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ORIGINAL ARTICLE

Novel polyelectrolytes containing perfluorocyclobutane and triazole units: synthesis, characterization and properties

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A new class of aryl trifluorovinyl ether monomers were designed and synthesized, and novel fluorinated polymers containing perfluorocyclobutane and 1H-1,2,3-triazole units were prepared from these monomers. These polymers were characterized by nuclear magnetic resonance spectroscopy, thermo-gravimetric analysis and differential scanning calorimetry. The temperatures of 5% weight loss of the polymers under nitrogen were up to $\sim 290\,^\circ\text{C}$, and the glass transition temperatures of the polymers were in the range of 79–110 °C. These new polymers showed good solubility in common organic solvents such as dimethyl sulfoxide and N,N-dimethylacetamide. In addition, the proton conductivity of the polymers was measured under anhydrous conditions using impedance spectroscopy, and a maximum conductivity of $2.85\,\mu\text{S cm}^{-1}$ was obtained at 200 °C.
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Keywords: fluorinated polymers; oligo(ethylene oxide); polyelectrolytes; triazole

INTRODUCTION

Proton-conducting polymers have attracted much attention as promising materials for membranes for fuel cells. The operation of proton exchange membrane fuel cells at medium temperatures (100–200 °C) can provide many advantages, such as improved carbon monoxide tolerance, higher energy efficiency and simplified heat management.[1–4] Thus far, many efforts have been made to develop proton-conducting materials for medium temperature fuel cells.[5–8]

One of these approaches involves finding compounds with an amphoteric nature to act as water substitutes. Recently, nitrogen-containing heterocyclic compounds, such as imidazole, pyrazole and benzimidazole, have been suggested as proton solvents for proton exchange membrane fuel cells, and they may also be covalently tethered to some suitable polymers to prepare fully polymeric materials.[9–18] Liu et al.[19] suggested that 1H-1,2,3-triazole has adequate electrochemical stability for fuel cell applications, and the 1H-1,2,3-triazole groups immobilized on a polymer backbone may open up new avenues in the design of polyelectrolytes. To date, several polymeric systems with tethered 1H-1,2,3-triazole moieties have been evaluated as polyelectrolytes.[13–17] However, most of these polymers derived from polyacrylate or polyethylene may have issues related to their electrochemical or dimensional stability for medium temperature fuel cells. During the past decade, partially fluorinated polymers containing perfluorocyclobutane (PFCB) rings have been developed.[19–21] These polymers exhibit high-thermal/oxidative/mechanical stability, good chemical resistance and flexibility. In addition, it was recently reported that this type of polymer could be promising for use in the membranes of fuel cells.[22,23] From this point of view, we have been trying to develop new partially fluorinated ionomers into which both PFCB and 1H-1,2,3-triazole units are incorporated. In these ionomers, triazole units are covalently grafted to the polymer backbone containing PFCB groups by flexible chains, which may increase the mobility of triazole units to facilitate proton transfer.

In this work, we report the synthesis and characterization of novel polymers containing PFCB and 1H-1,2,3-triazoles moieties. The polymer backbones and 1H-1,2,3-triazoles units are connected by flexible oligo(ethylene oxide) chains. These polymers were prepared from novel aromatic trifluorovinyl ether monomers (**6**) via thermal ($2\pi+2\pi$) cyclopolymerization. The preparation process, the corresponding composition and structure, and some physical properties of these polymers were investigated.

EXPERIMENTAL PROCEDURE

Materials

All chemicals were purchased from Sigma-Aldrich (Sigma-Aldrich Shanghai Trading Co. Ltd., Shanghai, China) with the exception of 1,2-dibromotetrafluoroethane (Shanghai Sinofluoro Scientific Co., Ltd, Shanghai, China). Acetonitrile and dimethyl sulfoxide (DMSO) were purified by standard methods before use. Zinc turnings were activated by treating with 5% aqueous hydrochloric acid. Propargyl mono-terminated oligo(ethylene oxide)s (**3**) and azidomethyl pivalate were prepared using previously published methods.[24,25] Other reagents or materials were used as received.

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Measurements

Gas chromatography/mass spectrometry was recorded on a Finnigan-MAT-8430 (Thermo Finnigan MAT GmbH, Bremen, Germany) instrument using EI ionization at 70 eV. Elemental analysis was carried out on a Carlo-Erba1106 system (Elementar Analysensysteme GmbH, Hanau, Germany). Infrared spectra (IR) were obtained on a Thermo Electron Nicolet Avatar 360 FT-IR spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). ^1H nuclear magnetic resonance (NMR; 400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Bruker Ultrashield 400 spectrometer (Bruker BioSpin AG, Fällanden, Switzerland). The relative molecular weights and distributions were measured with a Viscotek VE2001 GPC max system (Malvern Instruments, Worcestershire, UK). The system was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were conducted on a PerkinElmer 7 system (PerkinElmer, Waltham, MA, USA). Samples were heated from -50 to $250\,^\circ C$ for DSC and $50-800\,^\circ C$ for TGA at $10\,^\circ C\,min^{-1}$ under nitrogen. Proton conductivity of the polymers was measured using a previously published method.[17]

