Preparation and Properties of Novel AEPs Containing Perfluorocyclobutyl and Triazole Unites

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Abstract. A series of a novel class of linear aromatic ether polymers (AEP) containing perfluorocyclobutyl and triazole unites were synthesized by click chemistry and their structures and properties that were characterized by FT-IR, 1H NMR, GPC, TGA, DSC and WAXD. The results showed that these polymers exhibited relatively small molecular weight distributions (about 1.1), mostly were amorphous, and had good solubility in most dipole solvents and thermal stability. These polymers were reported to have potential value in material science. The reaction mechanism was well elucidated of the click chemistry indicated that it was efficient for polymerization.

Introduction

Fluoropolymers have been obtained increasing attention in the development of advanced materials with chemical resistance and superior electrical insulating ability, high thermal and oxidative stability[1-3]. In recent years, partially fluorinated polymers containing perfluorocyclobutane (PFCB) rings have been intensively studied[4]. PFCB aromatic ether polymers, combined with 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 [2π+2π] cyclopolymerization of aryl trifluorovinyl ethers in bulk or solution. However, this polymerization process generally need high temperature ( >150℃ ) and long reaction time[5-7].

The copper(I)-catalyzed azide-alkyne cycloaddition reaction is an effective and versatile representative of the click reactions, which are characterized by high yield, mild reaction condition, and extremely high compatibility with functional groups[8]. Click chemistry is widely used in polymer synthesis as well as the modification of surfaces nanometer- and mesoscale structures[9,10]. In this work, the synthesis and characterization 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 are amply carried out.

Experimental Part

Materials. DMSO, acetonitrile, and acetone were dried over calcium hydride, and distillated before use. THF was distilled under nitrogen over sodium. Granular zinnes were activated with 0.1 M hydrochloric acid, washed by using ethanol and ether, and dried at 120℃ under vacuum for 4h. Other reagents or materials were used as received.
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 obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. Mass spectrometry was 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$_4$Si ($^1$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 detector (RI), a Waters 2487 dual-wavelength λ absorbance detector and a set of Waters Styrage columns (HR3, HR4 and HR5, 7.8×300 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. Intrinsic viscosities were determined on DMSO solutions at a concentration of 0.5 g/dL using an Ubbelohde capillary viscometer with 0.5-0.6 mm diameter at 30.0±0.1 °C. 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 20 range of 5-60 °. Contact angles(CAs) and advancing/receding CAs were measured by OCA 40 (Dataphysics Co., Germany) at ambient temperature, and the values were averages from measurements on at least five different positions for each sample. The water repellency rating (spray test method) and oil repellency rating of the treated cotton fabrics were measured according to AATCC test methods 22-2001 and 118-2002, respectively[11].

Synthesis of compound Ⅰ-Ⅴ(Scheme 1).
Synthesis of 1-(2-bromo-1,1,2,2-tetrafluoroethoxy)-4-methylbenzene I. To a 1000 mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, a condenser, and a Dean-Stark azeotropic distillation assembly were added p-cresol (108.0 g, 1.00 mol), potassium hydroxide (80%, 70.0 g, 1.00 mol), DMSO (500 ml) and toluene (200 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 (312.0 g, 1.20 mol) was added dropwise while it was cooled 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 (1600 mL) and extracted with dichloromethane. The organic phase was washed for three times by using water, dried over MgSO₄. The solution was distilled under ambient pressure and then the pressure was reduced to give I as a colorless liquid (202.5 g, 71%): b.p. 43°C (ca. 8 mmHg).

1H NMR (400 MHz, CDCl₃) δ: 7.16 (2H, d, J = 8.48 Hz), 7.11 (2H, d, J = 8.56 Hz) and 2.37 (3H, s).

19F NMR (376 MHz, CDCl₃) δ: -67.8, -85.9. IR (KBr, cm⁻¹): ν 3040, 2959, 2930, 2854, 1597, 1508, 1328, 1220, 1196, 1164, 1127, 1101, 1020, 932, 844 and 778.

Synthesis of 1-methyl-4-trifluorovinyloxybenzene II. To a 1000 mL dry three-necked flask equipped with a magnetic stirrer, a thermometer and a condenser under nitrogen were added into compound I (190.0 g, 0.66 mol) slowly for over 1 h. Finally, they constructed a stirring mixture of granular Zn (39.0 g, 0.60 mol) in acetonitrile (700 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 II as a colorless liquid (81.3 g, 65%): b.p. 32°C (ca. 8 mmHg).

1H NMR (400 MHz, CDCl₃) δ: 7.15 (2H, d, J = 8.42 Hz), 6.99 (2H, d, J = 8.44 Hz) and 2.32 (3H, s).

