 21 64166128.
E-mail address: flq@mail.sioc.ac.cn (F.-L. Qing).

0022-1139/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2008.04.012



Scheme 1.

obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. MS spectra were recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Bruker AM-400 spectrometer with Me_4Si (^{1}H 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 (RI) detector, a Waters 2487 dual-wavelength λ absorbance detector 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 DMF as eluent at a flow rate of 1.0 μL/min. The system was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was conducted on a NetZSch (German) DSC 204 F1 system under nitrogen calibrated with indium and zinc standards. Initial sample weight was set as 1–2 mg for each operation. The specimen was heated from 25 to 280 °C at a heating rate of 10 °C/min. Dynamic thermo-gravimetric analysis (TGA) was performed on NetZSch (German) TGA 209 F1 system on powder samples at a heating rate of 10 °C/min under nitrogen atmosphere from 25 to 700 °C. Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature on a Rigaku D/Max-2550 powder diffractometer with a scanning speed of 5 °/min, and the patterns were recorded in the 2θ range of 5–60°.

2.3. Synthesis of 1-(2-bromo-1,1,2,2-tetrafluoroethoxy)-4-methylbenzene 1

To a 500 mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, a condenser, and a Dean-Stark azeotropic distillation assembly was added *p*-cresol (54.0 g, 0.50 mol), potassium hydroxide (80%, 35.0 g, 0.50 mol), DMSO (250 mL) and toluene (100 mL). The reaction mixture was refluxed for about 48 h until no water was existed in the separator. The solution was cooled to room temperature, and 1, 2-dibromotetrafluoroethane (156.0 g, 0.60 mol) was added dropwise under cooling by ice water. The solution was stirred at 20 °C for 12 h and then for at 35 °C for 10 h. Then the reaction mixture was diluted with water (800 mL) and extracted with dichloromethane. The organic phase was washed three times with water, dried over $MgSO_4$. The solution was distilled under ambient pressure and then reduced pressure to give **1** as a colorless liquid (100.8 g, 70%): b.p. 42–44 °C (ca. 8 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (2H, d, J = 8.48 Hz), 7.11 (2H, d, J = 8.56 Hz), 2.36 (3H, s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −67.8, −85.9. IR (thin film, cm^{-1}): ν 3040, 2959, 2929, 2854, 1597, 1508, 1328, 1220, 1196, 1164, 1127, 1101, 1020, 932, 844, 778.

2.4. Synthesis of 1-methyl-4-trifluorovinyloxybenzene 2

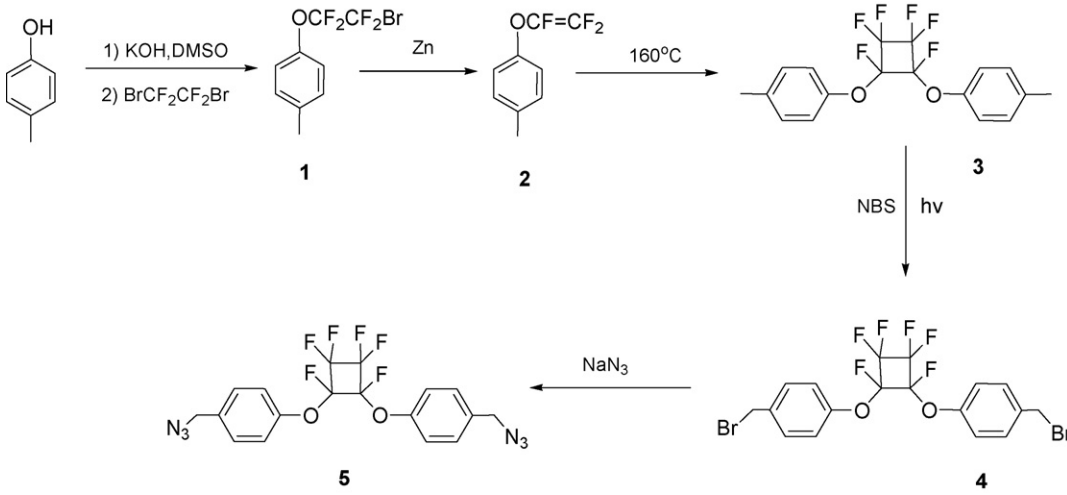
To a 500 mL dry three-necked flask equipped with a magnetic stirrer, a thermometer and a condenser under nitrogen was added compound **1** (95.0 g, 0.33 mol) slowly over 1 h to a stirring mixture of granular Zn (26.0 g, 0.40 mol) in acetonitrile (350 mL) at 80 °C. The reaction mixture was refluxed for 12 h and then evaporated; the crude product was extracted from the salts successively with hexane, concentrated, and distilled to give **2** as a colorless liquid (39.2 g, 63%): b.p. 31–32 °C (ca. 8 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (2H, d, J = 8.42 Hz), 6.99 (2H, d, J = 8.44 Hz), 2.33 (3H, s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −120.1, −127.1, −133.6. IR (thin film, cm^{-1}): ν 3040, 2960, 2930, 2855, 1833, 1611, 1507, 1314, 1284, 1278, 1195, 1168, 1140, 1017, 820, 739.

