СИНТЕЗ ПОЛІМЕРІВ

POLYMER SYNTHESIS

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SYNTHESIS OF FLUORINATED POLY (ARYLENE POLYETHER) COPOLYMERS WITH QUATERNARY PIPERIDINIUM AND MORPHOLINIUM GROUPS

Polymers functionalized with quaternary ammonium centers hold great promise for the development of universal ion-conducting membranes, enabling their application in energy conversion and storage technologies such as fuel cells, flow batteries, electrolyzers, etc. In this context, poly(arylene ether) polymer backbones with covalently attached quaternary ammonium moieties (e.g., imidazolium, piperidinium, guanidinium, pyrrolidinium, etc.) are utilized for the fabrication of such membranes. In this work, the strategy to the synthesis of the quaternary ammonium functionalized fluorinated poly(arylene ether) copolymers is proposed. The copolymers are synthesized by aromatic nucleophilic substitution reaction from decafluorobiphenyl and piperidine- or morpholine-based dihydroxyl-substituted monomers using resorcinol as comonomer in both cases. Quaternized polymers with piperidinium (QFPAE-PP) andmorpholinium (QFPAE-MP) side groups were synthesized via Menshutkin reactions with iodomethane in dimethylacetamide (DMAc) at room temperature. Free-standing films with a tensile strength of approximately 30 MPa were obtained from DMAc solutions of the quaternized polymers. The thermal properties of the quaternized polymers in the I^- form were studied using differential scanning calorimetry and thermogravimetric analysis. It was found that both copolymers exhibit dual glass transition temperatures, which is attributed to their

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copolymeric nature, leading to the formation of phases enriched and depleted in cationic centers. The polymer with piperidinium groups (QFPAE-PP) demonstrated higher thermal stability, with a 5 % weight loss occurring at 220 °C, compared to 200 °C for QFPAE-MP. Treatment of the quaternized polymers (QFPAE-PP and QFPAE-MP) with an aqueous alkaline solution resulted in the formation of polymeric ammonium bases (polymers in the OH^- form). The obtained IEC values indicate the potential of these systems for use as anion-exchange membranes in various applications.

Keywords: *poly(arylene ether)s, quaternary ammonium, ion exchange capacity, anion exchange membrane.*

Introduction

The development of thermally stable polymers with diverse functional capabilities remains a crucial area in polymer chemistry. Among such polymers, aromatic polyethers attract particular interest due to their high thermal and chemical stability provided by aromatic units [1-3]. Additionally, the presence of ether linkages in the polymer chains enhances their mechanical strength and flexibility, thereby increasing solubility [4]. The incorporation of fluorinated fragments into polymers further improves their thermal and chemical stability as well as enlarges solubility and transparency, reduces surface energy, dielectric constant, friction coefficient, and other properties [5, 6]. Significant progress was made in the development of proton- and anion- exchange membranes based on fluorinated polyarylene ethers (FPAEs) for applications in fuel cells, electrolyzers, and redox flow batteries (e.g., vanadium redox flow battery) [7—12]. In this context, one of the key advantages of poly(arylene ether)s is the excellent mechanical properties of their films, which are crucial for membrane technologies.

Generally, anion-exchange membranes (AEMs) have emerged as a highly promising alternative to commercially established proton exchange membranes (PEMs), such as the widely used Nafion, for applications in vehicles, power plants, and portable power sources [13]. Their advantages stem from enhanced oxygen reduction reaction activity and the ability to utilize cost-effective base metal electrocatalysts [14]. In contrast, Nafion-based fuel cells rely on platinum (Pt)-based catalysts, a costly and limited resource, thereby driving the search for more sustainable and economically viable alternatives. Both AEMs and PEMs play a crucial role in separating fuel and oxidant; however, unlike PEMs, which facilitate proton (H^-) transport in an acidic medium, AEMs operate in an alkaline environment, conducting hydroxide (OH^-) anions [15]. To enable anion conductivity, nitrogen-containing cationic groups are incorporated into the polymer structure, typically in the form of various quaternized amine groups, including ammonium, imidazolium, guanidinium, pyridinium, morpholinium, spiro-ammonium, and others [16, 17].