19F NMR (376 MHz, CDCl₃) δ: -120.1, -127.2, -133.6. IR (KBr, cm⁻¹): ν 3040, 2962, 2930, 2855, 1833, 1611, 1507, 1314, 1285, 1278, 1195, 1168, 1140, 1017, 820 and 739.

Synthesis of 1, 2-bis (4-methylphenoxy) perfluorocyclobutane III. Compound II (76.0 g, 0.40 mol) was heated neatly at 160°C for 36 h in a 100 mL single-necked round-bottom flask under N₂. The product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 90/1) to give III as clear oil (69.5 g, 92%).

1H NMR (400 MHz, CDCl₃) δ: 7.00-7.13 (8H, m), 2.31 (6H, s).

19F NMR (376 MHz, CDCl₃) δ: -128.4, -128.8, -129.8, -130.3, -130.4, -130.7, -131.2, -131.2. MS (EI): m/z 377, 376, 375, 269, 188, 168, 141, 108, 91, 77, 65. IR (KBr, cm⁻¹): ν 3039, 2958, 2868, 1612, 1596, 1508, 1455, 1403, 1382, 1319, 1285, 1266, 1197, 1170, 1116, 1019, 962, 899, 815 and 754.

Synthesis of 1, 2-bis (4-bromomethylphenoxy) perfluorocyclobutane IV. a mixture of compound III (60.2g, 0.16mol), N-bromosuccinimide (NBS, 57g, 0.32mol) and dry CCl₄ (700mL) were 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 by a rotary evaporator to produce crude product. The crude product was recrystallized from ethanol to produce compound IV as white solid (80.5 g, 94%): m.p. 99°C.

1H NMR (400 MHz, CDCl₃) δ: 7.35-7.38 (4H, m), 7.05-7.15 (4H, dd, J = 8.0 Hz, 8.5 Hz), 4.45 (4H, s).

13C NMR (100 MHz, CDCl₃) δ: 34.6, 120.8, 120.9, 132.8, 132.9, 137.4, 154.4. 19F NMR (376 MHz, CDCl₃) δ: -127.7, -127.9, -128.4, -128.6, -129.5, -130.2, -130.5, -131.3, -131.6. IR (KBr, cm⁻¹): ν 3042, 2970, 2927, 2856, 1608, 1508, 1322, 1288, 1198, 1177, 1117, 1018, 963, 833, 603. MS (EI): m/z 456, 455, 454, 453, 187, 106, 90, 89, 78. Anal. Calcd for C₁₈H₁₂Br₂F₆O₂: C, 40.21; H, 2.27. Found: C, 39.96; H, 2.25.

Synthesis of 1, 2-bis (4-azidomethylphenoxy) perfluorocyclobutane V. To a 500 mL single-necked flask equipped with a reflux condenser and a magnetic stirrer were added into a compound IV (75 g, 0.14 mol) and NaN₃ (18.2 g, 0.28 mol) in DMF (360 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 × 100 mL). The combined organic layer was washed with saturated brine solution (100 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 V as colorless liquid (43.5 g, 68%). 1H NMR (400 MHz, CDCl₃) δ: 7.28-7.32 (4H, m), 7.11-7.21 (4H, dd, J = 8.4 Hz, 8.5 Hz), 4.32 (4H, s). 13C NMR (100 MHz, CDCl₃) δ: 56.3, 120.7, 121.0, 132.0, 134.7, 135.1, 154.6. 19F NMR (376 MHz, CDCl₃) 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 C₁₈H₁₂F₆N₆O₂: C, 47.35; H, 2.65; N, 18.34. Found: C, 47.46; H, 2.70; N, 18.43.

**Synthesis of bisethynyl compounds VI a-d (Scheme 2).** To a solution of the benzenediol (0.10 mol) in dry acetone (240 mL) excess anhydrous K₂CO₃ (60.0 g) was added and the reaction mixture was refluxed for 0.5 h. Then propargyl bromide (26.2 g, 0.22 mol) was added dropwise over 2 h into 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 CH₂Cl₂ (300 mL) and the solution was washed with water (3×80 mL) followed by saturated brine solution (80 mL). The organic layer was dried over anhydrous MgSO₄ and then concentrated in vacuo. The residue was purified by column chromatography on silica gel by using petroleum ether/ethyl acetate (8 : 1) as eluent to give VI a-c.