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

Compound **2** (38.0 g, 0.20 mol) was heated neat at 160 °C for 36 h in a 50 mL single-necked round-bottom flask under N_2. The product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 90/1) to give **3** as clear oil (34.5 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.00–7.12 (8H, m), 2.31 (6H, s). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −128.3, −128.8, −129.8, −130.3, −130.4, −130.7, −131.1, −131.2. MS (EI): m/z 377, 376, 375, 269, 188, 168, 141, 108, 91, 77, 65. IR (thin film, cm^{-1}): ν 3039, 2958, 2928, 2867, 1611, 1596, 1508, 1455, 1402, 1382, 1319, 1285, 1266, 1197, 1170, 1116, 1019, 962, 899, 815, 754.

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

A mixture of compound **3** (30.1 g, 0.08 mol), *N*-bromosuccinimide (NBS, 28.5 g, 0.16 mol) and dry CCl_4 (350 mL) was stirred and refluxed under the light of two "IR 275 W" lamps until the starting material was complete transformed (ca. 1–3 h). The reaction mixture was cooled to room temperature, succinimide was filtered off and the solvent was removed on a rotary evaporator to give crude product. The crude product was recrystallized from ethanol to afford compound **4** as white solid (39.6 g, 93%): m.p. 98.4–99.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34–7.38 (4H, m), 7.04–7.15 (4H, dd, J = 8.0 Hz, 8.5 Hz), 4.45 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.6, 120.6, 120.9, 132.8, 132.9, 137.4, 154.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −127.7, −127.9, −128.4, −128.6, −129.5, −130.1, −130.7, −131.3, −131.6. IR (KBr, cm^{-1}): ν 3042, 2970, 2927, 2856, 1608, 1508, 1322, 1288, 1265, 1198, 1177, 1117, 1018, 963, 833, 603. MS (EI): m/z 456, 455, 454, 453, 187, 106, 90, 89, 78. Anal. Calcd for $C_{18}H_{12}Br_2F_6O_2$: C, 40.48; H, 2.26. Found: C, 39.96; H, 2.25.



Scheme 2. Synthesis of 1,2-bis(4-methylazidophenoxy)perfluorocyclobutane **5**.

2.7. Synthesis of 1,2-bis(4-azidomethylphenoxy)perfluorocyclobutane 5

To a 250 mL single-necked flask equipped with a reflux condenser and a magnetic stirrer were added compound **4** (37.5 g, 0.07 mol) and NaN_3 (9.1 g, 0.14 mol) in DMF (180 mL). The reaction mixture was stirred at 90 °C for 24 h. After the mixture was cooled to room temperature, the solution was diluted with water and extracted with ether (3 mL × 80 mL). The combined organic layer was washed with saturated brine solution (80 mL), dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10: 1) as eluent to give compound **5** as colorless liquid (21.5 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28–7.31 (4H, m), 7.10–7.21 (4H, dd, J = 8.4 Hz, 8.5 Hz), 4.32 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.3, 120.7, 121.0, 132.0, 134.7, 135.1, 154.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −127.8, −128.2, −128.5, −128.8, −129.5, −130.2, −130.8, −131.1, −131.5. IR (neat, cm^{-1}): ν 3045, 2930, 2878, 2099, 1610, 1508, 1449, 1422, 1317, 1263, 1202, 1171, 1120, 1018, 962. MS (EI): m/z 401, 388, 106, 104, 89, 90, 91, 78, 77, 51. Anal. Calcd for $C_{18}H_{12}F_6N_6O_2$: C, 47.17; H, 2.64; N, 18.34. Found: C, 47.47; H, 2.69; N, 18.43.

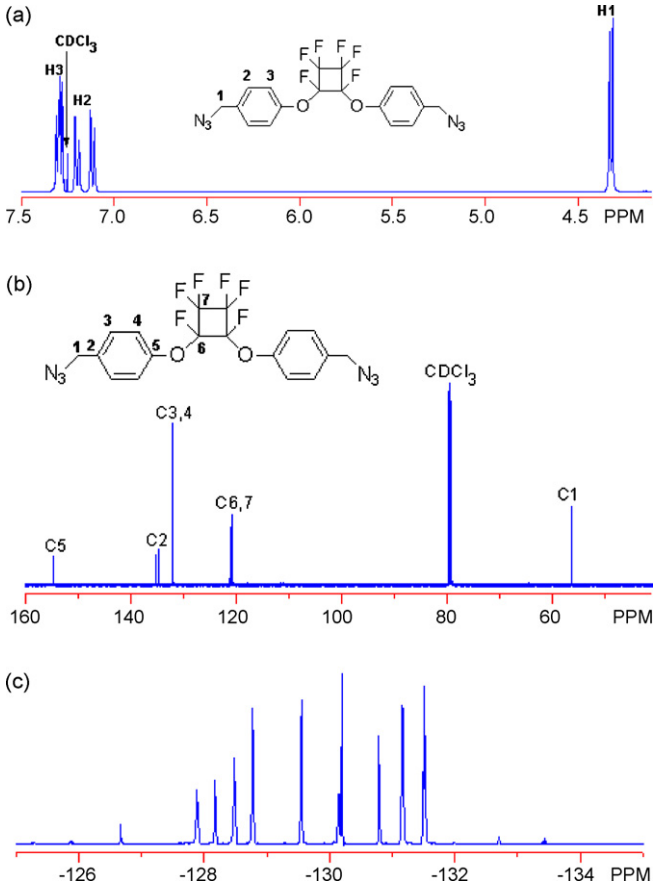


Fig. 1. ^{1}H NMR (a), ^{13}C NMR (b) and ^{19}F NMR (c) spectra of compound **5**.

