

УДК 678.746.4:547.539.1:547.63

New spirobisindane-based ladder-type poly(arylene ether) copolymer with perfluorinated biphenylene and trifluoromethyl fragments

I.M. Tkachenko, Y.L. Kobzar, O.V. Shekera, V.V. Shevchenko

Institute of Macromolecular Chemistry NAS of Ukraine
48, Kharkivske shose, Kyiv, 02160, Ukraine

A novel ladder-type fluorinated poly(arylene ether) copolymer containing perfluorinated biphenylene and trifluoromethyl fragments as well as dibenzodioxin and spirobisindane units was synthesized by the double-aromatic nucleophilic substitution reaction from 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane monomer and an equimolar amount of two fluorinated monomers. The chemical structure of the prepared copolymer was determined using ^1H , ^{19}F NMR and FTIR spectroscopy techniques. The obtained polymer was completely soluble in chloroform and tetrahydrofuran, but insoluble in such solvents as dimethylsulfoxide and dimethylformamide. It is shown that the synthesized polyether has average molecular weight (M_w) equal to 54600 and good thermo-oxidative stability (up to 400 °C). No glass transition temperature or other thermal transitions were found from the copolymer DSC curve up to 300 °C. The presence of both rigid ladder dibenzodioxin units and spirobisindane fragments (site of contortion) in its structure leads to decreasing the packing density of macromolecular chains that is promising for the regulation of transport properties of polymeric systems.

Keywords: core-fluorinated monomers, fluorinated poly(arylene ether)s, double-aromatic nucleophilic substitution reaction, ladder fragments, trifluoromethyl groups.

Fluorinated poly(arylene ether)s (FPAEs) show excellent properties, first of all, high thermal stability, good optical (low refractive index, optical losses and absorption in the near infrared) and low dielectric permeability. These properties make FPAEs attractive for modern hi-tech applications, especially, in microelectronics (for example, an interlayer dielectric material for microelectronic packaging devices) and in optical telecommunications (for example, waveguides in optoelectronic integrated circuits) [1–3].

Usage of CF_3 -containing monomers or core-fluorinated monomers is the main two methods for the introduction of fluorine into FPAEs [1, 2]. It is interesting that core-fluorinated compounds (mainly individual decafluorobiphenyl (DFB) and bis(pentafluorophenyl)-derivatives) can be used as monomers for the preparation of fluorinated ladder-type polyethers such as polymers of intrinsic microporosity (PIMs) [4–6]. PIMs are prepared via the dibenzodioxane forming reaction based on a double-aromatic nucleophilic substitution mechanism [4–7]. These polymers have potential applications as materials for gas permeation membranes because PIMs combine the adaptability of polymers with nano-engineered free volume elements for the high surface area that are larger than most other polymers and even many zeolites [4–8]. The micro-

porosity of PIMs is due to their rigid and contorted macromolecular structures, which cannot fill space efficiently, leaving molecular-sized interconnected voids. Thus, PIMs are composed of fused rings (as a rule, dibenzodioxane units) that provide rigidity, and sites of contortion, which are provided by spiro-centres. The most commonly reported such material having high molecular weight, termed PIM-1, is prepared from commercially available 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane and 2,3,5,6-tetrafluoroterephthalonitrile. It should be noted that the molecular scaffold used to synthesize PIMs is generally derived from an activated tetrafluorine-containing aromatic monomers (some syntheses utilize dichlorides) and aromatic tetrols to form a linear ladder-type polyethers. But as a result of dibenzodioxane-forming reaction the ladder polyethers are non-fluorinated [4–10].

Generally, to improve gas transport properties, an approach of introducing fluorinated moieties into the polymer chain can be used. Fluorinated amorphous polymers have shown high free volume and low cohesion energy which favors simultaneously the mobility and solubility of permeates inside of the polymer matrix. In addition, fluorinated polymers are not plasticized by organic vapors which usually results in a decreasing selectivity of

gas separation [11–13]. Consequently, the synthesis of new core-fluorinated as well as CF_3 -containing monomers suitable for use in the dibenzodioxane-forming reaction and ladder-type polyethers is crucial for further development of the gas separation materials. Despite the large number of studies that focuses on design of PIM polymers, only a few PIM structures with fluorinated fragments have been reported to date [4, 6, 13].