Synthesis of monomers (6)

Preparation of 1,3-bis(2-bromotetrafluoroethoxy)anisole (1). A mixture of 5-methoxyresorcinol (14.0 g, 0.100 mol), 1,2-dibromotetrafluoroethane (77.7 g, 0.300 mol) and Cs_2CO_3 (97.8 g, 0.300 mol) in dry DMSO (250 ml) was stirred for 3 days at $50\,^\circ C$. After cooling to room temperature, H_2O (300 ml) and CH_2Cl_2 (100 ml) were added. The aqueous phase was separated and washed with CH_2Cl_2 (2×20 ml). The combined organic phases were washed with H_2O (2×30 ml), brine (2×20 ml), and then dried over anhydrous $MgSO_4$. After the removal of the solvent, the residue was purified by silica column chromatography using hexane to give compound 1 as a liquid (30.1 g, 61%).

^1H NMR (CDCl$_3$; p.p.m.) δ 6.71 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (CDCl$_3$; p.p.m.) δ 161.1, 149.8, 115.8 (tt, 1C), 113.4 (tt, 1C), 107.5, 106.3, 56.0. ^{19}F NMR (CDCl$_3$; p.p.m.) δ -67.9 (t, 1F), -86.0 (t, 1F). MS: m/z 500, 498, 496. Anal. calcd for $C_{11}H_6Br_2F_8O_3$: C, 26.53%; H, 1.21%. Found: C, 26.47%; H, 1.17%.

Preparation of 1,3-bis(2-bromotetrafluoroethoxy)phenol (2). To a solution of 1 (10 g, 20 mmol) in anhydrous CH_2Cl_2 (50 ml), boron tribromide in CH_2Cl_2 (1 M, 60 ml) was added slowly with stirring at $0\,^\circ C$. The resulting mixture was allowed to warm to room temperature and stirred for 48 h. The solution was hydrolyzed by carefully adding H_2O (50 ml). The aqueous phase was separated and washed with CH_2Cl_2 (2×10 ml). The combined organic phases were washed with 5% aqueous $NaHCO_3$ (2×10 ml) and H_2O (2×10 ml) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by silica column chromatography using EtOAc-hexane (1:6, v/v) to give compound 2 as a liquid (9.3 g, 98%).

^1H NMR (CDCl$_3$; p.p.m.) δ 6.71 (t, 3H), 5.85 (s, 1H). ^{13}C NMR (CDCl$_3$; p.p.m.) δ 157.1, 149.9, 115.8 (tt, 1C), 113.3 (tt, 1C), 107.7. ^{19}F NMR (CDCl$_3$; p.p.m.) δ -68.3 (t, 1F), -86.4 (t, 1F). IR (neat; cm^{-1}) 3392 (–OH). MS: m/z 486, 484, 482. Anal. calcd for $C_{10}H_4Br_2F_8O_3$: C, 24.82%; H, 0.83%. Found: C, 24.80%; H, 0.82%.

Preparation of compound 4. Compound 3 (10 mmol) and azidomethyl pivalate (1.57 g, 10 mmol) were suspended in tetrahydrofuran (THF)-H_2O (20 ml, 1:1, v/v). To this mixture copper (II) sulfate pentahydrate (0.125 g, 0.5 mmol) and sodium ascorbate (0.594 g, 3 mmol) were added. The mixture was stirred at room temperature for 48 h. The resulting mixture was diluted with H_2O (20 ml) and then extracted with EtOAc (2×20 ml). The combined organic layers were washed with water (2×10 ml) and brine (2×10 ml) and dried over anhydrous $MgSO_4$. After the removal of solvent, the residue was purified by silica column chromatography using hexane-EtOAc (1:3, v/v) to give compound 4 as a colorless oil.

Compound 4a: Yield 96%. ^1H NMR (CDCl$_3$; p.p.m.) δ 7.80 (s, 1H), 7.77 (d, 2H), 7.30 (d, 2H), 6.19 (s, 2H), 4.62 (s, 2H), 4.11 (t, 2H), 3.53–3.65 (m, 6H), 2.39 (s, 3H), 1.14 (s, 9H). IR (neat; cm^{-1}) 1745 (C=O). MS: m/z 455.

Compound 4b: Yield 93%. ^1H NMR (CDCl$_3$; p.p.m.) δ 7.67 (d, 1H), 7.54 (d, 2H), 7.13 (d, 2H), 6.01 (s, 2H), 4.43 (s, 2H), 3.91 (t, 2H), 3.33–3.45 (m, 10H), 2.19 (s, 3H), 0.93 (s, 9H). IR (neat; cm^{-1}) 1744 (C=O). MS: m/z 499.

