

Synthesis of *meta*-linked fluorinated oligo(arylene ether) with hydroxyl end groups

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Reactive aromatic oligoethers with perfluoroaromatic units attract much interest as efficient building blocks for the construction low-loss optical waveguide materials and highly ion conductive membranes. Significant progress has been made on the synthesis of fluorine-terminated oligo(arylene ether)s (FAOs). Due to the side reactions as branching and crosslinking, hydroxyl-terminated FAOs are significantly less developed therefore efficient strategies of synthesis mentioned oligomers are paramount. In this work, the strategy to the synthesis of the hydroxyl-terminated FAO containing meta-oxyphenylene fragments was proposed. This oligomer is the first example of meta-linked FAO with reactive OH end-groups and was prepared by condensation polymerization of decafluorobiphenyl and resorcinol, where an excess of resorcinol was used. The structure of the synthesized oligomer was determined by Fourier transform infrared, ¹H NMR and ¹⁹F NMR spectroscopy techniques. The molecular weight and thermal properties of the synthesized fluorinated oligo(arylene ether) were studied.

Keywords: reactive oligomers, fluorinated aromatic oligomers, synthesis, properties, *meta*-fragments.

Fluorinated poly(arylene ether)s (FPAEs) show various excellent properties such as high thermal stability and chemical resistance, good dimensional stability, low dielectric constant and reduced friction coefficient, refractive index, optical losses and moisture absorption [1–3]. The main way of FPAEs synthesis is reaction nucleophilic substitution of fluorine atom(s) in a perfluorinated aromatic nucleus with a phenol-type hydroxyl group in the presence of an alkali. The polycondensation of perfluoroaromatic monomers (decafluorobiphenyl (DFB), hexafluorobenzene derivatives, etc.) with phenol-type monomers of various structures provides a wide spectrum of FPAEs [4–6]. The application of fluorinated oligomeric compounds represents another efficient way to obtain FPAEs [7–14].

Typically, in order to synthesize the fluorinated aromatic oligoethers (FAOs) an excess of core-fluorinated monomers relative to phenol-type monomers are used [7–12]. In contrast, the synthesis of FAOs with reactive OH end-groups through using excess phenol-type monomers are significantly less developed due to the side reactions that lead to the formation of branched and cross-linked structures [13, 14]. For these reasons very careful control of reaction temperature and/or time is necessary for the successful synthesis of hydroxyl-terminated oligomers. Meanwhile, OH groups are important functional groups which can participate in many reaction types.

Both perfluorophenyl rings end-capped and hydroxyl-terminated FAOs are widely used as hydrophobic blocks to prepare alternating hydrophilic-hydrophobic multiblock

(MB) copolymers [10–14]. The combination of microphase separation in MB copolymers with self ordering occurring on a molecular scale can provide interesting properties compared to random copolymers. The ionic-containing fluorinated MB copolymers have shown to be promising as proton or anion exchange membranes for fuel cells [10–15]. The oligomer approach is the preferred method for the production of the desired cross-linked FPAEs. For this purpose, FAOs bearing cross-linkable groups at the chain end have been synthesized. FPAEs based on cross-linkable FAOs are mainly designed for low-loss polymer optical waveguide devices as well as for proton-exchange membranes with improved chemical resistance and oxidative stability [7–9].

Our previous results demonstrated that *meta*-connecting fluorinated polymers and, in particular FPAEs, possess enhanced solubility, thermal stability, optical and mechanical properties [6, 16, 17]. In addition, *meta*-phenylene rings of the polymers can be selectively and almost completely sulfonated under mild reaction conditions [13]. To the best of our knowledge, there are no reports on the FAOs, containing core-fluorinated units along with *meta*-linked fragments in their structure.

Thus, here we demonstrate an evidently simple strategy to prepare a novel hydroxyl-terminated fluorinated aromatic oligoether containing *meta*-oxyphenylene fragments from commercially available monomers DFB and resorcinol. The *molecular weight and thermal properties of the synthesized fluorinated oligo(arylene ether)* were thoroughly studied.