Over the past decades, various poly(arylene ether)s, including fluorinated derivatives, were synthesized for the development of AEMs. The synthetic strategy typically involves the chloromethylation of aromatic units or the bromination of methylbenzene units in polyethers (a post-functionalization approach), followed by the reaction of chloromethyl/bromomethyl groups with tertiary amines of various structures (a quaternization reaction) [18—21]. The resulting cationic groups, initially associated with Cl^- (Br^-) counterions, are then converted to their hydroxide (OH^-) form through treatment with an aqueous alkaline (KOH or NaOH) solution, making them suitable for use in fuel cells and electrolyzers. Another approach to functionalization of polyethers with quaternary ammonium groups is to use aminomethylated phenolic-type monomers (such as bisphenols) [22—24]. The resulting polymers, containing a tertiary nitrogen atom, are then quaternized with various alkyl halides, typically methyl iodide. This strategy allows the introduction of functional groups in a well-defined arrangement, while the number of these groups can be easily controlled by adjusting the composition of comonomers with different structures.

Previously, tetrafluoro(diphenoxy)benzene-based phenolic monomers with aminomethylated moieties in the aromatic units, which allow the synthesis of ionogenic FPAEs, was developed [25, 26]. However, controlling the number of cationic centers in this case is challenging, as the polymer chains precipitate out of solution during the quaternization process, resulting in polymers that are insoluble in most organic solvents. Thus, the present study reports an approach to design FPAE copolymers with side piperidinium (PP) or morpholinium (MP) fragments and octafluorobiphenylene units in the main chain, using resorcinol as a comonomer to regulate the number of cationic centers. The combination of *meta*-isomeric units, flexible aromatic ether groups and contorted sites (non-coplanar units of octafluorobiphenylene) within the macromolecular chains results in polymers with exceptional solubility and film-forming capabilities, opening the way for their versatile applications.

Experimental section

Materials. Fluorinated aminomethylated monomers 4,4'-((perfluoro-1,4-phenylene)bis(oxy))bis(2-(piperidin-1-ylmethyl)phenol) (1-PP) and 4,4'-((perfluoro-1,4-phenylene)bis(oxy))bis(2-(morpholinomethyl)phenol) (1-MP) were prepared according to the earlier described procedure [26, 27]. Decafluorobiphenyl (2) (99 %) and resorcinol (3) (99 %) are purchased from Aldrich Chemical Co. and used as received. Anhydrous potassium carbonate (K_2CO_3, 99 %) is purchased from Acros Organic Inc and dried at 120 °C for 24 hours before it is used. The other reagents and solvents were purified routinely.

Polymers Preparation

Synthesis of FPAE-PP. 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 monomer 1-PP (0.248 g, 0.439 mmol), decafluorobiphenyl (0.250 g, 0.748 mmol), and 4.1 mL of N,N-dimethylacetamide (DMAc). After dissolving the monomers, anhydrous potassium carbonate (0.111 g, 0.804 mmol) was added to the flask. The solution was then heated to 85 °C and stirred at this temperature for 1 hour. A solution of resorcinol (0.032 g, 0.292 mmol) in DMAc (1 ml) was then added to the reaction mixture. The molar ratio of OH-based components to decafluorobiphenyl was 0.977 : 1 respectively. After an additional 1-hour reaction at 90 °C, the reaction mixture was cooled to room temperature and poured into 30 mL of ethanol containing a few drops of glacial acetic acid to precipitate the polymer. The precipitate was collected, dried, and dissolved in chloroform, filtered to remove any insoluble solid, and reprecipitated by adding the solution dropwise into ethanol. The copolymer was collected and dried in vacuo for 24 h at 60 °C overnight. Yield is 85 %.

Copolymer FPAE-MP with side morpholine moieties was prepared using similar procedure as outlined above. Yield is 82 %.

Quaternization of FPAE-PP and FPAE-MP (QFPAE-PP and QFPAE-MP). FPAE-PP and FPAE-MP were quaternized via the Menshutkin reaction using iodomethane. The reactions were performed in 8—10 wt % polymer solutions in DMAc at room temperature in the dark with K_2CO_3 ensuring the neutrality and availability of all amine groups for quaternization. In a typical procedure, FPAE-PP or FPAE-MP (1 equiv) and K_2CO_3 (1 equiv) were dispersed in DMAc to form a heterogeneous mixture. Iodomethane (3 equiv) was then added, and the reaction proceeded in darkness for 24 h. The reaction mixture was subsequently poured into a large volume of ethyl acetate and washed several times. The purified polymers in iodine (I^-) forms were further dried at 60 °C for one day.