Compound 4c: Yield 92%. ^1H NMR (CDCl$_3$; p.p.m.) δ 7.78 (d, 1H), 7.74 (d, 2H), 7.29 (d, 2H), 6.16 (s, 2H), 4.63 (s, 2H), 4.09 (t, 2H), 3.55–3.70 (m, 14H), 2.38 (s, 3H), 1.12 (s, 9H). IR (neat; cm^{-1}) 1744 (C=O). MS: m/z 543.

Preparation of compound 5. A mixture of 2 (4.84 g, 0.01 mol), 4 (0.01 mol) and anhydrous K_2CO_3 (2.76 g, 0.02 mol) in CH_3CN (50 ml) was stirred at reflux for 48 h. After the removal of the solvent, the residue was diluted with H_2O and EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2×10 ml). The combined organic layers were washed with H_2O (2×10 ml) and brine (2×10 ml) and dried over anhydrous $MgSO_4$. After the removal of the solvent, the residue was purified by silica column chromatography using hexane-EtOAc (2:7, v/v) to give compound 5 as a colorless oil.

Compound 5a: Yield 89%. ^1H NMR (CDCl$_3$; p.p.m.) δ 7.79 (s, 1H), 6.73 (d, 3H), 6.19 (s, 2H), 4.68 (s, 2H), 4.13 (t, 2H), 3.84 (t, 2H), 3.71 (s, 4H), 1.16 (s, 9H). ^{19}F NMR (CDCl$_3$; p.p.m.) δ -67.9 (t, 1F), -86.0 (t, 1F). MS: m/z 769, 767, 765. Anal. calcd for $C_{23}H_{25}Br_2F_8N_3O_7$: C, 36.00%; H, 3.28%. Found: C, 35.95%; H, 3.25%.

Compound 5b: Yield 87%. ^1H NMR (CDCl$_3$; p.p.m.) δ 7.67 (s, 1H), 6.72 (d, 3H), 6.20 (s, 2H), 4.63 (s, 2H), 4.11 (t, 2H), 3.82 (t, 2H), 3.64–3.68 (m, 8H), 1.14 (s, 9H). ^{19}F NMR (CDCl$_3$; p.p.m.) δ -67.9 (t, 1F), -86.0 (t, 1F). δ 21.3. MS: m/z 813, 811, 809. Anal. calcd for $C_{25}H_{29}Br_2F_8N_3O_8$: C, 37.01%; H, 3.60%. Found: C, 36.97%; H, 3.57%.

Compound 5c: Yield 83%. ^1H NMR (CDCl$_3$; p.p.m.) δ 7.69 (s, 1H), 6.73 (d, 3H), 6.21 (s, 2H), 4.64 (s, 2H), 4.12 (t, 2H), 3.83 (t, 2H), 3.52–3.73 (m, 12H), 1.16 (s, 9H). ^{19}F NMR (CDCl$_3$; p.p.m.) δ -67.9 (t, 1F), -86.0 (t, 1F). MS: m/z 857, 855, 853. Anal. calcd for $C_{27}H_{33}Br_2F_8N_3O_9$: C, 37.91%; H, 3.89%. Found: C, 37.88%; H, 3.87%.

Preparation of compound 6. To a flame-dried 100-ml flask was added 5 (10 mmol), zinc (1.95 g, 30 mmol) and CH_3CN (30 ml). The resulting mixture was stirred at reflux for 48 h. After removal of the solvent, the residue was diluted with CH_2Cl_2 and then filtered. The filtrate was washed with H_2O and brine and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by silica column chromatography using hexane-EtOAc (1:3, v/v) to give compound 6 as a colorless oil.

Compound 6a: Yield 77%. MS: m/z 569. Anal. calcd for $C_{23}H_{25}F_6N_3O_7$: C, 48.51%; H, 4.43%. Found: C, 48.50%; H, 4.43%.

Compound 6b: Yield 75%. MS: m/z 613. Anal. calcd for $C_{25}H_{29}F_6N_3O_8$: C, 48.94%; H, 4.76%. Found: C, 48.92%; H, 4.75%.