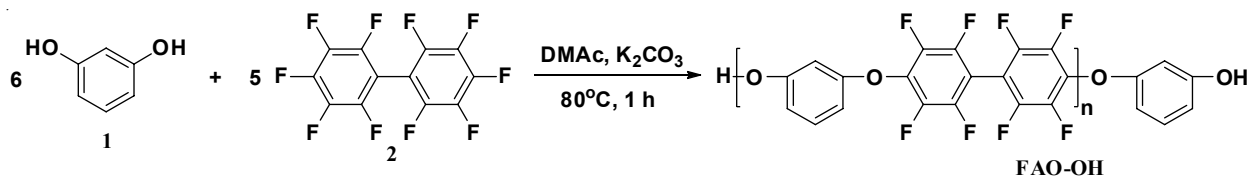


Fig. 1. The schematic representation synthesis of FAO-OH oligomer

Experimental.

Materials. Initial monomers resorcinol (**1**, 99 %) and DFB (**2**, 99 %) were purchased from Aldrich Chemical Co. and used as received. Anhydrous potassium carbonate (K₂CO₃, 99+ %) was purchased from Acros Organic Inc and dried at 120 °C for 24 h before used. All the organic solvents were obtained from commercial sources and purified by conventional methods.

Synthesis of the hydroxyl-terminated fluorinated aromatic oligoether (FAO-OH). A dry, 25 ml three-necked flask equipped with an oil bath, a mechanical stirrer, a cold water condenser, an argon inlet/outlet, and a thermometer was charged with resorcinol **1** (0,200 g, 1,816 mmol), DFB **2** (0,506 g, 1,514 mmol), and 4,3 ml of dimethylacetamid (DMAC). After dissolving of the monomers, anhydrous potassium carbonate (0,3 g, 2,179 mmol) was added into the flask. The solution was then heated to 80 °C and stirred vigorously at this temperature for 1 h. After cooling to room temperature, the solution was then poured into 100 ml of methanol containing a few drops of glacial acetic acid to precipitate the oligomer. The precipitate was collected, dried, and dissolved in chloroform, filtered to remove insoluble solid, and reprecipitated by adding the solution dropwise into methanol. The separated oligomer was dried in vacuo at 60 °C overnight. Yield 85 %. ¹H NMR (CDCl₃, 500 MHz, δ, ppm): 6,56 (*s*, terminal ArH-OH), 6,61 (*m*, terminal ArH-OH), 6,80 (*d*, 2H, *J*=7,1 Hz, ArH), 6,86 (*s*, 1H, ArH), 7,21 (*t*, *J*=8,2 Hz, terminal ArH), 7,34 (*t*, 2H, *J*₁=7,7, *J*₂=8,2 Hz, ArH). ¹⁹F NMR δ(CDCl₃, 188,1 MHz, δ, ppm): -138,57 (*d*, 4F, *J*=24,3 Hz, ArF), -153,77 (*d*, 4F, *J*=16,1 Hz, ArF). FTIR ν (cm⁻¹): 982, 1003 (C-F), 1244 (Ph-O-Ph), 1485 (C=C_{arom}), 1601 (Ph), 2800–3000 (CH), 3200–3600 (OH).

Characterization and measurement.