![Scheme 2. Synthesis of compound VI a-d](image)

**Compound VI a:** white solid (16 g, 86%): m.p. 48°C. 1H NMR (400 MHz, CDCl₃) 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 VI b:** white solid (22.5 g, 72%): m.p. 80°C. 1H NMR (400 MHz, CDCl₃) 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 VI c:** pale white solid (24.5 g, 75%): m.p. 181°C. 1H NMR (400 MHz, CDCl₃) 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, 3098, 2923, 2868, 2129, 1592, 1581, 1492, 1456, 1417, 1386, 1311, 1298, 1242, 1144, 1107, 1072, 833.
Synthesis of 1,2-bis(4-ethynylphenoxy)-perfluorocyclobutane VI d. Compound of VI d was prepared according to the reference [12].

Synthesis of polymer VI a-d (Scheme 3 and Scheme 4). CuSO₄·5H₂O (14 mg, 10 mol%) and sodium ascorbate (24 mg, 20 mol%) dissolved in H₂O (20 mL) were added dropwise into a solution of bis ethynyl compound VIa-d (1.00 mmol) and 1, 2-bis (4-azidomethylphenoxy) perfluorocyclobutane V (458 mg, 1.00mmol) in DMSO (30 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 H₂O (40 mL) and concentrated ammonia (10 mL) for another 1 h. The mixture was filtered and the resulting filter cake was washed by using H₂O (3 × 40 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 VII a-d were obtained as pale yellow solids, respectively.

Scheme 3. Synthesis of polymers VII a-c

Scheme 4. Synthesis of polymer VII d

Compound VII a: 76%. ¹H NMR (400 MHz, CDCl₃) δ: 8.25 (2H, s), 7.38 (4H, br), 7.18 (4H, br), 6.91 (4H, br), 5.59 (4H, br), 5.03 (4H, s). ¹³C NMR (100MHz, CDCl₃) δ: 54.9, 64.5, 118.4, 121.1,
121.6, 127.4, 129.8, 132.7, 136.5, 146.2, 154.1, 155.4. $^{19}$F NMR (376MHz, CDCl$_3$) δ: -127~132. IR (KBr, cm$^{-1}$): ν 3138, 3075, 2938, 2868, 1606, 1508, 1461, 1433, 1382, 1320, 1304, 1263, 1202, 1171, 1113, 1045, 1013, 961, 823. Mn = 72484, Mw = 79732, PI = 1.10.

Compound VII b: 84%. $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.30 (2H, s), 7.41 (4H, br), 7.27 (4H, br), 7.10 (4H, br), 6.93 (4H, br), 5.62 (4H, s), 5.10 (4H, s), 1.57 (6H, s). $^{13}$C NMR (100MHz, CDCl$_3$) δ: 33.5, 44.2, 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 (376MHz, CDCl$_3$) δ: -127~132. IR (KBr, cm$^{-1}$): ν 3135, 3070, 2958, 2876, 1593, 1509, 1495, 1464, 1318, 1292, 1258, 1203, 1177, 1151, 1107, 1049, 1017, 963, 834, 718. Mn = 58304, Mw = 66467, PI = 1.14.

Compound VII c: 72%. $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.30 (2H, s), 7.84 (4H, br), 7.46 (4H, br), 7.25–7.17 (8H, br), 5.62 (4H, s), 5.21 (4H, s). $^{13}$C NMR (100MHz, CDCl$_3$) δ: 54.9, 64.4, 118.3, 121.1, 121.6, 127.7, 129.8, 132.1, 132.5, 136.4, 136.5, 145.0, 154.5, 164.8. $^{19}$F NMR (376MHz, CDCl$_3$) δ: -127~132. IR (KBr, cm$^{-1}$): ν 3141, 3070, 2958, 2870, 1593, 1509, 1495, 1464, 1318, 1292, 1258, 1203, 1177, 1151, 1107, 1049, 1017, 963, 834, 718. Mn = 58304, Mw = 66467, PI = 1.14.

Compound VII d: 78%. $^1$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 (100MHz, 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 (376MHz, CDCl$_3$) δ: -127~132. IR (KBr, cm$^{-1}$): ν 3137, 3045, 2946, 2928, 2847, 1614, 1560, 1510, 1496, 1459, 1320, 1266, 1201, 1169, 1117, 1045, 1017, 958, 839, 772. Mn = 33728, Mw = 36764, PI = 1.09.

Results and Discussion

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 was seen that these perfluorocyclobutyl-containing polymers showed good solubility in dipole organic solvents, such as NMP, DMAc, DMSO and DMF. But they cannot dissolve or can just swell in non-polar solvents such as acetone, THF and CHCl$_3$ with the exception of polymer VII d which can be dissolved in THF because of two PFCB groups in one repeating unit that make the polymer backbone more flexible. All PFCB polymers can swell in conc. H$_2$SO$_4$ owing to the effect of hydrogen bonds between the solution and the polymers.

