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New acetyl-containing aromatic polyether with perfluorinated mono- and biphenylene fragments

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A novel fluorinated poly(arylene ether) containing tetrafluorobenzene and octafluorobenzene fragments and acetyl side groups was synthesized by polycondensation of 1,4-bis(3-acetyl-4-hydroxyphenoxy)-2,3,5,6-tetrafluorobenzene and decafluorobiphenyl. Some properties of this polymer were examined, and its keto groups were reduced into alcohol ones.

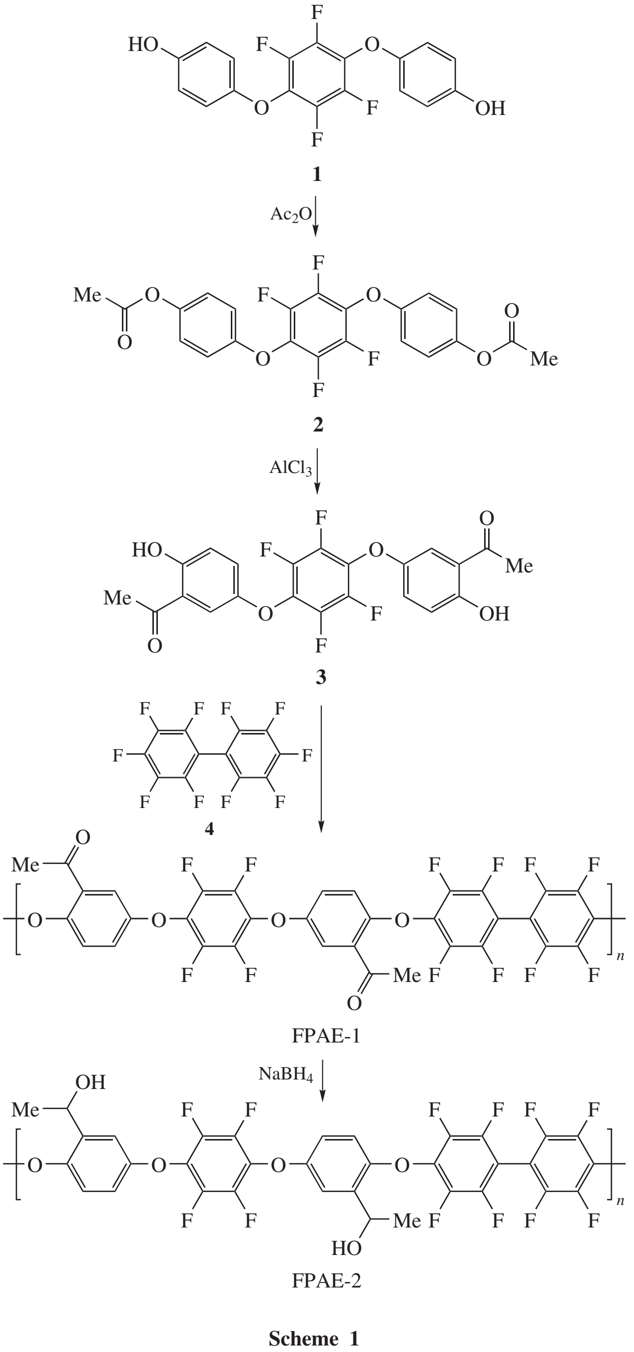
Fluorinated poly(arylene ether)s (FPAEs) possess high thermal stability along with good optical (low refractive index, optical losses and absorption in the near infrared) and dielectric characteristics. These properties make them attractive for microelectronics and optical telecommunications.[1–3]

A broader application of polymers depends on diversification of their chemical functionalization through polymeranalogous transformations (‘post’ route), or by means of monomer units containing functional groups or fragments (‘pre’ route). Both of them were applied to FPAEs, thus incorporating sulfonic[4] and phosphonic acid,[5] aldehyde,[6] epoxide[7] and curable aliphatic moieties.[8,9]

Previously we reported on the first successful synthesis of FPAEs bearing both tetrafluorobenzene (TFB) and octafluorobiphenyl (OFB) units in the backbone.[10] Functionalization of such polymers with allyl[11] and aminomethyl[12] fragments offers interesting opportunities for their use as intermediate insulators in multilayer integrated systems and ion-exchange membranes, respectively. Therefore, synthesis and functionalization of new FPAEs containing TFB and OFB units seem topical.