Fourier transform infrared (FTIR) spectrum of the synthesized oligomer was recorded with a TENSOR 37 spectrometer in the absorption region of 600–4000 cm⁻¹. ¹H and ¹⁹F NMR spectra were recorded with Bruker Avance DRX 500 and Varian Mercury 200 spectrometers respectively at room temperature in CDCl₃. Chloroform was used as an internal chemical shift reference for ¹H NMR (7.25 ppm). For ¹⁹F NMR spectroscopy, fluorotrichloromethane was used as the internal standard. Intrinsic viscosity [η] of oligomer solution was determined with an Ubbelohde viscometer in dimethylformamide at 30 °C. Gel permeation chromatography (GPC) of FAO was carried out using a Waters Breeze 1515 GPC system. Waters Styragel columns with tetrahydrofuran (THF) as an eluent were

used in the study. Glass transition temperature was determined by *differential scanning calorimetry* (DSC) using the second heating run with a TA Instruments Q-2000 apparatus (USA) at a heating rate of 20 K min⁻¹. The thermo-oxidative destruction of oligomer was studied using thermogravimetric analysis (TGA) with a TA Instruments Q-50 apparatus (USA). A heating rate of 20 K min⁻¹ with a temperature from 25 to 800 °C was applied.

Results and discussion.

The desired hydroxyl-terminated (namely, resorcinol-terminated) oligomer (FAO-OH) was prepared in good yield from DFB (**2**) and an excess amount of resorcinol (**1**) in DMAC in the presence of potassium carbonate as a base (Fig. 1).

The repeating unit of the oligomer was targeted as *n*=5 by controlling the molar ratio of DFB to resorcinol. The oligomer FAO-OH was obtained at 80 °C for 1 h. Note that an increase in the reaction temperature or an extended reaction time at FAO-OH synthesis yields cross-linked products. This result indicates that except the fluorine at *para*-site, the fluorine atoms at other sites of the perfluorophenyl can also react under appropriate conditions [6].

All the FTIR, ¹H NMR, and ¹⁹F NMR spectroscopic data support the suggested structure of FAO-OH. Thus, the FTIR spectrum shows peaks which correspond to C-F, C-O-C, and C=C_{arom} groups (Fig. 1). The broad but weak peak around 3450 cm⁻¹ in the FTIR spectrum of the FAO-OH indicates the presence of phenolic end groups.

All peaks in the ¹H NMR spectrum of representative oligomer can be readily assigned (Fig. 3). The shifts between 6,75 and 7,40 ppm correspond to the aromatic

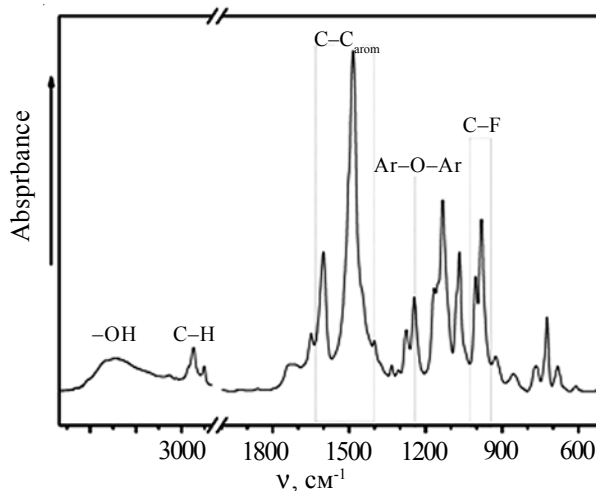
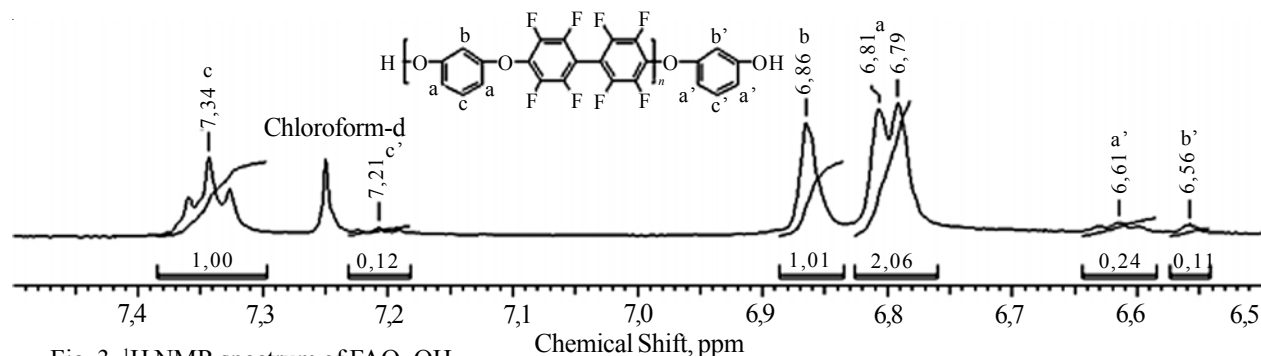
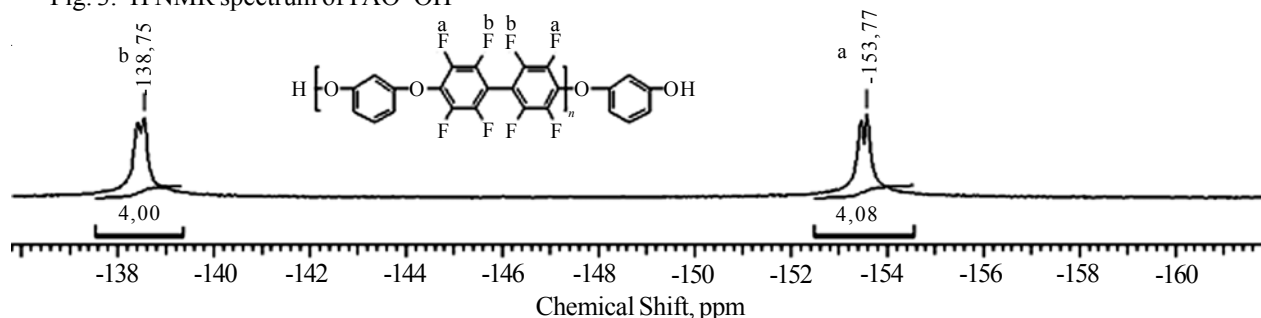