2.8. Synthesis of bisethynyl compounds 6a–e

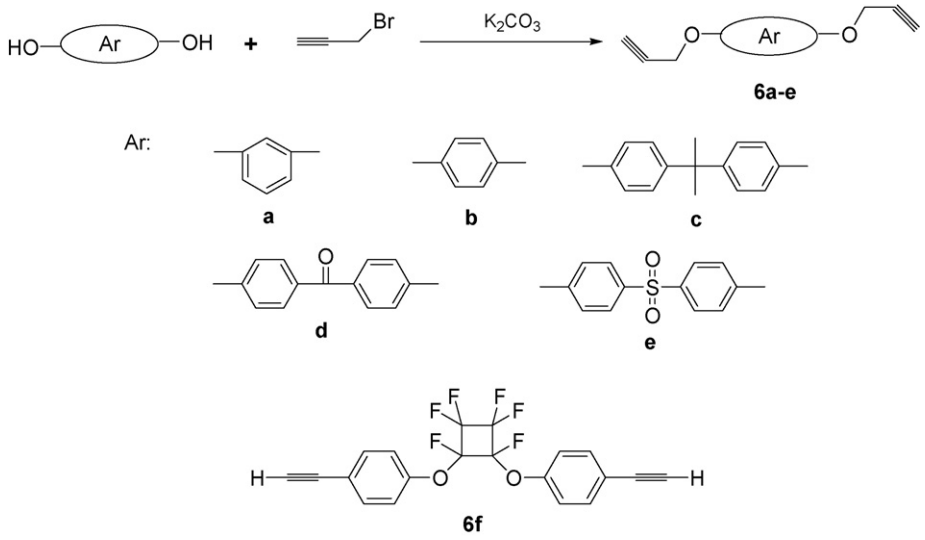
To a solution of the benzenediol (0.05 mol) in dry acetone (120 mL) was added excess anhydrous K_2CO_3 (40.0 g) and the reaction mixture was refluxed for 0.5 h. Then propargyl bromide (13.1 g, 0.11 mol) was added dropwise over 2 h to the above reaction mixture. The resulting mixture was refluxed for 20 h and then cooled, filtered and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 (150 mL) and the solution was washed with water (3 mL × 40 mL) followed by saturated brine solution (40 mL). The organic layer was dried over anhydrous $MgSO_4$ and then concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (8: 1) as eluent to give **6a–e**.

Compound **6a**: colorless liquid (7.5 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (1H, t, J = 7.25 Hz), 6.54 (2H, dd, J = 4.45 Hz), 6.49 (1H, t, J = 4.45 Hz), 4.65 (4H, d, J = 2.40 Hz), 2.50 (2H, t, J = 2.40 Hz). IR (neat, cm^{-1}): ν 3284, 3032, 2916, 2868, 2122, 1595, 1495, 1470, 1368, 1302, 1235, 1201, 1112, 1017, 935, 834, 695.

Compound **6b**: white solid (7.9 g, 86%): m.p. 48.2–48.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.93 (4H, s), 4.65 (4H, d, J = 2.40 Hz), 2.51 (2H, t, J = 2.40 Hz). IR (KBr, cm^{-1}): ν 3289, 3033, 2922, 2866, 2121, 1604, 1507, 1451, 1366, 1299, 1222, 1202, 1105, 1028, 923, 827.

Compound **6c**: white solid (11.3 g, 73%): m.p. 80.0–80.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 (4H, m), 6.86 (4H, m), 4.66 (4H, d, J = 2.40 Hz), 2.51 (2H, t, J = 2.40 Hz), 1.64 (6H, s). IR (KBr, cm^{-1}): ν 3285, 3035, 2967, 2870, 2116, 1604, 1508, 1454, 1364, 1297, 1264, 1221, 1182, 1028, 830.

Compound **6d**: white solid (10.4 g, 72%): m.p. 90.5–90.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (4H, d, J = 7.12 Hz), 7.04 (4H, d,



Scheme 3. Synthesis of bisethynyl compounds **6a–f**.

J = 7.12 Hz), 4.78 (4H, d, J = 2.40 Hz), 2.57 (2H, t, J = 2.40 Hz),. IR (KBr, cm^{-1}): ν 3289, 3065, 2923, 2868, 2123, 1647, 1598, 1506, 1452, 1417, 1373, 1309, 1232, 1166, 1020, 929, 845.

Compound **6e**: pale white solid (12.3 g, 75%): m.p. 180.0–181.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (4H, d, J = 7.12 Hz), 7.02 (4H, d, J = 7.12 Hz), 4.66 (4H, d, J = 2.40 Hz), 2.48 (2H, t, J = 2.40 Hz). IR (KBr, cm^{-1}): ν 3283, 3272, 3098, 2923, 2868, 2129, 1592, 1581, 1492, 1457, 1417, 1386, 1311, 1297, 1242, 1143, 1107, 1072, 833.

2.9. Synthesis of 1,2-bis(4-ethynylphenoxy)-perfluorocyclobutane 6f

Compound of **6f** was prepared according to the reference [5].