In this work, we prepared new acetyl-containing fluorinated poly(arylene ether) with both perfluorinated mono- and biphenylene fragments from acetyl-substituted monomer and decafluorobiphenyl (DFB) (Scheme 1, ‘pre’-functionalization route). Properties of the synthesized polymer, such as solubility, molecular-weight characteristics, tensile strength, and thermal stability were thoroughly investigated. In addition, we demonstrated pathway for further functionalization of the acetyl-containing FPAE with alcohol groups (‘post’-functionalization route).

The required acetylated monomer **3** was obtained in two steps according to the published method.[13] First, acetylation of the TFB-containing bis-phenol **1** gave its diester **2**. Next, the $AlCl_3$-assisted Fries rearrangement afforded diketone **3** (see Scheme 1).[†]



Scheme 1

[†] Compounds **1**–**3** were prepared as reported previously.[13] Decafluorobiphenyl **4** and other reagents were purchased from Aldrich Chemical Co. All solvents were purified before the use.

Polymer FPAE-1. A mixture of compound **3** (0.2 g, 0.444 mmol) and monomer **4** (0.15 g, 0.444 mmol) was dissolved in 2 ml of DMA, and K_2CO_3 (0.13 g, 0.98 mmol) was added. The mixture was stirred under nitrogen flow at 90 °C for 25 min and then was poured into a 1% AcOH solution. The precipitated polymer was washed with hot methanol and water several times and dried *in vacuo* at 80 °C for 8 h. Yield 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.77 (s, 6H, Me), 6.92 (d, 2H, Ph, J 9.3 Hz), 7.22 (br. s, 2H, Ph), 7.48 (s, 2H, Ph). ^{19}F NMR (188 MHz, $CDCl_3$) δ: –139.06 (br. s, 4F, Ph), –154.73 (br. s, 4F, Ph), –155.32 (br. s, 4F, Ph). FTIR (ν/cm^{-1}): 978, (C–F), 1238 (Ph–O–Ph), 1472 (C=C$_{arom}$), 1690 (C=O). 2850–3100 (CH).

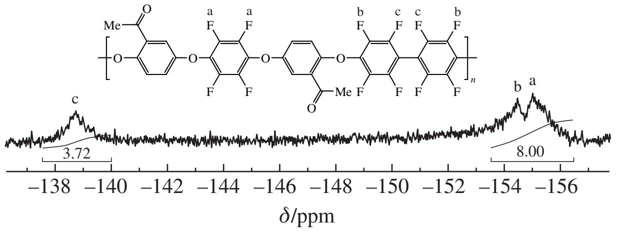


Figure 1 ^{19}F NMR spectrum of polymer FPAE-1.

Condensation of monomer **3** with DFB led to the acetyl-containing FPAE-1 with TFB and OFB moieties alternating along the polymer chain. The FTIR spectrum of FPAE-1 shows a characteristic peak of the C=O group near 1690 cm^{-1}, while its ^{1}H NMR spectrum exhibits a distinct resonance at 2.77 ppm for the acetyl protons. In the nucleophilic substitution reactions, the fluorine atom in a *para*-position in pentafluorophenyl unit is very reactive with the activated dihydroxyl-substituted monomers;[1] anyway, the fluorine atoms at other sites can sometimes also react to form cross-linking products.[6] The ^{19}F NMR spectrum of FPAE-1 contains two equal signals corresponding to OFB fluorine atoms in the *meta*- and *ortho*-positions along with a singlet of the equivalent fluorine atoms of TFB fragment (Figure 1). This is an evidence that the nucleophilic substitution occurred exclusively at *para*-positions of perfluorobiphenyl moiety.

The synthesized polymer is easily soluble in DMF, DMSO, DMA, CHCl$_3$, toluene and THF, and insoluble in hexane and ethanol. The number-average molecular weight (M_n) and the polydispersity index ($M_\mathrm{w}/M_\mathrm{n}$) of the polymer FPAE-1 calibrated with polystyrene standards were 10000 and 2.16, respectively.[‡] The intrinsic viscosity [η] of prepared polymer solution in DMF was 0.16 dl g^{-1}. Polymer FPAE-1 has good film-forming ability. Thus, the film of this polymer possesses tensile strength of 13 MPa and relative elongation of 3%.