Therefore, the present work focuses on the synthesis of new advanced ladder-type FPAE copolymer (coFPAE) derived from bis(nonafluorophenyl)-containing monomer having 1,1,1,3,3,3-hexafluoropropane fragments as central units. Properties of the synthesized copolyether, such as solubility, molecular-weight characteristics, tensile strength, and thermal stability were thoroughly investigated.

Experimental.

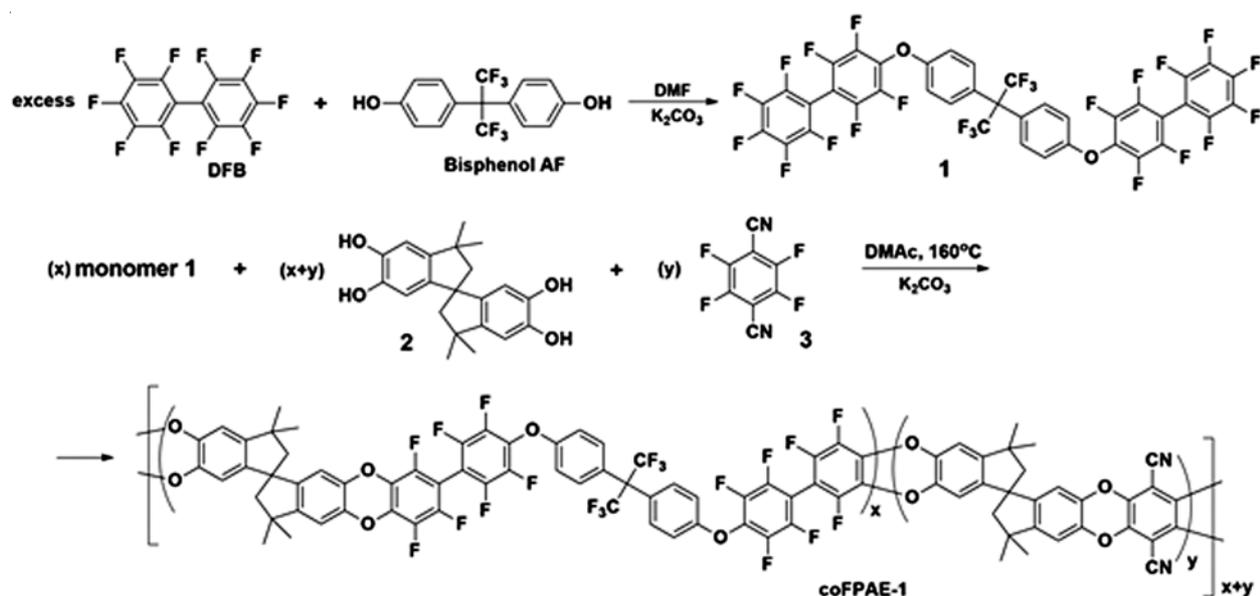
Materials. Bis(nonafluorobiphenyl)-containing monomer **1** with bis(oxyphenyl)hexafluoropropane central unit was synthesized according to the previously described procedure [14]. Hydroxyl-containing monomer 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane (**2**) was synthesized according to the previously reported protocol [15]. Tetrafluoroterephthalonitrile (**3**, 98 %) purchased from Alfa Aesar was purified by crystallization from methanol. All solvents were purified before the use.

Copolymer coFPAE-1. A dry, 25 mL three-necked flask equipped a mechanical stirrer, a cold water condenser, an argon inlet/outlet, and a thermometer was charged with bis-catechol **2** (0,300 g, 0,881 mmol), compound **3** (0,088 g, 0,441 mmol), monomer **1** (0,425 g, 0,441 mmol), and 2,0 mL of dimethylacetamide (DMAc). After dissolving of the monomers, anhydrous potassium carbonate (0,268 g, 1,938 mmol) was added into the flask. After stirring for about 10 min, the flask was transferred into a 160 °C oil