2.10. General procedure for polymerization

$CuSO_4{\cdot}5H_2O$ (7 mg, 5 mol%) and sodium ascorbate (12 mg, 10 mol%) dissolved in H_2O (10 mL) were added dropwise to a solution of bisethynyl compound **6a–f** (0.50 mmol) and 1,2-bis(4-azidomethylphenoxy)perfluorocyclobutane **5** (229 mg, 0.50 mmol) in DMSO (15 mL). The reaction mixture was stirred at 45 °C overnight. The solvent was decanted to leave a gum residue in the flask. The residue was then stirred in H_2O (20 mL) and concentrated ammonia (5 mL) for another 1 h. The mixture was filtered and the resulting filter cake was washed with H_2O (3 mL × 20 mL). The filter cake was then dissolved in DMSO, filtered again and precipitated into a 2:1 solution of water and methanol. The solid was separated and washed repeatedly with aqueous methanol before dried in a vacuum oven. The desired polymers **7a–f** were obtained as pale yellow solids, respectively.

Compound **7a**: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (2H, s), 7.61–7.54 (4H, br), 7.38–7.27 (4H, br), 7.10–7.05 (1H, br), 6.84 (1H, br), 6.55 (2H, d), 5.76 (4H, s), 5.18 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.0, 64.1, 104.4, 110.1, 120.6, 121.2, 127.4, 128.9, 131.9, 132.5, 136.4, 146.0, 154.5, 161.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −127 to −132. IR (KBr, cm^{-1}): ν 3138, 3075, 2944, 2876, 1596, 1509, 1491, 1463, 1432, 1384, 1319, 1304, 1263, 1201, 1176, 1149, 1113, 1048, 1017, 958, 899, 820. Mn = 72102, Mw = 85290, PI = 1.18.

Compound **7b**: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (2H, s), 7.37 (4H, br), 7.18 (4H, br), 6.92 (4H, br), 5.59 (4H, s), 5.03 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 54.9, 64.4, 118.4, 121.1, 121.6, 127.4, 129.7, 132.7, 136.5, 146.2, 154.0, 155.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −127 to −132. IR (KBr, cm^{-1}): ν 3137, 3075, 2938, 2869, 1606, 1508, 1461, 1432, 1382, 1320, 1304, 1263, 1201, 1171, 1113, 1047, 1013, 961, 823. Mn = 62230, Mw = 78715, PI = 1.26.

Compound **7c**: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (2H, s), 7.42 (4H, br), 7.27 (4H, br), 7.10 (4H, br), 6.92 (4H, br), 5.63 (4H, s), 5.10 (4H, s), 1.57 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 33.5, 44.1, 55.0, 64.0, 116.8, 120.8, 121.4, 127.9, 129.9, 130.5, 132.4, 136.4, 145.6, 146.0, 154.4, 158.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −127 to −132. IR (KBr, cm^{-1}): ν 3137, 3070, 2938, 2876, 1595, 1508, 1491, 1459, 1384, 1321, 1305, 1263, 1199, 1177, 1150, 1119, 1047, 1018, 962, 819. Mn = 64656, Mw = 78604, PI = 1.22.

Compound **7d**: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (2H, s), 7.69 (4H, br), 7.40 (4H, br), 7.24 (4H, br), 7.17 (4H, br), 5.63 (4H, s), 5.24 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 54.9, 64.2, 117.3, 121.1, 121.6, 127.6, 129.9, 132.3, 134.5, 134.8, 136.4, 145.3, 154.2, 164.4, 195.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −127 to −132. IR (KBr, cm^{-1}): ν 3138, 3066, 2928, 2876, 1647, 1600, 1508, 1462, 1421, 1310, 1251, 1204, 1169, 1116, 1048, 1013, 962, 928, 848, 770. Mn = 53608, Mw = 64376, PI = 1.20.

Compound **7e**: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (2H, s), 7.84 (4H, br), 7.46 (4H, br), 7.25–7.18 (8H, br), 5.61 (4H, s), 5.21 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 54.9, 64.4, 118.3, 121.1, 121.6, 127.6, 129.8, 132.1, 132.5, 136.4, 136.5, 145.0, 154.5, 164.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −127 to −132. IR (KBr, cm^{-1}): ν 3141, 3070, 2958, 2870, 1593, 1509, 1495, 1464, 1318, 1292, 1258, 1203,

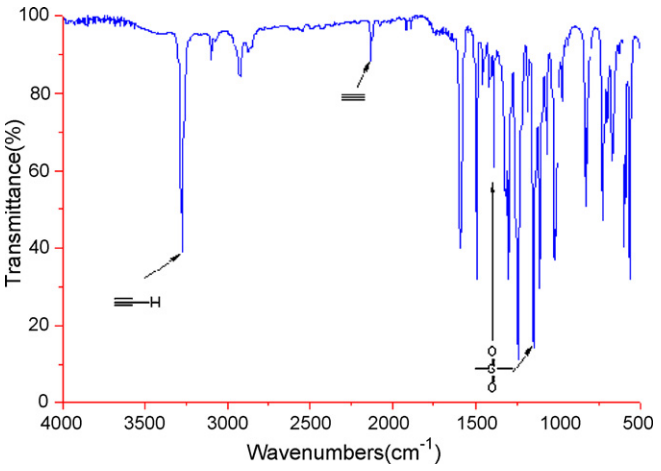


Fig. 2. IR spectrum of monomer **6e**.

1177, 1151, 1107, 1049, 1017, 963, 834, 718. Mn = 51499, Mw = 61457, PI = 1.19.