Film preparation and ion exchange. QFPAE-PP and QFPAE-MP were dissolved in DMAc to prepare 5 wt. % polymer solutions. The solutions were filtered through 0.45 μm syringe filters onto glass Petri dishes and dried at 80 °C for 48 h to form membranes. The resulting membranes were then treated with a 1M NaOH solution at room temperature for 24 h to exchange I^- for OH^- anions. Afterward, the membranes were soaked in deionized water to remove residual NaOH.

Characterization. ^1H and ^{19}F NMR spectra were recorded at room temperature using a Bruker Avance instrument in $CDCl_3$ or DMSO-d_6 as the solvents. Fourier transform infrared (FTIR) spectra (4000—400 cm^{-1}) of the synthesized compounds were recorded on a TENSOR 37 spectrometer (Bruker Optics) using KBr pellets. The intrinsic viscosity of polymer solutions was measured using an Ubbelohde viscometer in dimethylacetamide at 30 °C. The ion exchange capacity (IEC) of the obtained polymers was determined by back titration [28], while the water uptake (WU) was assessed based on the weights change of the polymers before and after swelling at room temperature [16]. Tensile strengths of the samples were measured on a 2166 P-5 tensile-testing machine with a stretching speed of 50 mm/min. The glass transition temperature (T_g) of the polymers was determined by differential scanning calorimetry (DSC) using a Q-2000 TA Instruments (USA) device at a heating rate of 20 °C/min. Thermal stability was evaluated by thermogravimetric analysis (TGA) on a Q-50 TA Instruments (USA) device in air with a heating rate of 20 °C/min over a temperature range of 25—1000 °C.

Results and Discussion

In this study, two novel partially fluorinated copoly(arylene ether)s functionalized with pendant ammonium groups, specifically piperidinium (PP) and morpholinium (MP) groups, were synthesized. The synthesis was carried out via aromatic nucleophilic substitution reactions using aminomethylated dihydroxyl-substituted monomers containing either piperidine (monomer 1-PP) or morpholine (monomer 1-MP) units along with decafluorobiphenyl (monomer 2) and resorcinol (monomer 3) as comonomers. The resulting polymers, FPAE-PP and FPAE-MP, were obtained following the procedure outlined in Fig. 1. The FPAE-PP and FPAE-MP copolymers were obtained as white fibers with a yield of approximately 85—90 %. The required phenolic monomers with a central tetrafluorobenzene core, 1-PP and 1-MP, were synthesized using the Mannich reaction following the procedures described in [57—59].

In order to prepare cationic quaternized polymers, FPAE-PP and FPAE-MP were treated with an excess of iodomethane in DMAc solution leading to the conversion of tertiary amine groups into quaternary ammonium groups (piperidinium and morpholinium). This reaction yielded the corresponding cationic quaternized polymers, QFPAE-PP and QFPAE-MP (Fig. 1). All quaternized polymers were soluble in DMAc, NMP and DMSO, and insoluble in diethyl ether, IPA, water and chloroform.

In our previous work, we demonstrated that the quaternization of an FPAE-PP homopolymer, synthesized with an equimolar ratio of monomer 1-PP to monomer 2 in acetone, led to the formation of an insoluble polymer [25]. A similar result was observed when DMAc was used as the solvent. Next, numerous studies showed that controlling the amount of quaternary ammonium cations is crucial for managing the trade-off between the physicochemical properties of polymers and their electrochemical characteristics [11]. For example, while an increased number of cationic groups can enhance anionic conductivity, it also tends to