Table 1. Solubility of PFCB polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Acetone</th>
<th>THF</th>
<th>CHCl$_3$</th>
<th>Conc. H$_2$SO$_4$</th>
<th>NMP</th>
<th>DMSO</th>
<th>DMAc</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII a</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>VII b</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>VII c</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>VII d</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Note: (+): soluble; (+−): swell; (−): insoluble.
Molecular weights and their distributions of polymers VIIa-d. The corresponding data of GPC analysis in DMF for VIIa-d were listed in Table 2. The molecular weights were reduced from VIIa to VIIId. The shorter the repeating unit of the polymer chain was, the higher the molecular weight was. All the polydispersities of fluoropolymers VIIa-d were about 1.1 which indicated that the click chemistry was efficient for polymerization.

Table 2. Physical properties of PFCB polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>M_n</th>
<th>M_w</th>
<th>(M_w/M_n)</th>
<th>T_g(°C)</th>
<th>T_d(°C)</th>
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<tbody>
<tr>
<td>VII a</td>
<td>72484</td>
<td>79732</td>
<td>1.10</td>
<td>106</td>
<td>345</td>
</tr>
<tr>
<td>VII b</td>
<td>70271</td>
<td>78703</td>
<td>1.12</td>
<td>123</td>
<td>332</td>
</tr>
<tr>
<td>VII c</td>
<td>58304</td>
<td>66467</td>
<td>1.14</td>
<td>-</td>
<td>339</td>
</tr>
<tr>
<td>VII d</td>
<td>33728</td>
<td>36764</td>
<td>1.09</td>
<td>156</td>
<td>370</td>
</tr>
</tbody>
</table>

Thermal properties of polymers. Thermal properties of the PFCB polymers were evaluated by means of thermo- gravimetric analysis (TGA, Figure 1) and differential scanning calorimetry (DSC, Figure 2). The resulting data are listed in Table 2. The polymers VIIa-d 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 VIIb is more rigid than VIIa. So its T_g is high. It is not easy to determine the T_g of polymers VIIc, because there is no apparent transformation in their DSC curves. The polymer VIIId contains more fluorine than others, which makes its T_g and T_d higher. The curves of DSC (Figure 2) also show that all PFCB polymers mostly are amorphous, which had been further confirmed by the X-ray of these polymers (Figure 3).

Surface free energy and wettabilities of VIIa-d/the treated cotton fabrics. Surface free energy of VIIa-d (calculated by Wu’s method) was determined by measuring the CAs of different test liquids on the smooth cast films. When water, n-hexadecane, and n-decane are used as the wetting
liquids, corresponding CAs are listed in Table 3, and 110-115 for water, 78-91 for n-hexadecane, and 77-84 for n-decane, respectively. The very low surface energy (14.11-14.38 mJ/m²) of the hyperbranched polymers and the short fluoroalkyl chains. The results also imply that the molecular weights and DBs of VIIa-d have little effects on the surface free energy.

Table 3 Static CAs of VIIa-d smooth films/the treated cotton fabrics for different wetting liquids and the surface free energy

<table>
<thead>
<tr>
<th>Samples</th>
<th>Water</th>
<th>C16b</th>
<th>C10b</th>
<th>surface free energy</th>
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<tr>
<td></td>
<td>S.F.</td>
<td>T.F.</td>
<td>S.F.</td>
<td>T.F.</td>
</tr>
<tr>
<td>VIIa</td>
<td>112</td>
<td>145</td>
<td>80</td>
<td>121</td>
</tr>
<tr>
<td>VIIb</td>
<td>110</td>
<td>143</td>
<td>78</td>
<td>119</td>
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<tr>
<td>VIIc</td>
<td>113</td>
<td>143</td>
<td>79</td>
<td>118</td>
</tr>
<tr>
<td>VIIId</td>
<td>115</td>
<td>152</td>
<td>91</td>
<td>126</td>
</tr>
</tbody>
</table>

Notes: *S.F.=smooth films, T.F.=treated fabrics; bC16= n-hexadecane, C10= n-decane.

Conclusion

A novel monomer V was prepared. The click chemistry of bis azide compound V and bis ethynyl compounds VI a-d 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. Due to the characteristics of fluorine atoms, the enhanced appearance of fluorinated portions on the surfaces of fluorine-containing polymers is important in the potential applications, e.g. anti-thermal, water repellency, chemical proof and electric insulation materials.

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References