Compound **7f**: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (2H, s), 7.91 (4H, br), 7.40 (4H, br), 7.27 (8H, br), 5.65 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 54.9, 121.1, 121.3, 121.5, 124.6, 129.8, 129.9, 132.7, 132.8, 136.4, 136.6, 148.3, 153,9, 154.0, 154.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −127 to −132. IR (KBr, cm^{-1}): ν 3137, 3046, 2946, 2928, 2847, 1614, 1560, 1510, 1496, 1459, 1320, 1266, 1201, 1169, 1117, 1045, 1017, 958, 839, 772. Mn = 29070, Mw = 35968, PI = 1.24.

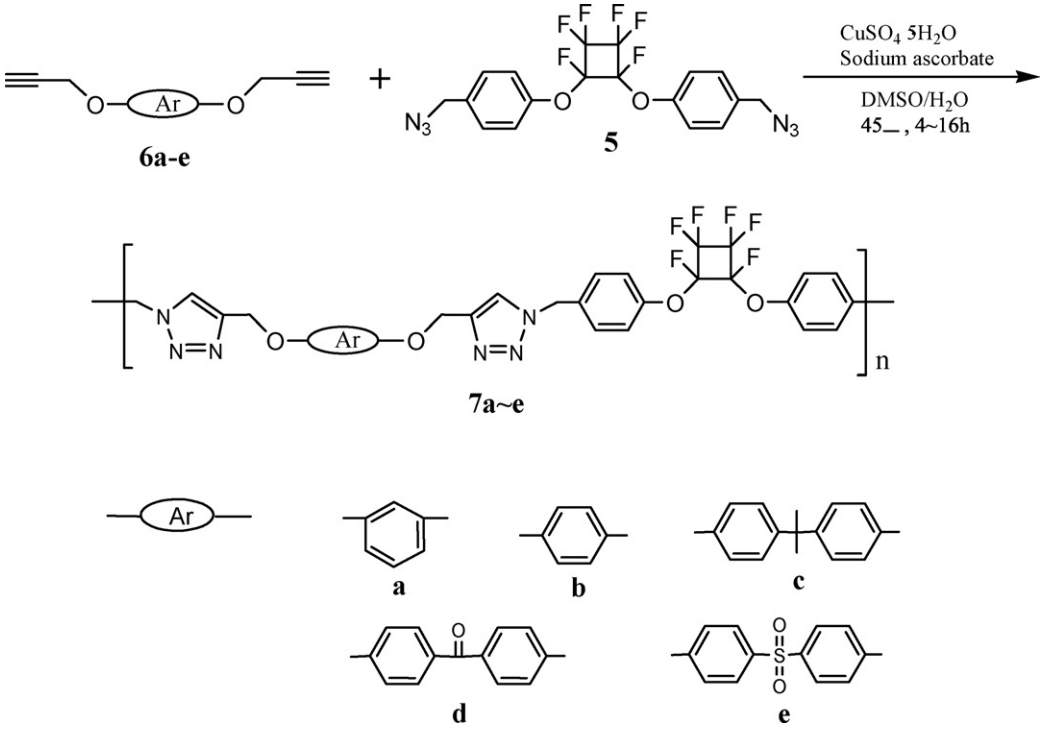
3. Results and discussion

3.1. Synthesis and characterization of 1,2-bis(4-azidomethylphenoxy)perfluorocyclo-butane 5

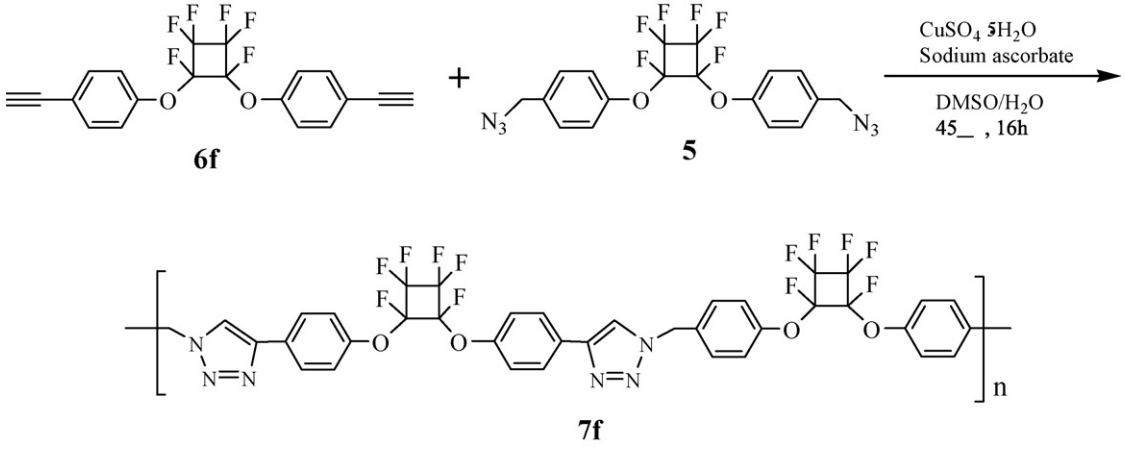
The synthesis of compound **5** was outlined in Scheme 2. Compound **2** was synthesized in high purity by treatment of potassium 4-methylphenolate with $BrCF_2CF_2Br$ followed by dehalogenation with zinc. Although a series of p-substituted aromatic trifluorovinyl ethers were prepared [6], to the best of our knowledge, there was no report about the synthesis of 1-methyl-4-trifluorovinyloxybenzene **2**. The thermal [2π + 2π] cyclodimerization of **2** at 160 °C provided 1,2-bis(4-methylphenoxy)perfluorocyclobutane **3** in 91% yield. The light-induced bromination of **3** with *N*-bromosuccinimide gave compound **4** in 93% yield [7]. Finally, treatment of **4** with NaN_3 provided the desired compound **5** in 67% yield. There was a strong stretch vibration at 2100 cm^{-1} in the IR spectrum of compound **5**. The structure of **5** was further confirmed by ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra (Fig. 1).