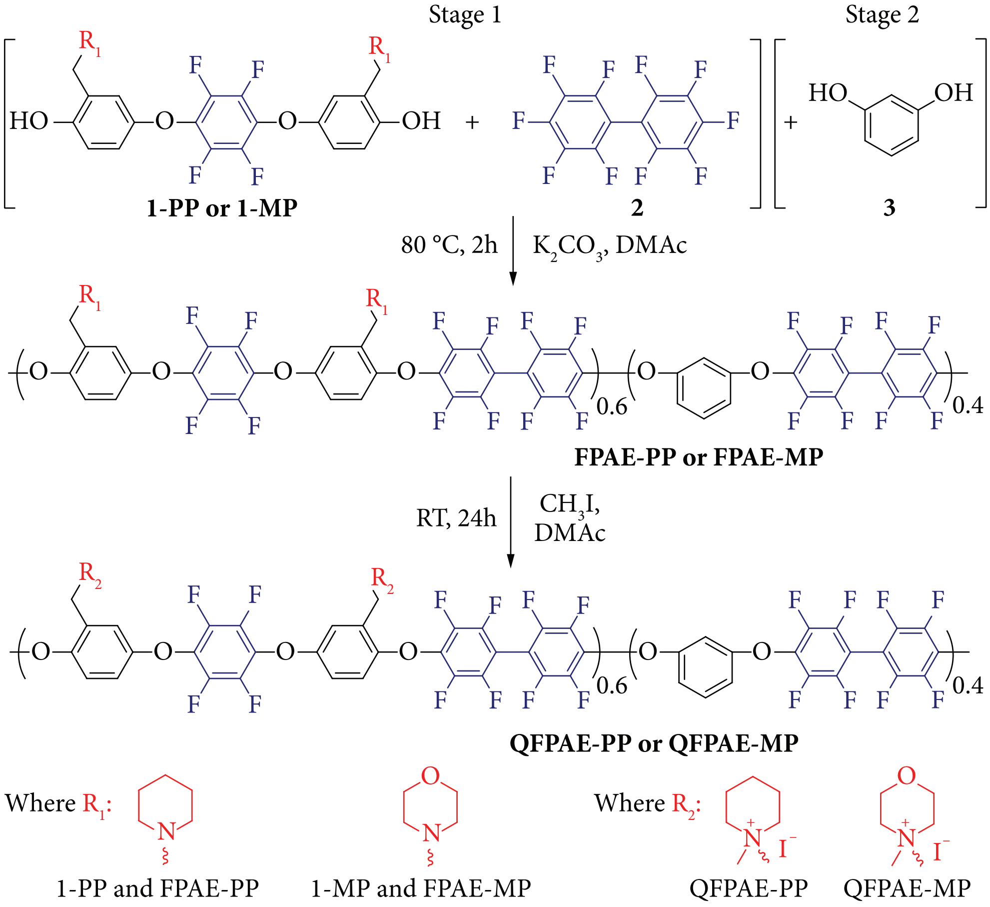


Fig. 1. Synthetic pathways to QFPAE-PP and QFPAE-MP polymers

cause excessive water absorption by the polymer, compromising the stability of the resulting membranes in terms of their geometric dimensions and making them unsuitable for practical applications.

Based on data from the literature [24], a molar ratio of aminomethylated monomer 1-PP (or monomer 1-MP) to resorcinol of 60:40 mol % for the polymer synthesis was chosen in this study. As a result, complete quaternization of these copolymers occurred in DMAc solution without subsequent precipitation. Moreover, the combination of *meta*-isomeric units and flexible aromatic ether groups in macromolecular chains leads to the formation of polymers with exceptional solubility and film formation ability, setting the stage for their versatile applications. The fluorinated component (tetrafluorobenzene and octafluorobenzene fragments) aims to maintain the high thermal stability of functionalized polymers [4].

The success of the synthesis of the FPAE copolymers was confirmed with ^{1}H, 19F NMR and FTIR spectroscopy techniques. The chemical shifts corresponding to protons of the aromatic units in the neutral FPAE-PP and FPAE-MP are observed in their ^{1}H NMR spectra within the range of 6.6—7.4 ppm (Fig. 2).

The peak for proton *d* of the methylene groups directly connected to the aromatic fragments appears at approximately 3.7 ppm. The ^{1}H NMR spectra of the cation-active polymers QFPAE-PP and QFPAE-MP are recorded in deuterated DMSO with the addition of 5 vol % TFA to shift