Compound 6c: Yield 72%. MS: m/z 657. Anal. calcd for $C_{27}H_{33}F_6N_3O_9$: C, 49.32%; H, 5.06%. Found: C, 49.30%; H, 5.05%.
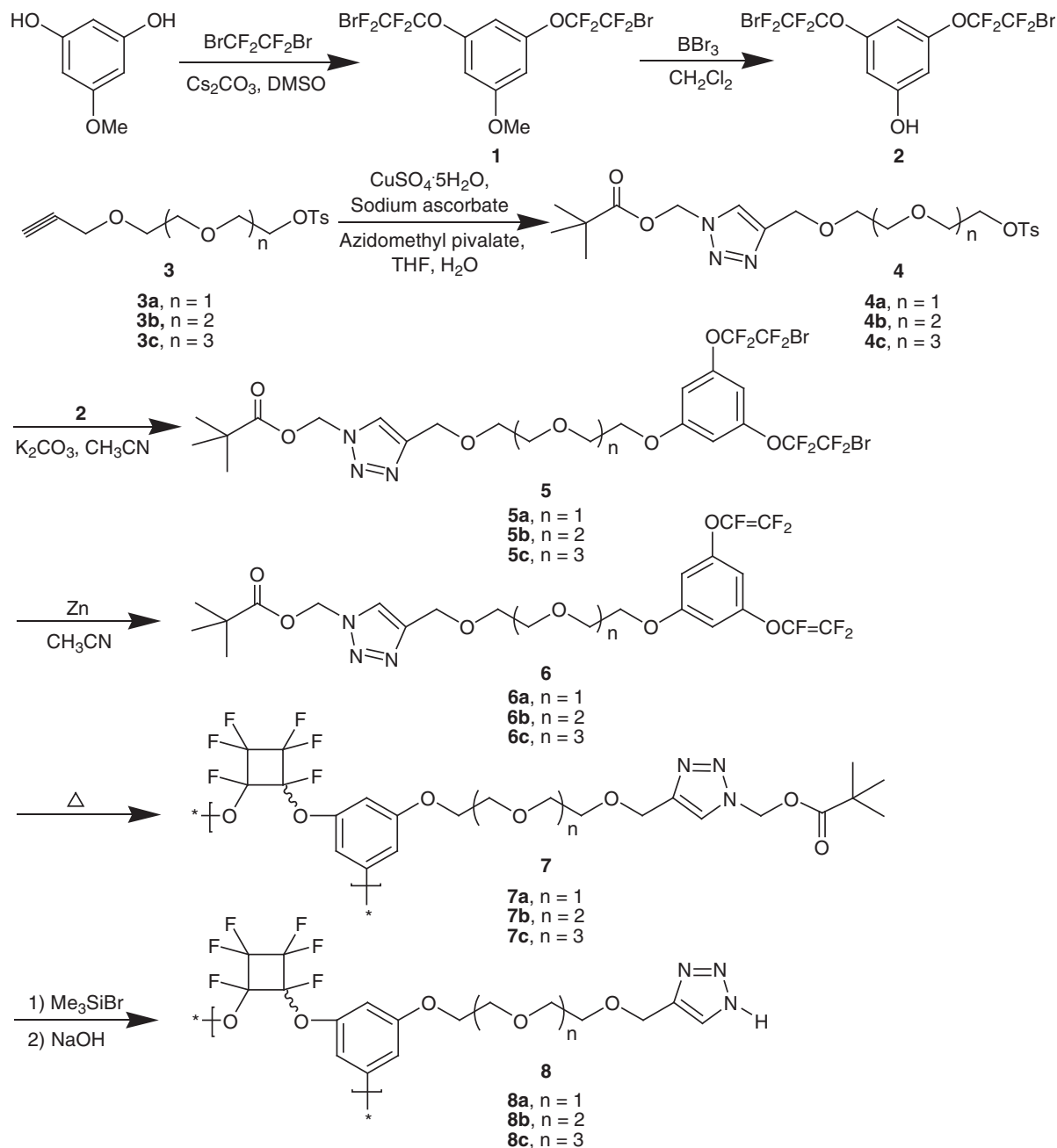
Synthesis of polymers 7 and 8

Compound 6 (1 mmol) was added to a pre-dried 50-ml flask. After three cycles of freeze-pump-thaw, the flask was heated at $190\,^\circ C$ for 48 h. After cooling to room temperature, the residue was dissolved in CHCl$_3$ (10 ml) and then precipitated in hexane to give polymer 7 (90–95%). To a solution of polymer 7 (0.5 g) in methanol (10 ml) aqueous NaOH (1 M, 1 ml) was added. The resulting mixture was stirred at room temperature for 12 h and subsequently neutralized with 5% aqueous hydrochloric acid. The solution was concentrated under vacuum and then dissolved in methanol (5 ml). The resulting solution was triturated with excess diethyl ether. After filtration, the obtained solid was dried at $100\,^\circ C$ for 24 h to give polymer 8 (82–87%).

RESULTS AND DISCUSSION

Monomer syntheses

The preparation procedure for the monomers (6) is shown in Scheme 1. The synthesis of 1 initially focused on traditional methods.[23–25] However, 6 was obtained in very low yield (<20%). Most of the products were derived from the bromination of the benzene ring, which was confirmed by ^1H NMR and gas chromatography/mass spectrometry. Following a new route,[26] the yield of 6 could be increased to 61%. In this route, the phenoxides were generated *in situ*, which not only avoided using harsh conditions to prepare moisture sensitive phenoxides but also gave the desired products in higher yield.[26] Using boron tribromide, demethylation of 1 was

Scheme 1 Synthesis of polymer **8**. DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

achieved successfully with relatively high yield (>96%). Treatment of **3** with azidomethyl pivalate gave **4** in high yield (92–96%) by a typical 'click' reaction. Using potassium carbonate as a base, the coupling reaction between **4** and **2** proceeded smoothly to give **5** in good yield (83–89%). In the last step, **6** was synthesized from **5** by zinc-mediated elimination in anhydrous acetonitrile.