3.2. Synthesis of bisethynyl compounds 6a–f

The monomers **6a–e** were prepared from the phenols and propargyl bromide in the presence of K_2CO_3 (Scheme 3). They were



Scheme 4. Synthesis of polymers **7a–e** via click chemistry.



Scheme 5. Synthesis of polymer **7f** via click chemistry.

characterized by FT-IR which showed the characteristic absorption owing to –H bond of the propargyl groups near 3285 cm^{-1}. The absorption owing to the C≡C appeared as a weak band at about 2120 cm^{-1}. The typical IR spectrum of **6e** was shown in Fig. 2. The monomer **6f** was prepared from 4-bromophenol through five steps and the detailed procedures were reported in our published paper [5].

3.3. Synthesis and characterization of polymers 7a–f

The polymers containing perfluorocyclobutyl and triazole unites **7a–f** were obtained in 67–82% from the click reactions of monomers **5** and **6a–f** respectively (Schemes 4 and 5). Click reactions were carried out in a 3:2 solvent ratio of DMSO to H_2O using 5 mol% $CuSO_4{\cdot}5H_2O$ with 10 mol% sodium ascorbate as the in situ reducing agent to generate the active Cu(I) species [8]. The reaction temperature played key role in the formation of fluorinated polymers. It was found that the polymers with reasonable molecular weight were obtained when the click reactions were carried out at 45 °C.

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 perfluorocyclobutyl 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. The monomers **5** and **6f** and polymer **7f** all have PFCB groups which were confirmed in their IR spectra (Fig. 3). The perfluorocyclobutyl groups in PFCB polymers were characterized further by ^{19}F NMR (Fig. 4), in which fluorine signals of these groups were presented from −127 to −132 ppm. The 1,2-disubstituted perfluorocyclobutyl group was further identified in the ^{13}C NMR spectrum of polymers **7a–f** by the presence of several separated multiplets near 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 polymers **7a–f** adjacent (*ipso*) and *ortho* to the perfluorocyclobutyl ether linkage did give separate signals dictated by the 1,2-disubstituted *cis*/*trans* configuration of the ring: the *ipso* carbon signals near 154.0 (presumably *trans*) and 154.2 ppm (*cis*) (Fig. 4c). The 1,2,3-triazole rings of the polymer were characterized by signals near 8.3 ppm of the triazole protons in the ^1H NMR spectrum (Fig. 4a), and signals at 148.3

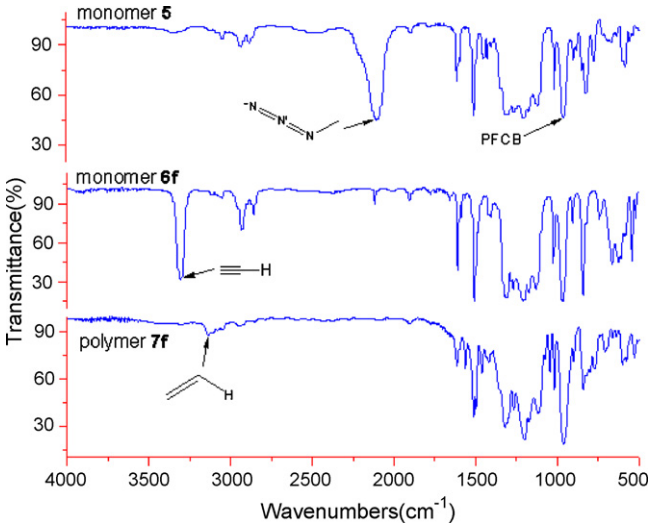


Fig. 3. IR spectra of monomers **5**, **6f** and polymer **7f**.