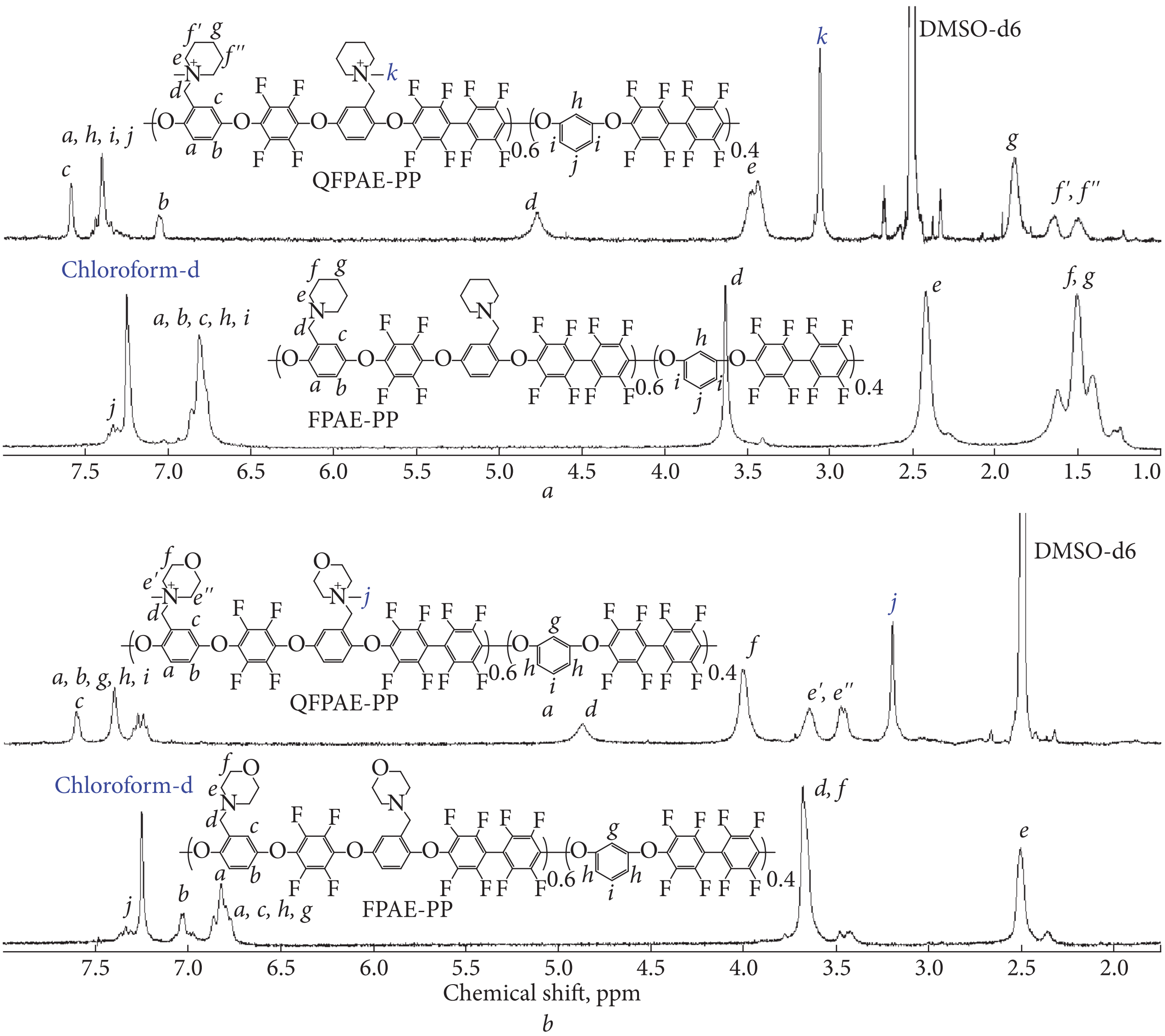


Fig. 2. ^{1}H NMR spectra of synthesized piperidine- (*a*) and morpholine-containing (*b*) polymers