The composition and structure of **6** were confirmed by Fourier transform infrared (FT-IR), ^{1}H-, ^{13}C- and ^{19}F-NMR. Compound **6b** is discussed as a typical example. In the ^{1}H NMR spectrum of **6b** (Figure 1), the signals of methyl (at 1.13 p.p.m.) and ethylene (at 6.21 p.p.m.) in the pivaloyloxymethyl (POM) moieties were observed, and the singlet peak at 4.63 p.p.m. indicated the two protons adjacent to the triazole ring. In the ^{13}C NMR spectrum of **6b** (Figure 2), the typical signals of –OCF=CF$_2$ groups were detected. The signals

between 134.0 and 135.5 p.p.m. and 143.0 and 151.5 p.p.m. were attributed to the units of –OCF= and =CF$_2$, respectively. These peaks overlapped with the signals of the carbon atoms in triazole rings, which appeared at 147.2 and 135.5 p.p.m. In addition, the four peaks at 26.9, 38.9, 74.2 and 177.0 p.p.m. were assigned to the carbon atoms in the POM moiety. The ^{19}F NMR spectrum (Figure 3a) exhibited three doublets centered at −119.0, −125.7 and −134.6 p.p.m., which were assigned to the fluorine atoms in –OCF=CF$_2$. Figure 5a displays the FT-IR spectrum of **6b**. The sharp band at 1832 cm^{-1} is the typical signal of –OCF=CF$_2$ groups, and the strong band at 1746 cm^{-1} was attributed to the carbonyl in the POM moieties. The characterization of **6** by gas chromatography/mass spectrometry and elemental analysis further confirmed the successful synthesis of the high-purity monomers.
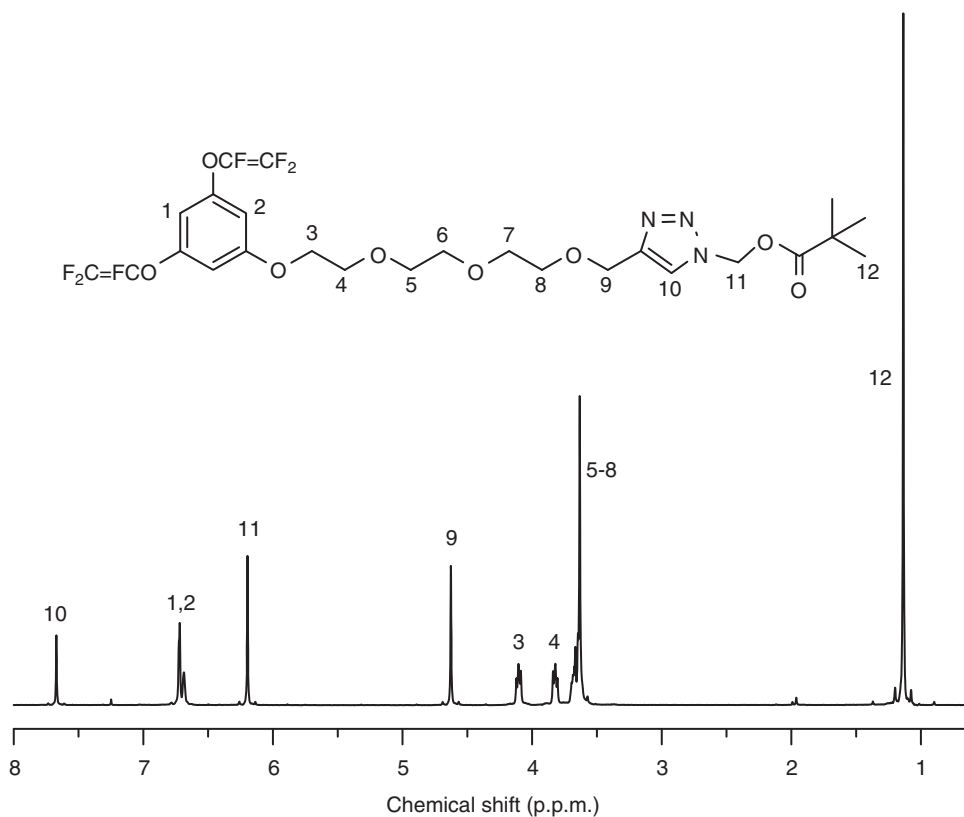
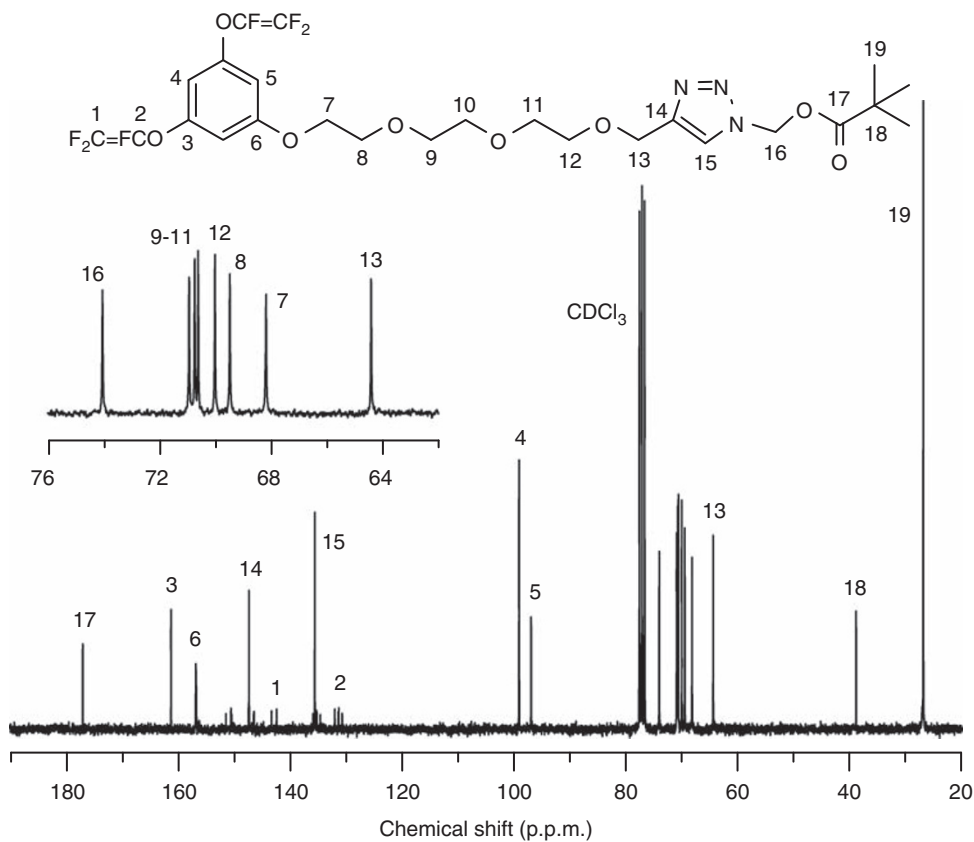**Figure 1** [1]H nuclear magnetic resonance spectrum of compound **6b**.