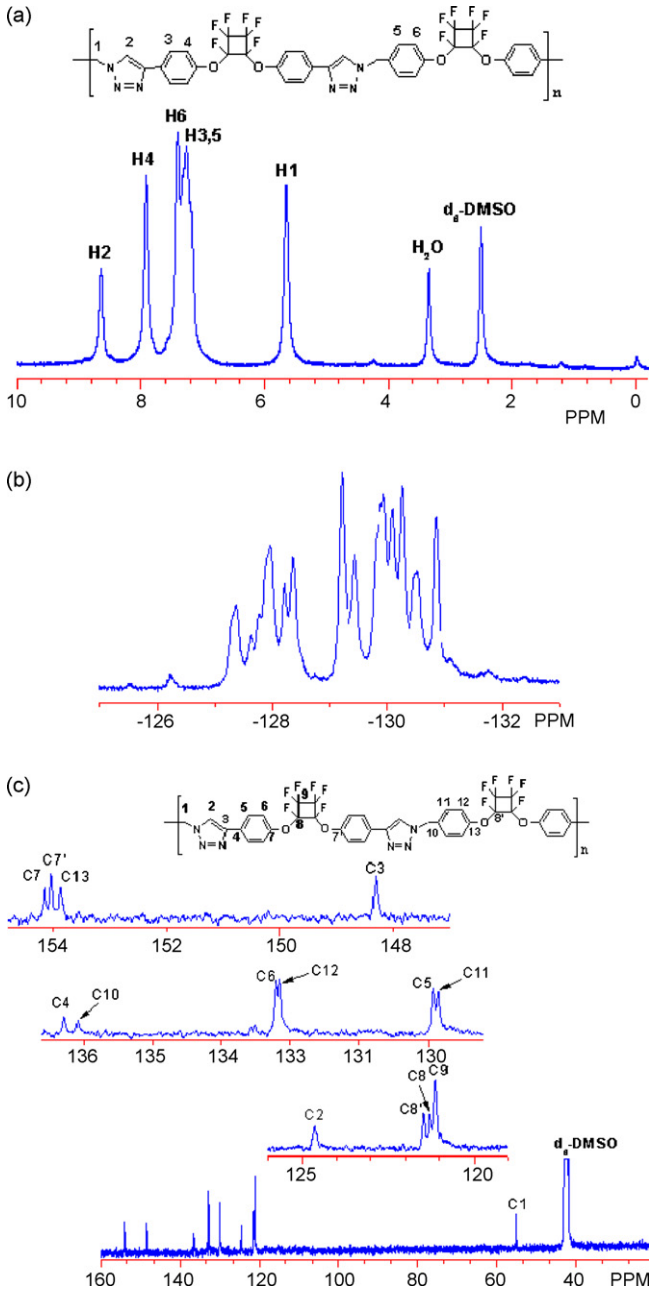


Fig. 4. ^1H NMR (a), ^{19}F NMR (b) and ^{13}C NMR (c) spectra of polymer **7f**.

and 124.6 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 vibration near 3135 cm^{-1} in the FT-IR spectrum (Fig. 3).

Table 1
Solubility of PFCB polymers

Polymers	Acetone	THF	$CHCl_3$	Conc. H_2SO_4	NMP	DMAc	DMSO	DMF
a	±	±	±	±	+	+	+	+
7b	±	±	±	±	+	+	+	+
7c	±	±	±	±	+	+	+	+
7d	–	–	–	±	+	+	+	+
7e	–	–	–	±	+	+	+	+
7f	±	+	–	±	+	+	+	+

Note: (+) Soluble; (±) swell; (–) insoluble.

Table 2
Physical properties of PFCB polymers

Polymers	Mn[a]	Mw[a]	(Mw/Mn)[a]	T_g[b] (°C)	T_d[b] (°C)
7a	72,102	85,290	1.18	91	340
7b	62,230	78,715	1.26	106	345
7c	64,656	78604	1.22	98	332
7d	53,608	64,376	1.20	–	334
7e	51,499	61,457	1.19	–	339
7f	29,070	35,968	1.24	156	370

[a] GPC in DMF vs. polystyrene at 35 °C.
[b] DSC and TGA at 10 °C/min in N_2.

3.4. Properties of polymers

3.4.1. Solubility of polymers

The solubility of the PFCB polymers in common organic solvent was determined quantitatively by dissolving 5.0 mg of solid polymers in 1.0 mL of solvents (Table 1). It can be seen that these perfluorocyclobutyl-containing polymers showed good solubility in dipole organic solvents, such as NMP, DMAc, DMSO and DMF. But they can not dissolve or can just swell in acetone, THF and $CHCl_3$ with the exception of polymer **7f** which can be dissolved in THF because of two PFCB groups in one repeating unit that make the polymer backbone more flexible. Polymers **7a**–**f** can swell in conc. H_2SO_4 owing to the effect of hydrogen bonds between the solution and the polymers.

3.4.2. Molecular weights and their distributions of PFCB polymers

The corresponding data of GPC analysis in DMF for **7a**–**f** were listed in Table 2. The molecular weights were reduced from **7a** to **7f**. The shorter the repeating unit of the polymer chain was, the higher the molecular weight was. All the polydispersities of fluoropolymers **7a**–**f** were about 1.2 which indicated that the click chemistry was efficient for polymerization.

3.4.3. Thermal properties of polymers

Thermal properties of the PFCB polymers were evaluated by means of thermo-gravimetric analysis (Fig. 5) and differential scanning calorimetry (Fig. 6). The resulting data are listed in Table 2. The polymers **7a**–**e** started to decompose at about 340 °C, and there were the second stage of weight loss at 420 °C, which might be caused by the decomposition of triazole rings. The values of T_g were determined from the DSC curves. The molecular structure of **7b** is more rigid than **7a**, so its T_g is higher. It is a little difficult to determine the T_g of polymers **7d** and **7e**, because there is no apparent transformation in their DSC curves. The polymer **7f** contains more fluorine than others, which makes higher T_g and T_d. The curves of DSC (Fig. 6) also showed that all PFCB polymers mostly were amorphous, which had been further confirmed by the X-ray of these polymers (Fig. 7).