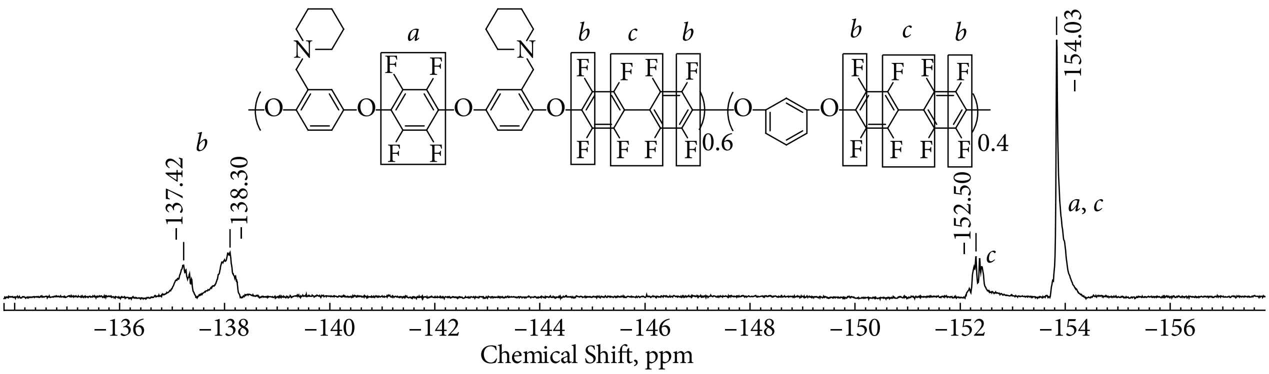


Fig. 3. ^{19}F NMR spectra of FPAE-PP

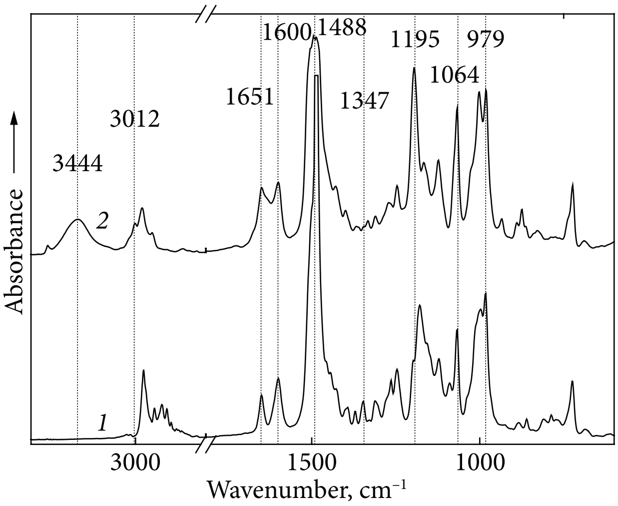


Fig. 4. FTIR spectra of copolyethers FPAE-PP (*1*) and QFPAE-PP (*2*)

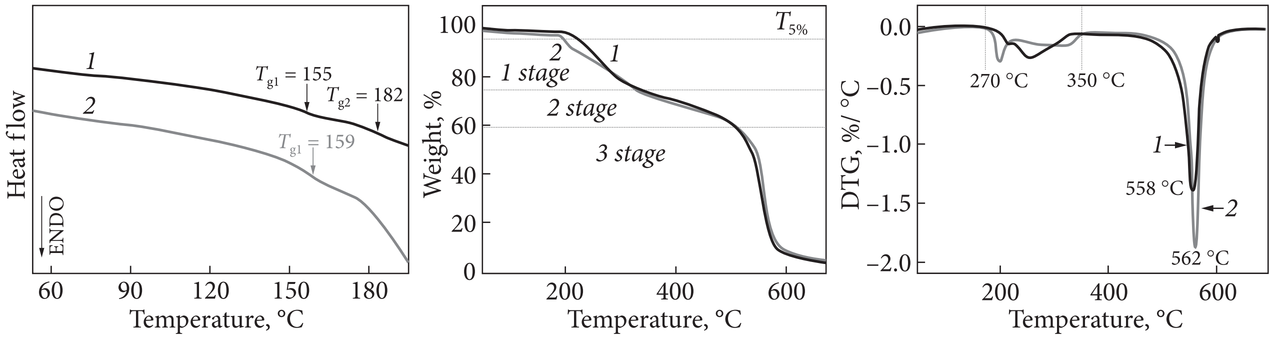
the water peak present in DMSO, facilitating spectrum interpretation. Evidence of quaternization is provided by the appearance of a new peak in the ^{1}H NMR spectra of QFPAE-PP and QFPAE-MP at approximately 3.1 ppm, corresponding to the protons *k*/*j* of the methyl group introduced into the polymers using iodomethane. The introduction of a new methyl group into the polymer significantly alters the chemical environment of the methylene groups in the cyclic amine component, leading to changes in the distribution pattern of the corresponding proton signals (Fig. 2). The formation of quaternary ammonium groups also causes a slight chemical shift of the aromatic protons and a substantial shift of the methylene protons *d* (to approximately 4.8 ppm) into a weaker field (Fig. 2).

The ^{19}F NMR spectra of the FPAE-PP and FPAE-MP polymers do not show signals characteristic of decafluorobiphenyl atoms in the *para*-positions, indicating their substitution [29]. Due to the copolymeric nature of polymers (which results in variations in the chemical environment of the fluorinated fragments), the signals from the fluorinated units are broadened and exhibit complex splitting patterns. For instance, the fluorine atoms of the octafluorobiphenylene fragment in the *meta*- and *ortho*-positions relative to the ether bond appear as two signals, with one of the ortho-substituted fluorine signals overlapping with the signal from the fluorine atoms of the tetrafluorobenzene core. As an example, the spectrum of the FPAE-PP polymer is presented in Fig 3.