bath. The mixture was vigorously stirred for 2 min and then 0,6 mL toluene was added into the reaction mixture. The reaction was continued for 2 min and another 0,6 mL toluene was added. After another six minutes the polymer was isolated by precipitation in methanol and filtered. The total time of reaction was 10 min at 160 °C. After reprecipitation in a chloroform/methanol mixture, the polymer was boiled in hot water to remove the salt and solvent, and then filtered off. The separated copolymer was dried in vacuo at 80 °C overnight. Yield 88 %. $^1\text{H NMR}$ (CDCl_3 , 500 MHz, δ , ppm): 1,30 (br.s, 6H, $-\text{CH}_3$); 1,36 (br.s, 6H, $-\text{CH}_3$); 2,17 (br.s, 2H, $-\text{CH}_2-$); 2,33 (br.s, 2H, $-\text{CH}_2-$); 6,44 (br.s, 2H, Ph); 6,80 (br.s, 2H, Ph); 7,02 (br.s, 2H, Ph); 7,38 (br.s, 2H, Ph). $^{19}\text{F NMR}$ (CDCl_3 , 376.32 MHz, δ , ppm): -162,59 (s, 2F, Ph); -153,56 (s, 4F, Ph); -141,66 (s, 2F, Ph); -138,98 (s, 2F, Ph); -138,01 (d, 2F, $J=24.25$ Hz Ph); -64,57 (s, 6F, $-\text{CF}_3$). FTIR (ν , cm^{-1}): 989, 1012 (C–F); 1176 (C–O); 1228 (Ph–O–Ph); 1481 ($\text{C}=\text{C}_{\text{arom}}$); 2241 (CN); 2850"3000 (CH).

Characterization and measurement.

Fourier transform infrared (FTIR) spectrum of synthesized copolymer was recorded with a TENSOR 37 spectrometer in the range of 600–4000 cm^{-1} . $^1\text{H NMR}$ and $^{19}\text{F NMR}$ spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer at room temperature with CDCl_3 . Chemical shifts are reported relative to chloroform ($\delta=7,25$ ppm) for $^1\text{H NMR}$. For $^{19}\text{F NMR}$ fluorotrichloromethane was used as the internal standard. Intrinsic viscosities $[\eta]$ of polymer solution was determined with an Ubbelohde viscometer in chloroform at 25 °C. The molecular weight was determined via gel permeation chromatography (GPC) on a Shimadzu LC-10AD chromatograph equipped with Waters Styragel HT 6E columns (7,8 mm diameter \times 300 mm) and PL gel Mixed-D columns (7,5 mm diameter \times 300 mm). Tetrahydrofuran (THF) was used as the eluent, the flow rate was 0,5 mL/min, the concentration of the investigated



Scheme. Synthetic routes of monomer **1** and coFPAE-1

polymer was 3 mg/mL in THF, and the test-solution volume was 100 mL. Differential scanning calorimetry (DSC) was carried out using a TA Instruments Q-2000 apparatus (United States) at the heating rate of 20 °C/min. The thermooxidative destruction of coFPAE-1 were studied by thermogravimetric analysis (TGA) on a TA Instruments Q-50 apparatus (United States). A heating rate of 20 °C/min with a temperature range from 25 to 700 °C was applied.

Results and discussion.

In order to prepare spirobisindane-based ladder coFPAE with perfluorinated biphenylene and trifluoromethyl fragments, bis(nonafluorophenyl)-containing monomer **1** with 1,1,1,3,3,3-hexafluoropropane fragments as central units was synthesized according to the published method [14]. The monomer **1** was prepared in good yield by the interaction of DFB with 4,4'-(hexafluoroisopropylidene)diphenol (bisphenol AF) in *N,N*-dimethylformamide (DMF) in the presence of potassium carbonate as a base (Scheme 1). In order to prevent formation of oligomeric products during the synthesis of monomer **1** we use an excess DFB which can be easily removed by simple vacuum distillation. Importantly, similar to *bis*-catechol **2**, which contains a site of contortion such as a spiro-center, bis(nonafluorobiphenyl)-containing monomer **1** provides a site of contortion due to covalent bond (between perfluorinated phenylene fragments) about which there is restricted rotation [14].

The ladder-type polyether coFPAE-1 was synthesized by the dibenzodioxane formation reaction from spiro *bis*-catechol **2** and an equimolar amount of fluorinated monomers **1** and **3** in the ratio of 1:1 in DMAc in the presence of potassium carbonate (Scheme 1). The precipitation of the polymer during the reaction is avoided by the addition of toluene solvent to the DMAc.

