SULFONATION OF STYRENE – ALLYL GLYCIDYL ETHER COPOLYMERS

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ABSTRACT. Sulfonated polymeric materials are widely applied in the development of high-performance proton-conducting membranes. In terms of sulphating agents, concentrated sulphuric- and chlorosulfonic acids, a mixture of methanesulfonic- and concentrated sulphuric acid, and acetyl sulphate are most commonly used. A high degree of sulfonation of membrane materials provides efficient proton transport and excellent current-voltage characteristics of fuel cells. In order to develop a new proton-conducting membrane, the sulfonation of copolymers of styrene and allyl glycidyl ether is carried out, the composition and structure were confirmed by elemental analysis, IR and NMR spectroscopy. Obtained copolymers represent powdery substances, having a cream to dark brown colour, and are characterised by good solubility in benzene and acetone. The degree of sulfonation varies from 12 to 98 mol. %. Additionally, a quantum chemical study of the sulfonation mechanism of styrene and allyl glycidyl ether copolymers is studied using Gaussian 09 software; MP2//B3LYP level of theory and 6-311++G(d,p) basis set and composite CBS-QB3 method. Studying the process of copolymers sulfonation and comparing the obtained results with the data of quantum chemical calculations is essential for the development of additional methods for obtaining effective proton-conducting membranes.

Keywords: sulfonated copolymers, allyl glycidyl ether, styrene, quantum chemical calculations

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СУЛЬФИРОВАНИЕ СОПОЛИМЕРОВ СТИРОЛА И АЛЛИГЛИЦИДИЛОВОГО ЭФИРА

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**INTRODUCTION**

Currently, a wide range of sulfonated macro-

molecular compounds based on perfluorinated poly-

mers and aromatic condensation polymers – as well as aromatic polymerisation products, for exam-

ple, polystyrene – are used in the creation of pro-

ton-conducting membranes [1–6].

Sulfonated aromatic condensation polymers manifest themselves as promising compounds for making of proton-conducting membranes. These polymers are characterised by high heat resistance, good mechanical properties and high moisture absorption while having good plasticity and proton conductivity. The simplest and most common method for the synthesis of such membranes consists in sulfonation of various class polymers, such as, poly(1,4-phenylene) [2, 7], poly-п-xylene [8, 9], poly(1,4-oxyphenylene) [4, 9–14], polyarene ether sulfo-

nes [15–17], polyphenylene sulphides [18], polyphenylquinolines [19, 20], polybenzimidaz-

oles [2] and several dozen of other aromatic cond-

ensation polymers.

In terms of sulphating agents, the most com-

monly used are concentrated sulphuric and chloro-

sulfonic acids, a mixture of methanesulfonic and con-

centrated sulphuric acids, and acetyl sulphate. The degree of sample sulfonation ranges from 30 to 100%. At the same time, the chemical destruction and «crosslinking» are not observed, and the resulting membranes demonstrate sufficiently high proton conductivity [2].

The development of polystyrene-based proton-conducting membranes is promising due to its commercial availability and low cost [21]. The first industrial proton-conducting membranes [22], having a level of conductivity comparable to that of commercial perfluorinated membranes, were obtained from sulfonated polystyrene [22]. It should be noted the main disadvantage of polystyrene membranes is their short lifetime due to their low thermal-oxidative stability and mechanical strength.

Chemical modification of polystyrene materi-

als by copolymerisation of styrene with functional-

ised vinyl monomers (for example, allyl glycidyl ether), as well as the formation of hybrid composite materials based on it, which include blocks of inorganic components, provides an opportunity to reduce these disadvantages and obtain proton conducting materials comparable to commercially-available per-

fluorinated membranes (Nafion, MF-4SK) [23].

It has been shown that the proton conductivity of polymer membranes is determined not only by the presence of functional groups that provide proton transfer, but also by the structure of the mem-

brane itself [24]. In particular, macromolecules for-

ming membrane structure should be capable of forming clusters to effectively adsorb water.

Noteworthy, hybrid composites microstructure is formed, among other things, at the stage of co-

polymer sulfonation. Therefore, in order to develop additional methods for obtaining proton-conducting membranes on this basis, an understanding of the mechanism of styrene and allyl glycidyl ether copolymer sulfonation is of great importance.

The aim of this work is to study the products of sulfonation of styrene and allyl glycidyl ether copolymer and to compare the obtained results with the data of quantum-chemical calculations.
DISCUSSION OF THE RESULTS

Copolymers of styrene (St) and allyl glycidyl ether (AGE) are obtained using the suspension radical copolymerisation method according to [25]. Sulfonation of copolymers is carried out with concentrated sulphuric acid (p=1.825 g/cm³) in a solution of benzene or toluene at a temperature varying from 60 to 90 °C for 2 hours. AGE-St sulfonated copolymers represent powdery substances coloured from cream to dark brown with good solubility in benzene and acetone. According to the elemental analysis, the degree of sulfonation ranges from 12 to 98 mol. % (see Table below).