Figure 4 presents the FTIR spectra of the FPAE-PP (spectrum 1) and QFPAE-PP (spectrum 2) polymers as examples. Both spectra contain absorption bands corresponding to C–F bonds ((979—1001) cm^{-1}), aromatic C = C bonds (~1488 and ~1600 cm^{-1}), and fluorinated aromatic C = C bonds (~1651 cm^{-1}).

In contrast, the FTIR spectrum of QFPAE-PP exhibits an additional absorption band at 3012 cm^{-1} and the disappearance of the C-N linkage band at 1347 cm^{-1}, indicating the formation of a new H_3C—N^+ bond due to the methylation of tertiary amine groups in FPAE-PP. The broad band at 3444 cm^{-1} in the FTIR spectrum of QFPAE-PP indicates the presence of bound moisture, which is characteristic of high-molecular-weight quaternary ammonium compounds. Additionally, the intensity of the band at 1064 cm^{-1} (C-N) increases, and the band at 1195 cm^{-1} (C-O) shifts, reflecting the transition from a neutral polymer to a cation-active polymer.

The DSC results (second heating cycle, heating rate — 20 °C/min; nitrogen atmosphere) point out an amorphous structure of the obtained quaternized polymers (Fig. 5*a*). Due to the copolymer



a *b* *c*

Fig. 5. DSC curves (*a*), TGA curves (*b*) and DTG curves (*c*) of the synthesized cationic-active polymers (curve *1* — QFPAE-PP; curve *2* — QFPAE-MP)

nature, QFPAE-PP exhibits two glass transition temperatures (T_{g1} and T_{g2}), indicating the presence of two types of amorphous phases in its structure. The corresponding T_{g1} and T_{g2} values for QFPAE-PP are 155 °C and 182 °C. It is evident that QFPAE-MP may also have two types of amorphous phases, but the T_{g2} value, which is above 180 °C, is difficult to determine precisely, as thermal degradation of the polymer begins at a temperature slightly above 180 °C (see TGA data below). The T_{g1} value for QFPAE-MP is 159 °C (Fig. 5*a*).

It is evident that the lower glass transition temperature (below 160 °C) for QFPAE-PP and QFPAE-MP corresponds to the “mobile” phase, where macromolecular chains containing fewer quaternized nitrogen centers exhibit greater flexibility and mobility. The higher thermal transition (T_{g2}) indicates a relatively rigid amorphous phase formed by macromolecules saturated with quaternized amino groups. As shown in reference [25], quaternization of FPAEs significantly increases their glass transition temperatures compared to corresponding FPAEs containing only tertiary nitrogen atoms. Similar thermal behavior, characterized by the presence of two glass transition temperatures, also was observed in other polymers and copolymers containing perfluoroaromatic fragments and *meta*-oxyphenylene units [30, 31].

The study of the thermal oxidative stability of the synthesized quaternized polymers revealed that the $T_{5\,\%}$ values are 220 °C for QFPAE-PP and 200 °C for QFPAE-MP. The decomposition of the polymers occurs in three stages, with a minor mass loss observed below 170 °C, attributed to the evaporation of residual solvent (Fig. 5*b*). The first stage (180—320 °C) corresponds to the elimination of the quaternary nitrogen atom and the decomposition of aliphatic fragments [32]. The second stage (320—500 °C) involves further degradation of aliphatic groups and the initial breakdown of ether bonds. In the third stage (500—640 °C), the decomposition of aromatic fragments occurs [31]. Derivative thermogravimetry (DTG) curves for both polymers show the most intense weight loss peak at ~550 °C, indicating the highest degradation rate (Fig. 5*c*). Broad, less intense peaks in the 270—350 °C range indicate a more prolonged degradation process resulting from the gradual cleavage of the aforementioned chemical bonds. Notably, the presence of piperidinium centers enhances the thermal oxidative stability of QFPAE-PP compared to QFPAE-MP during the first stage of decomposition. However, there are no significant differences in the decomposition behavior of the two polymers during the second and third stages.