All spectroscopic data from FTIR, ¹H, and ¹⁹F NMR spectroscopy support the suggested structure of the ladder-type coFPAE-1. Thus, the FTIR spectrum of copolymer shows peaks which correspond to C–F, –C–O–C–, –

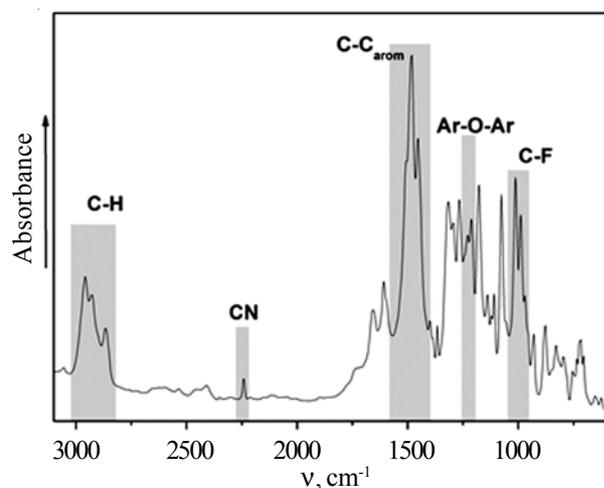


Fig. 1. FTIR spectrum of coFPAE-1

C=C_{arom} - and CN groups (Fig. 1). Additionally, the absence of intense bands of OH groups of the initial monomer **2** in the FTIR spectrum of the obtained polymer in the range of 3600–3100 cm⁻¹ indicates that these groups have been consumed during the polycondensation reaction.

All peaks in the ¹H NMR spectrum of representative coFPAE-1 can be readily assigned to the protons in the corresponding repeat units (Fig. 2).

In Figure 3 the ¹⁹F NMR spectrum of the obtained ladder-type polyether is displayed. The ¹⁹F NMR spectrum contains one singlet at -64,57 ppm corresponding to the fluorine atoms of the trifluoromethyl groups. The position and intensity of the fluorine peaks from perfluorinated aromatic units in the ¹⁹F NMR spectrum of the final copolymer are observed. These results indicate polymer formation by a double-aromatic nucleophilic substitution of fluorine atoms of bis(perfluoroaromatic) fragments in the *para*- and *ortho*-positions.

The synthesized copolymer is readily soluble in CHCl₃ and THF, and can be cast from solution to form self-supporting membrane. On the other hand, coFPAE-1 limited soluble in DMF and DMAc that are typical for the PIM polymers [16]. The number-average molecular weight (*M_n*) and the polydispersity index (*M_w/M_n*) of the coFPAE-1 calibrated with polystyrene standards were 14000 and 3,9, respectively. The intrinsic viscosity [*η*] of copolymer solution in DMF was 0,32 dL g⁻¹. Note that the coFPAE-1 sample holds a higher molar weight and narrower molar weight distribution than the PIM polymer, which was obtained from individual DFB and spirobis-catechol **2** (*M_n* = 8400, *M_w* = 36000, *M_w/M_n* = 4,3) [4].

Thermal properties of the resulting coFPAE-1 were investigated using DSC and TGA. Typically, due to their