Figure 2 ^{13}C nuclear magnetic resonance spectrum of compound **6b**.

Polymer syntheses

The preparation procedures of polymers **7** and **8** are shown in Scheme 1. polymer **7** was prepared by the thermal ($2\pi+2\pi$) cyclopolymeriza-
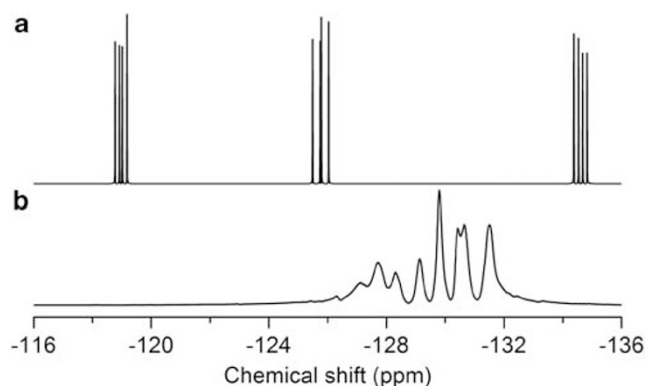

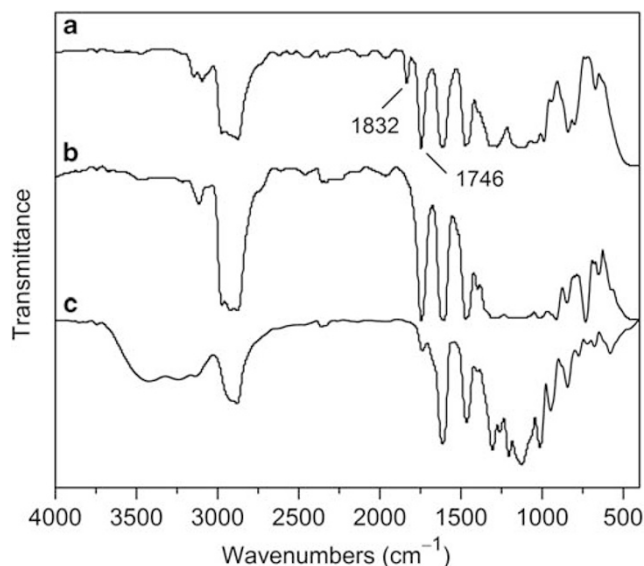**Figure 3** ^{19}F nuclear magnetic resonance spectra of (**a**) compound **6b** and (**b**) polymer **7b**.