Fig. 2. FTIR spectrum of FAO-OH

Fig. 3. ^1H NMR spectrum of FAO-OHFig. 4. ^{19}F NMR spectrum of FAO-OH

protons of the oligoether FAO-OH backbone. Additionally, the ^1H NMR spectrum of the FAO-OH contains the aromatic protons of the terminal benzene ring appeared at 6,54 and 7,23 ppm as relatively weak signals.

Two peaks were clearly detected in the ^{19}F NMR spectrum of oligomer corresponding to *ortho*- and *meta*-fluorine atoms of the perfluorinated biphenylene units to the ether linkage (Figure 4).

The resulting oligomer is soluble in most common organic solvents and insoluble in methanol, benzene, and *n*-hexane. The solubility of FAO-OH oligomer in THF enabled investigation of their molecular mass distribution by GPC using polystyrene standards. According to the GPC measurements, the M_n value of FAO-OH is 4000, whereas the M_w/M_n value is 2,2. The inherent viscosity of the oligomer in DMAc is 0,14 dL/g, measured at 30 °C.

Based upon the integrating intensity of the sub-peaks (the proton shifts of phenolic fragment) and the major peaks, the degree of polymerization of the obtained oligomer FAO-OH can be estimated using ^1H NMR analysis. Thus, the numbers of repeat units of FAO-OH were estimated from the ^1H NMR spectrum ($n=8,1$) and GPC measurement (9,6), which were somewhat greater than those expected from the feed monomer ratio ($n=5$). Evidently, this is due to the fact that the free phenoxide end groups remaining at the chain ends of FAO-OH can react with the fluorine atoms of the octafluorobiphenylene moieties along the oligomers chains, leading to further

polycondensation reaction.