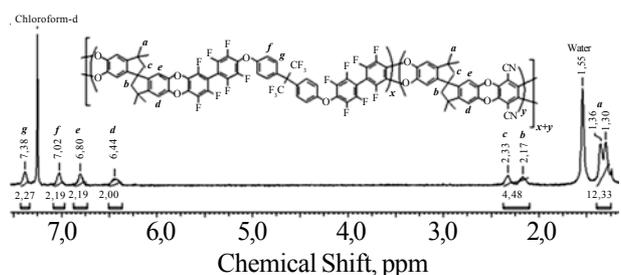


Fig. 2. ¹H NMR spectrum of coFPAE-1

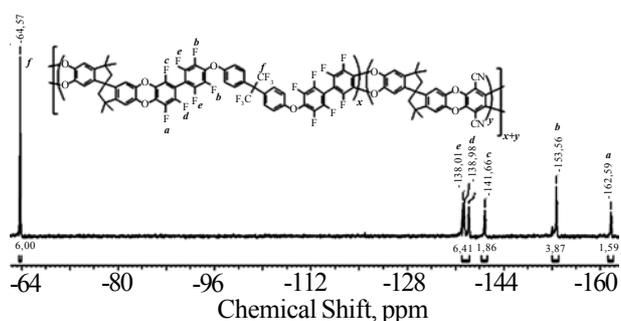


Fig. 3. ¹⁹F NMR spectrum of representative coFPAE-1

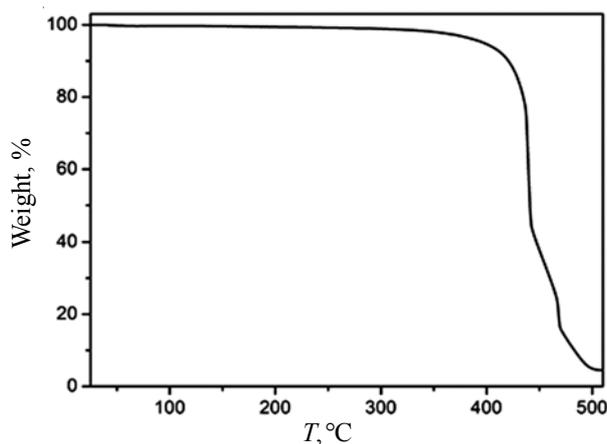


Fig. 4. TGA curve of coFPAE-1

rigid chain structure, PIMs exhibit no glass transition temperature below their decomposition temperature [17]. Hence, no glass transition temperature or other thermal

transitions were found from the DSC curve up to 300 °C. TGA experiment showed that the polymer has excellent thermal stability (Fig. 4). The synthesized coFPAE-1 exhibited one-step pattern of decomposition and the temperature of 5 % weight loss ($T_{5\%}$) for it is 400 °C.

In a summary, we have synthesized new ladder-type fluorinated copoly(arylene ether) having perfluorinated aromatic units and CF_3 -groups as well as both rigid dibenzodioxin and spirobisindane fragments. Our studies demonstrate that coFPAE-1 is characterized with an extensive solubility and shows both a relatively high molecular weight and good thermal stability. The obtained copoly-ether has good prospects for the use as gas separation materials with controlled permeability and selectivity. The presence of highly fluorinated units in the obtained fluorinated copolymer offers interesting opportunities for further functionalization of such system (for example, creation of cross-linked materials for a gas storage area).

References

1. Shevchenko V.V., Tkachenko I.M., Shekera O.V. Nucleus-fluorinated aromatic polyethers. *Polymer Sci. B.*, 2010, **52**, no. 7–8: 408–430.
2. Dhara M.G., Banerjee S. Fluorinated high-performance polymers: poly(arylene ether)s and aromatic polyimides containing trifluoromethyl groups. *Prog. Polym. Sci.*, 2010, **35**, no. 8: 1022–1077.
3. Maier G. Low dielectric constant polymers for microelectronics. *Prog. Polym. Sci.*, 2001, **26**, no. 1: 3–65.0
4. Budd P.M., Ghanem B.S., Makhseed S., McKeown N.B., Msayib K.J., Tattershall C.E. Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials. *Chem. Commun.*, 2004, no. 2: 230–231.
5. McKeown N.B., Budd P.M., Msayib K.J., Ghanem B.S., Kingston H.J., Tattershall C.E., Makhseed S., Reynolds K.J., Fritsch D. Polymers of intrinsic microporosity (PIMs): bridging the void between microporous and polymeric materials. *Chem. Eur. J.*, 2005, **11**, no. 9: 2610–2620.
6. Makhseed S., Samuel J., Bumajdad A., Hassan M. Synthesis and characterization of fluoropolymers with intrinsic microporosity and their hydrogen adsorption studies. *J. Appl. Polym. Sci.*, 2008, **109**, no. 4: 2591–2597.
7. Ramimoghadam D., Gray E.M., Webb C.J. Review of polymers of intrinsic microporosity for hydrogen storage applications. *Int. J. Hydrogen Energy*, 2016, **41**, no. 38: 16944–16965.
8. Kim S., Lee Y.M. Rigid and microporous polymers for gas separation membranes. *Prog. Polym. Sci.*, 2015, **43**: 1–32.
9. Du N., Robertson G.P., Pinnau I., Guiver M.D. Polymers of intrinsic microporosity derived from novel disulfone-
10. based monomers. *Macromolecules* 2009, **42**, no. 16: 6023–6030.
11. Makhseed S., Ibrahim F., Samuel J. Phthalimide based polymers of intrinsic microporosity. *Polymer* 2012, **53**, no. 14: 2964–2972.
12. Belov N.A., Zharov A.A., Shashkin A.V., Shaikh M.Q., Raetzke K., Yampolskii Yu.P. Gas transport and free volume in hexafluoropropylene polymers. *J. Membr. Sci.*, 2011, **383**, no. 1–2: 70–77.
13. Yampolskii Y. Polymeric gas separation membranes. *Macromolecules* 2012, **45**, no. 8: 3298–3311.
14. Du N., Robertson G.P., Song J., Pinnau I., Thomas S., Guiver M.D. Polymers of intrinsic microporosity containing trifluoromethyl and phenylsulfone groups as materials for membrane gas separation. *Macromolecules* 2008, **41**, no. 24: 9656–9662.
15. Tkachenko I.M., Belov N.A., Kobzar Ya.L., Dorokhin A.V., Shekera O.V., Shantarovich V.P., Bekeshev V.G., Shevchenko V.V. Synthesis of fluorinated poly(arylene ether)s with dibenzodioxin and spirobisindane units from new bis(pentafluorophenyl)- and bis(nonafluorobiphenyl)-containing monomers. *J. Fluorine Chem.* 2017, **195**: 1–12.
16. W. Baker. The condensation of catechol with acetone. *J. Chem. Soc.*, 1934, 1678–1681.
17. Song J., Du N., Dai Y., Robertson G.P., Guiver M.D., Thomas S., Pinnau I. Linear high molecular weight ladder polymers by optimized polycondensation of tetrahydroxytetramethylspirobisindane and 1,4-dicyanotetrafluorobenzene. *Macromolecules* 2008, **41**, no. 20: 7411–7417.
18. McKeown N.B. Polymers of intrinsic microporosity. *ISRN Materials Science* 2012, **2012**: 16.