Figure 4 Fourier transform infrared spectra of (**a**) compound **6b**, (**b**) polymer **7b** and (**c**) polymer **8b**.

tion of **6** in bulk. This polymerization process did not require catalysts or initiators and gave polymer **7** in high yield. The formation of polymer **7** was confirmed by FT-IR, ^{1}H- and ^{19}F NMR. Polymer **7b** is discussed as a typical example. In the FT-IR spectrum of polymer **7b** (Figure 4b), the sharp band at 1834 cm^{-1} disappeared, and a new band at 989 cm^{-1} appeared, which represented the PFCB groups. In Figure 3b, the resonance signals of the –OCF=CF$_2$ groups disappeared, and a series of new peaks between -126.7 and -132.1 p.p.m. appeared, which are typical fluorine signals of PFCB groups. The molecular weights of polymer **7** determined by gel permeation chromatography in THF using polystyrene as the standard ranged from 37 900 to 38 800 for M_w with M_w/M_n values of 2.5–2.8 (Table 1).

Treatment of polymer **7** with NaOH gave polymer **8** in good yield. The conversion of polymer **7** to polymer **8** was confirmed by ^{1}H NMR and FT-IR spectra. The disappearance of the peaks at 1.14 and 6.20 p.p.m. (Figure 5b) indicated the successful removal of the POM moieties, which was further confirmed by the FT-IR spectrum of polymer **8b** (Figure 4c). In Figure 4c, a broad band from 2500 to 3500 cm^{-1} was attributed to the –NH groups in 1*H*-1,2,3-triazole moieties, and the disappearance of a strong band at 1746 cm^{-1} indicated the absence of the carbonyl groups in the POM moieties.
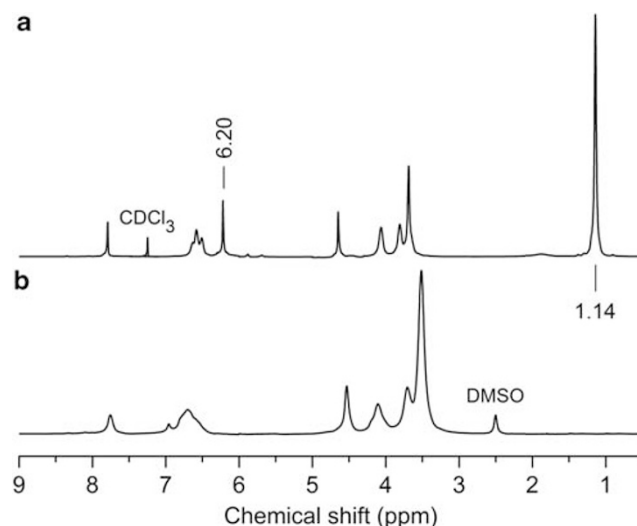

Figure 5 ^{1}H nuclear magnetic resonance spectra of (**a**) polymer **7b** and (**b**) polymer **8b**. DMSO, dimethyl sulfoxide.

Table 1 Properties of polymers 7 and 8

Polymer	Triazole (wt%)	M_w[a]	(M_w/M_n)[a]	$T_{d\,5\%}$ (°C)[b]	DSC (°C)[b]	Solubility				
						THF	CHCl$_3$	DMSO	DMAc	DMF
7a	—[c]	38 800	2.5	267	48	+	+	+	+	+
7b	—[c]	37 900	2.6	274	43	+	+	+	+	+
7c	—[c]	38 100	2.8	249	36	+	+	+	+	+
8a	14.9	—[c]	—[c]	314	110	–	–	+	+	+
8b	13.6	—[c]	—[c]	328	97	–	–	+	+	+
8c	12.5	—[c]	—[c]	295	89	–	–	+	+	+

Abbreviations: +, soluble; –, insoluble; DMAc, N,N-dimethylacetamide; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; DSC, differential scanning calorimetry; GPC, gel permeation chromatography; TGA, thermo-gravimetric analysis; THF, tetrahydrofuran.
[a]GPC in THF at 25 °C.
[b]TGA and DSC at 10 °C min^{-1} in N$_2$.
[c]Not available.
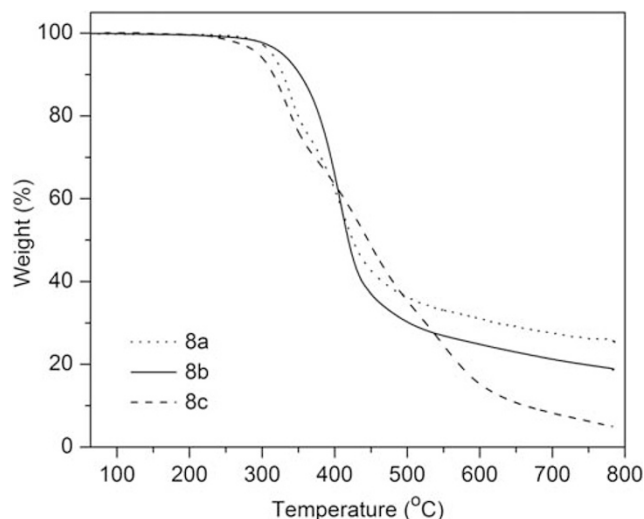
Figure 6 Thermo-gravimetric analysis curves of polymer **8** under nitrogen.