Thermal properties of the resulting oligomer were investigated using DSC and TGA. DSC measurements revealed the amorphous nature of the oligomer because no melting endotherm peak is found from the DSC curves. The glass transition (T_g), heat capacity (ΔC_p) and glass transition region (ΔT_g) values of the FAO-OH are 115 °C, 0,131 J/(g·°C) and 6 °C, respectively. The oligomer has a good thermal stability and exhibited a one-step pattern of decomposition with a negligible weight loss up to approximately 500 °C. The temperature of 5 % weight loss ($T_{5\%}$) for FAO-OH is 550 °C, while value $T_{10\%}$ is about 570 °C.

In a summary, we have developed synthetic route for a novel *meta*-linked FAO with the hydroxyl end groups. Optimal conditions for the reactive oligomeric compound preparation were found and described. Note due to the presence of high reactive phenoxide end groups, it is difficult enough to control accurately the molecular weight of OH-terminated oligomer. The obtained oligomer has excellent solubility in common organic solvents and exhibited good thermal properties. The prepared hydroxyl-terminated oligomer could be considered as a new building block for the synthesis of a wide range of fluorinated multiblock copolymers. The presence of both nonfluorinated and fluorinated aromatic fragments in the obtained fluorinated oligoether offers interesting opportunities for further functionalization of such compounds (namely, creation of multifunctional cross-linked materials polymer systems).

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Синтез *мета*-заміщеного фторованого ароматичного олігоетеру з кінцевими гідроксильними групами

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*Реакційноздатні ароматичні олігоетери з перфторароматичними фрагментами викликають великий інтерес як ефективні будівельні блоки для отримання волоконно-оптичних матеріалів з низькими оптичними втратами та мембран з високою іонною провідністю. Значний прогрес досягнутий у синтезі фторованих в ядро ароматичних олігомерів (ФАО) з кінцевими атомами фтору. В той же час, внаслідок побічних реакцій, таких як розгалуження та зшивання, методи синтезу ФАО з кінцевими гідроксильними групами майже не розроблені. Тому розробка способів синтезу зазначених олігомерів є важливим завданням полімерної хімії. Запропоновано ефективний спосіб синтезу першого представника ФАО, що одночасно містить кінцеві гідроксильні групи та *мета*-заміщені фрагменти. Такий олігомер з кінцевими реакційноздатними ОН-групами отриманий поліконденсацією декафторбіфенілу з мольним надлишком резорцину. Будова синтезованого олігомеру досліджена методами ІЧ-, ¹H- та ¹⁹F ЯМР-спектроскопії. Охарактеризовано молекулярно-масові та термічні властивості отриманого фторованого в ядро ароматичного олігоетеру.*

Ключові слова: реакційноздатні олігомери, фторовані ароматичні олігомери, синтез, властивості, *мета*-фрагменти.

Синтез *мета*-замещенного фторированного ароматического олигоэфира с концевыми гидроксильными группами

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*Реакционноспособные ароматические олигоэфиры с перфторароматическими фрагментами вызывают большой интерес как эффективные строительные блоки для получения волоконно-оптических материалов с низкими оптическими потерями и мембран с высокой ионной проводимостью. Значительный прогресс достигнут в синтезе фторированных в ядро ароматических олигомеров (ФАО) с концевыми атомами фтора. В то же время, вследствие побочных реакций, таких как разветвление и сшивание, методы синтеза ФАО с концевыми гидроксильными группами почти не разработаны. Поэтому разработка способов синтеза указанных олигомеров является важной задачей полимерной химии. Предложен эффективный способ синтеза первого представителя ФАО, который одновременно содержит концевые гидроксильные группы и *мета*-замещенные фрагменты. Такой олигомер с концевыми реакционноспособными ОН-группами получен поликонденсацией декафторбифенила с мольным избытком резорцина. Строение синтезированного олигомера исследовано методами ИК-, ¹H- и ¹⁹F ЯМР-спектроскопии. Изучены молекулярно-массовые и термические свойства полученного фторированного в ядро ароматического олигоэфира.*

Ключевые слова: реакционноспособные олигомеры, фторированные ароматические олигомеры, синтез, свойства, *мета*-фрагменты.