Надійшла до редакції 2018 р.

Новий спіробісінданвмісний драбинчастий кополімерний поліариловий етер з перфторованими біфеніленовими та трифторметильними групами

І.М. Ткаченко, Я.Л. Кобзар, О.В. Шекера, В.В. Шевченко

Інститут хімії високомолекулярних сполук НАН України
48, Харківське шосе, Київ, 02160, Україна

Розроблено спосіб синтезу нового драбинчастого фторованого кополімерного поліарилового етеру, який містить перфторовані біфеніленові та трифторметильні фрагменти, а також дибенздиоксинові та спіробісінданові ланки. Такий кополімер отримано реакцією подвійного ароматичного нуклеофільного заміщення на основі 5,5',6,6'-тетрагідрокси-3,3',3',3''-тетраметил-1,1'-спіробісіндану та еквімолярної кількості двох фторованих мономерів. Будова синтезованого кополімеру досліджена методами ІЧ-, ¹H- та ¹⁹F ЯМР-спектроскопії. Отриманий полімер добре розчиняється в хлороформі та тетрагідрофурані. Показано, що такий поліетер має середньомолекулярну масу (M_w) 54600 і високу термоокиснювальну стабільність (до $T=400$ °C). Поєднання жорстких дибенздиоксинових та спіробісінданових фрагментів (вузли зігнутості) в структурі синтезованого кополіетеру веде до пониження щільності упаковки макромолекулярних ланцюгів, що перспективно для регулювання транспортних характеристик полімерних систем.

Ключові слова: фторовані в ядро мономері, фторовані ароматичні поліетери, синтез, реакція подвійного ароматичного нуклеофільного заміщення, драбинчасті фрагменти, трифторметильні групи.

Новый спиросиндансодержащий лестничный сополимерный полиариловый эфир с перфторированными бифениленовыми и трифторметильными группами

І.М. Ткаченко, Я.Л. Кобзар, О.В. Шекера, В.В. Шевченко

Інститут хімії високомолекулярних сполук НАН України
48, Харьковское шоссе, Киев, 02160, Украина

Разработан способ синтеза нового лестничного фторированного сополимерного полиарилового эфира, содержащего перфторированные бифениленовые и трифторметильные фрагменты, а также дибенздиоксиновые и спиросиндановые звенья. Такой сополимер получен реакцией двойного ароматического нуклеофильного замещения на основе 5,5',6,6'-тетрагидрокси-3,3',3',3''-тетраметил-1,1'-спиросиндана и эквимольного количества двух фторированных мономеров. Строение синтезированного сополимера исследовано методами ИК-, ¹H- и ¹⁹F ЯМР-спектроскопии. Полученный полимер хорошо растворяется в хлороформе и тетрагидрофуране. Показано, что такой полиэфир имеет средневесовую молекулярную массу (M_w) 54600 и высокую термоокислительную стабильность (до $T=400$ °C). Сочетание жестких дибенздиоксиновых и спиросиндановых фрагментов (узлы изогнутости) в структуре синтезированного сополиэфира ведет к понижению плотности упаковки макромолекулярных цепей, что является перспективным для регулирования транспортных характеристик полимерных систем.

Ключевые слова: фторированные в ядро мономеры, фторированные ароматические полиэфиры, синтез, реакция двойного ароматического нуклеофільного замещения, лестничные фрагменты, трифторметильные группы.