Figure 7 Proton conductivities of polymer **8**.

Properties of polymers

Solubility of polymers. Table 1 shows solubility of the polymers determined quantitatively by dissolving 0.1 g polymer in 1.0 g organic solvents. Polymer **7** showed good solubility in common organic solvents such as DMSO, CHCl₃ and THF. After removal of POM moieties, however, the resulting polymers (polymer **8**) were not soluble in solvents with low dielectric constants and non-polar solvents such as THF and CHCl₃, which might be attributed to the strong hydrogen-bonding action between the 1*H*-1,2,3-triazole and oligo(ethylene oxide) units.

Thermal properties of polymers. The thermal properties of the polymers were evaluated by DSC and TGA. As shown in Table 1, the glass transition temperature (T_g) values of polymer **8** were much higher than those of polymer **7**, and the T_g value (polymer **8**) distinctly decreased with the reduction of the triazole content, which was attributed to the highly hydrogen bonded network formed between the triazole and oligo(ethylene oxide) units. The weight percent of triazole contained in each polymer was calculated by dividing the equivalent weight of the triazole units ($68 \, g \, mol^{-1}$) by the equivalent weight of the polymer repeat unit. Figure 6 shows the TGA traces of polymer **8** under nitrogen. These polymers were stable up to $\sim 290 \,°C$, which is much higher than that of previously reported polymers.[16,17]

Proton conductivity. The proton conductivity of polymer **8** was measured from 40 to 200 °C under anhydrous conditions using impedance spectroscopy. In general, the proton conductivity of polymers containing *N*-heterocyclic moieties is known to be influenced by several factors such as the glass transition temperature of the polymer and the proton charge carrier density.[12–14] As expected, polymer **8** exhibited very similar conductivity (Figure 7) because they possessed identical polymeric structure. A maximum conductivity of $2.85 \, \mu S \, cm^{-1}$ was obtained at 200 °C under anhydrous conditions. The proton conductivities of polymer **8** were lower than the values previously reported,[16,17] which could be attributed to the higher T_g and lower triazole content of polymer **8**. The introduction of more than one triazole per repeat unit did not result in an increase in conductivity because there was an accompanying increase in T_g;[16] thus, two methods are suggested to improve the proton conductivity. The first one is the reduct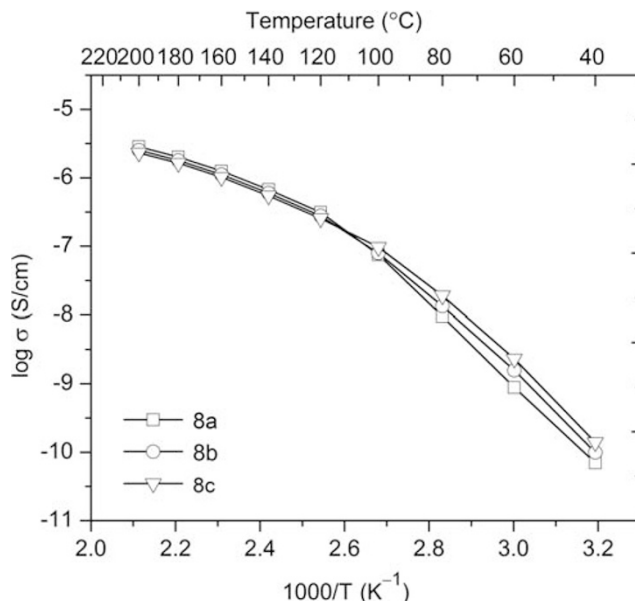ion of T_g by the incorporation of poly(ethylene oxide) (PEO) blocks to prepare copolymers. The second one is the increase of the acidity via the incorporation of electron withdrawing groups such as a trifluoromethyl group into the triazole rings.

CONCLUSIONS

A new class of perfluorocyclobutyl poly(arylene ether)s containing oligo(ethylene oxide) and 1*H*-1,2,3-triazole units were prepared and characterized. TGA show that these polymers had good thermal stability. DSC analysis indicated that the T_g value of these polymers decreased with the triazole content. These polymers also showed good solubility in common organic solvents such as DMSO and DMF. All polymers exhibited a proton conductivity comparable to that previously reported.[16] Systematic investigations of these polymers as solid electrolyte membranes for fuel cells applications are in progress.

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