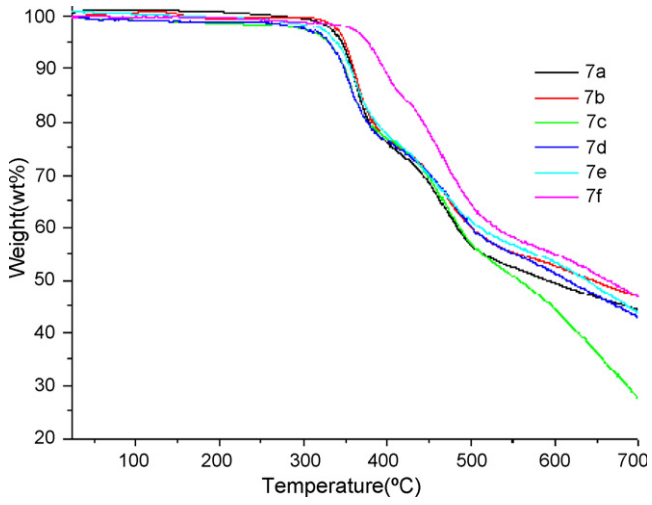


Fig. 5. TG curves of polymers **7a**–**f**.

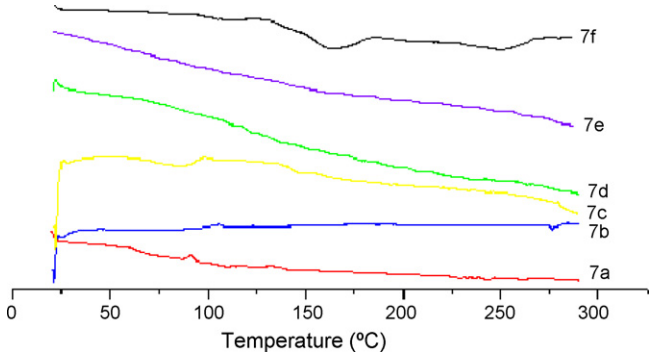


Fig. 6. DSC curves of polymers **7a**–**f**.

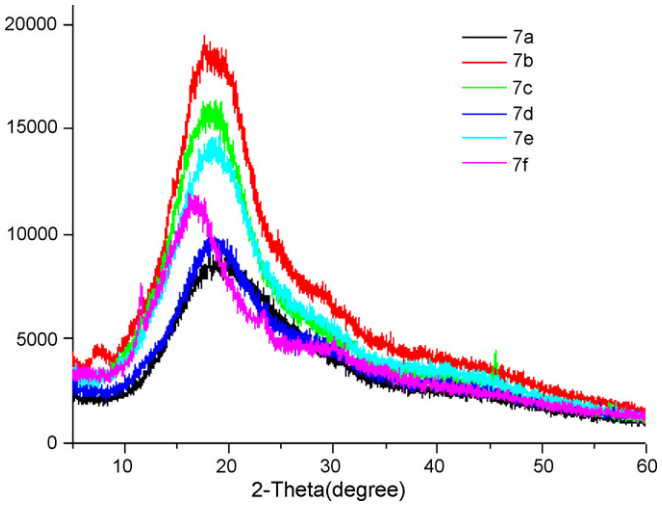


Fig. 7. Wide-angle X-ray diffraction patterns of polymers **7a**–**f**.

4. Conclusion

A novel monomer 1,2-bis(4-azidomethylphenoxy) perfluorocyclobutane was prepared. The click chemistry of 1,2-bis(4-azidomethylphenoxy) perfluorocyclobutane and bisethynyl compounds provided a novel class of linear aromatic ether polymers containing perfluorocyclobutyl and triazole unites. The resulting polymers mostly are amorphous and have good solubility in most dipole solvents and thermal stability.

Acknowledgments

We are grateful to National Natural Science Foundation of China, the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT0526) and Shanghai Municipal Scientific Committee for the financial support.

References

[1] H.C. Kolb, M.G. Finn, K.B. Sharpless, Angew. Chem. Int. Ed. 40 (2001) 2004–2021.
[2] For reviews see:
(a) J.F. Lutz, Angew. Chem. Int. Ed. 46 (2007) 1018–1025;
(b) W.H. Binder, R. Sachsenhofer, Macromol. Rapid Commun. 28 (2007) 15–54;

(c) H. Nandivada, X. Jiang, J. Lahann, Adv. Mater. 19 (2007) 2197–2208;
(d) D. Fournier, R. Hoogenboom, U.S. Schubert, Chem. Soc. Rev. 36 (2007) 1369–1380.
[3] J. Scheirs (Ed.), Modern Fluoropolym., J. Wiley & Sons, England, 1997.
[4] (a) D.W. Smith Jr., D.A. Babb, H.V. Shah, Macromolecules 29 (1996) 852–860;
(b) D.W. Smith Jr., D.A. Babb, H.V. Shah, A. Hoeglund, R. Traiphol, D. Perahia, H.W. Boone, C. Langhoff, M. Radler, J. Fluorine Chem. 104 (2000) 109–117;
(c) X.Y. Huang, R.W. Wang, P.Q. Zhao, G.L. Lu, S. Zhang, F.L. Qing, Polymer 46 (2005) 7590–7597.
[5] Y.Q. Zhu, Y.G. Huang, W.D. Meng, H.Q. Li, F.L. Qing, Polymer 47 (2006) 6272–6279.
[6] B.K. Spraul, S. Suresh, J. Jin, D.W. Smith Jr., J. Am. Chem. Soc. 128 (2006) 7055–7064.
[7] G.J.M. Gruter, O.S. Akkerman, F. Bickelhaupt, J. Org. Chem. 59 (1994) 4473–4481.
[8] B. Helms, J.L. Mynar, C.J. Hawker, J.M.J. Frechet, J. Am. Chem. Soc. 126 (2004) 15020–15021.