Free-standing, flexible, and tough QFPAE-PP and QFPAE-MP films, with a stress at break of 36 MPa and 28 MPa, respectively, were successfully fabricated from a DMAc solution. These films were then immersed into a 1M sodium hydroxide aqueous solution at room temperature for 24 hours to convert them from the iodine form to the hydroxide form. Due to their high fluorine content, the synthesized unquaternized FPAE-PP and FPAE-MP exhibit low water uptake (QFPAE-PP: 8 %, QFPAE-MP: 11 %). However, upon quaternization, the incorporation of hydrophilic quaternary ammonium groups increases water uptake, reaching 26 % for QFPAE-PP and 31 % for QFPAE-MP in the OH^- form. Theoretically calculated values of the ionic exchange capacity (IEC), which express the concentration of charge carriers, are approximately 1.68 meq/g for both polymers in their

OH^- form. Experimentally determined IEC values (using the back-titration method) for the polymer bases were slightly lower than the theoretical predictions, particularly, 1.35 meq/g for QFPAE-PP and 1.42 meq/g for QFPAE-MP. These lower IEC values are attributed to incomplete exchange of iodide anions for hydroxyl anions, as well as to the sensitivity of the measurement method.

Conclusion

In this study, successful synthesis of quaternary ammonium-functionalized fluorinated poly(arylene ether) copolymers via aromatic nucleophilic substitution, followed by quaternization through the Menshutkin reaction with iodomethane, was performed. The incorporation of resorcinol enabled precise tuning of the aminomethylated (piperidinium/morpholinium) fragment content. Spectroscopic analysis (NMR and FTIR) confirmed the chemical structure of the synthesized copolymers, while DSC and TGA investigations provided insight into their thermal behavior. According to DSC, the polymers are amorphous and primarily exhibit two glass transitions between 150 and 190 °C. Notably, the quaternized piperidinium-based copolymer exhibited slightly higher thermal stability than the morpholinium-based copolymer, with $T_{5\,\%}$ values of 220 °C for QFPAE-PP and 200 °C for QFPAE-MP. The synthesized cationic-active FPAEs (QFPAE-PP and QFPAE-MP) was able to be readily solution-processed into mechanically stable, free-standing films. Additionally, ion-exchange capacity measurements indicated values of 1.35 meq/g for QFPAE-PP and 1.42 meq/g for QFPAE-MP, confirming their suitability as anion-exchange membranes. These properties make them promising candidates for applications in energy conversion and storage technologies.

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СИНТЕЗ ФТОРОВАНИХ КОПОЛІАРИЛОВИХ ПОЛІЕТЕРІВ З КВАТЕРНІЗОВАНИМИ ПІПЕРИДИНІЄВИМИ ТА МОРФОЛІНІЄВИМИ ГРУПАМИ

Полімери, функціоналізовані кватернізованими амонієвими центрами, мають великий потенціал для розроблення різноманітних іонопровідних мембран, які застосовують у технологіях перетворення та зберігання енергії, таких як паливні елементи, проточні батареї, електролізери тощо. Для створення таких мембран використовують поліарилові етери з ковалентно зв'язаними четвертинними амонієвими групами (наприклад імідазольними, піперидинієвими, гуанідинієвими, піролідинієвими та ін.). У цій роботі запропоновано метод синтезу фторованих поліарилових кополіетерів з функціональними четвертинними амонієвими фрагментами. Синтез цих полімерів здійснено шляхом реакції ароматичного нуклеофільного заміщення між декафторбіфенілом і дигідроксизаміщеними мономерами, які містять піперидинові або морфолінові групи, із застосуванням резорцину як комономеру в обох випадках. Кватернізовані полімери з піперидинієвими (QFPAE-PP) і морфолінієвими (QFPAE-MP) бічними групами були отримані запри реакцією Меншуткіна з йодистим метилом у диметилацетаміді (ДМАА) за кімнатної температури. З розчинів кватернізованих полімерів у ДМАА отримано механічно стабільні плівки міцністю на розрив близько 30 МПа. Методами диференціальної сканувальної калориметрії та термогравіметричного аналізу вивчено теплофізичні властивості кватернізованих полімерів в I$^-$ формі. Встановлено, що обидва кополімери мають по дві температури склування, що пояснюється їх кополімерною природою, яка приводить до утворення фаз, збагачених і збіднених катіонними центрами. Полімер з піперидинієвими групами (QFPAE-PP) продемонстрував вищу термостабільність: 5 %-ва втрата маси відбувалася за температури 220 °C порівняно з 200 °C для QFPAE-MP. Оброблення кватернізованих полімерів (QFPAE-PP і QFPAE-MP) водним розчином лугу зумовило утворення полімерних амонієвих основ (полімерів у формі OH$^-$). Отримані значення статичної обмінної ємності вказують на потенціал цих систем при використанні як аніонообмінних мембран у різних галузях застосування.

Ключові слова: поліарилові етери, четвертинні амонієві групи, іонообмінна ємність, аніонообмінна мембрана.