Thermal properties of the resulting FPAE were investigated using DSC and TGA. DSC measurements revealed the amorphous nature of the polymer. No melting endotherm peak was found from the DSC curve. The glass transition (T_g), heat capacity (ΔC_p) and glass transition region (ΔT_g) values of FPAE-1 are 165 °C, 0.17 J g^{-1} deg^{-1} and 20 °C, respectively.

Thermal and thermo-oxidative stabilities of the synthesized polyether were evaluated by TGA analysis in nitrogen and air atmospheres. The polymer exhibited an almost one-step pattern of decomposition with a negligible weight loss up to 380 °C in both atmospheres. As expected, the prepared polymer is more stable in nitrogen. Thus, the temperature of 5% weight loss ($T_{5\%}$) for FPAE-1 is 405 °C in nitrogen and 390 °C in air. The char yield of FPAE-1 is about 45 wt% at 700 °C.

Note that analogous polymer lacking acetyl groups is not soluble in CHCl$_3$ and, forms brittle film, as well as shows lower T_g (109 °C) and $T_{5\%}$ (300 °C in air) values compared to the acetylated FPAE-1.[10] Better solubility of FPAE-1 can be attributed to the presence of bulky acetyl groups, which prevent close packing of the polymer chains. The enhancement of mechanical and thermal properties for the acetyl-derivative FPAE-1 is most likely caused by the presence of strong intermolecular forces due to acetyl groups.

The polymer chain design of acetyl-containing FPAE-1 enables further chemical modifications to introduce a multitude of functional groups and fragments through specific Mannich-type reaction, Claisen–Schmidt condensation, *etc.*[14,15] As an example, FPAE-1 was transformed into polymer FPAE-2 containing OH groups by the ketone group reduction with NaBH$_4$ (‘post’-modification route, see Scheme 1). The structure of FPAE-2 was confirmed by FTIR, ^{1}H and ^{19}F NMR spectroscopy.[§]

In summary, we have developed synthetic protocol for the preparation of new acetyl-containing fluorinated poly(arylene ether) consisting of perfluorinated mono- and biphenylene units using ‘pre’-modification route. This polymer possesses a better solubility and shows both high T_g value and good thermal stability in comparison with non-functionalized FPAE. The presence of acetyl groups in the polyether offers interesting opportunities for its further functionalization and creation of multifunctional polymer systems.

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[‡] Intrinsic viscosities [η] of polymer solutions were determined with an Ubbelohde viscometer in DMF at 30 °C. Gel permeation chromatography (GPC) of FPAE-1 was carried out using a Waters Breeze 1515 GPC system. Waters Styragel columns with THF as an eluent were used. The tensile strength and relative elongations of FPAE-1 film were measured on a 2166 P-5 tensile testing machine with uniaxial tension applied at the rate of clamp movement of 50 mm min^{-1}. Glass-transition temperature (T_g) was determined by DSC using the second heating run on a TA Instruments Q-2000 apparatus (USA) at the heating rate of 20 K min^{-1}. The thermo- and thermooxidative destruction of FPAE-1 were studied by TGA on a TA Instruments Q-50 apparatus (USA) under nitrogen atmosphere or in air, respectively. A heating rate of 20 K min^{-1} with a temperature range from 25 to 700 °C was applied.

[§] *Polymer FPAE-2*. NaBH$_4$ (0.41 g, 1.076 mmol) was added to a stirred suspension of polymer FPAE-1 (0.2 g, 0.269 mmol) in ethanol (5 ml) at 15 °C within 10 min. The resulting mixture was continuously stirred at room temperature for 12 h (the suspension became almost transparent after 4 h). Diluted HCl was added under stirring. The precipitated polymer FPAE-2 was filtered and washed several times with deionized water and dried *in vacuo* at 80 °C for 8 h. Yield 96%. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 1.37 (s, 6H, Me), 5.15 (s, 2H, CH), 5.48 (br. s, 2H, OH), 6.93–7.10 (m, 4H, Ph), 7.35 (s, 2H, Ph). ^{19}F NMR (188 MHz, DMSO-d_6) δ: –138.06 (d, 4F, Ph, J 24.25 Hz), –153.87 (d, 4F, Ph, J 24.25 Hz), –154.67 (s, 4F, Ph). FTIR (ν/cm^{-1}): 1005 (C–F), 1240 (Ph–O–Ph), 1483 (C=C$_\mathrm{arom}$), 2850–3000 (CH), 3200–3600 (OH).