Absorption IR bands of sulfonated copolymers are observed in the regions of 1260-1150 cm⁻¹, 1080-1010 cm⁻¹ and 700-600 cm⁻¹, which can be assigned to asymmetric and symmetric stretching vibrations of sulfogroups. The presence of oxirane cycle is confirmed by the presence of absorption bands in the following regions: 810 and 950 cm⁻¹ – asymmetric and 1250 cm⁻¹ – symmetric stretching vibrations of oxirane ring; 3040 cm⁻¹ – vibrations of the methylene group in oxirane ring.

The reactive oxirane cycle of AGE and aromatic fragments of St represent the main active centres for sulfonation. The ¹³C NMR spectroscopy data confirm the reaction course toward to both aromatic ring and epoxy group, indicating the formation of corresponding products.

Quantum chemical calculations are performed using the Gaussian 09 software [26]. Geometry optimization of structures is studied using B3LYP DFT functional [27] with 6-311++G(d,p) basis set [28] with zero-point vibrational energy correction. The refinement of the total energy is performed at Møller-Plesset MP2 level of theory [29] with the same basis set. At all stages of the calculations, toluene is used as a solvent and non-specific solvation is accounted for in the framework of IEF-PCM approximation [30]. For transition states, a descent along the internal reaction coordinate (IRC) is also performed [31] to prove the relationship between the transition state and initial reagents, as well as the reaction products. The relative energies presented in the text are given for the MP2/6-311++G(d,p)/B3LYP/6-311++G(d,p) method taking into account zero-point vibrational energy (ZPVE) calculated at B3LYP/6-311++G(d,p).

In order to study the sulfonation mechanism of the obtained copolymers, model molecules ethylbenzene (EB) and 2-(propoxymethyl)oxirane (PO) are used as structural elements of the AGE-St copolymer. The choice of these structures is justified by the fact that in the case of an atactic polymer, consideration of the three-units-block is not enough due to possible conformational changes, while involving a larger number of units in the calculation significantly increases the calculation cost. It should be noted that for model structures, in contrast to the copolymer, steric effect reveals much lesser extent. This must be considered when switching to the real object of study, such as AGE-St copolymer.

As in the case of other aromatic hydrocarbons, sulfonation of polystyrene proceeds through the initial attack by a S-electrophile (A₃). However, the precise role of the S-electrophile in this process is still debatable. The nature of «true» electrophile in the reaction between aromatic hydrocarbons and sulfuric acid H₂SO₄ depends on the concentration of the latter [18]. Thus, in diluted solutions, H₂SO₄⁺ (or H₂SO₄ and H₂O⁺ associate) acts as S-electrophile, while at concentrations above 80-85% it is H₂SO₄⁻ (or H₂SO₄ and SO₃ associate) that performs this function [32]. However, the true electrophile in the A₃ reaction of aromatic hydrocarbons is presented by SO₃ in free form or its associate.

In order to clarify the nature of the true electrophile and to study the sulfonation mechanism of obtained copolymers, model experiments are carried out. Energy profiles for generation of various S-electrophiles (H₂SO₄⁺, HSO₃⁻, SO₃ and H₂SO₄⁻) presented in Figure 1, energy values are obtained using precision composite CBS-QB3 method developed by Peterson et al. [33] taking into account the polarity of the solvent (toluene) in the framework of IEF-PCM model.

As can be seen from Figure 1, due to strong hydrogen bonds, the association of two H₂SO₄ molecules with the formation of dimer (H₂SO₄)₂ leads to energy decrease of 15.8 kcal/mol. Further protonation of one of the molecules in (H₂SO₄)₂ by the other with the formation of H₂SO₄⁺HSO₃⁻ ion pair requires high energy input (93.7 kcal/mol).

### Table

**General features of the process of AGE-St copolymers sulfonation**

| Composition of copolymer, mol.% | Temperature, °C | Composition of sulfonated copolymer, mol.% | Sulfonation degree, α, % |
|---------------------------------|-----------------|-------------------------------------------|-------------------------|
| St                             | AGE             |                                           |                         |
| 97.65                          | 2.35            | 60                                        | 86.60                   | 12.00                   | 1.40 | 12.29 |
| 97.65                          | 2.35            | 80                                        | 71.97                   | 26.51                   | 1.51 | 27.15 |
| 97.65                          | 2.35            | 90                                        | 3.69                    | 94.13                   | 2.17 | 96.40 |
| 97.78                          | 2.22            | 60                                        | 81.84                   | 16.80                   | 1.36 | 17.18 |
| 97.78                          | 2.22            | 80                                        | 46.99                   | 51.39                   | 1.61 | 52.56 |
| 97.78                          | 2.22            | 90                                        | 2.03                    | 95.87                   | 2.10 | 98.05 |

**Общие закономерности процесса сульфирования сополимеров АГЭ-Ст**

| Состав сополимера, мол. % | Температура, °C | Состав сульфированных сополимеров, мол. % | Степень сульфирования, α, % |
|--------------------------|-----------------|-------------------------------------------|-----------------------------|
| St                       | AGE             |                                           |                             |
| 97.65                    | 2.35            | 60                                        | 86.60                       | 12.00                     | 1.40 | 12.29 |
| 97.65                    | 2.35            | 80                                        | 71.97                       | 26.51                     | 1.51 | 27.15 |
| 97.65                    | 2.35            | 90                                        | 3.69                        | 94.13                     | 2.17 | 96.40 |
| 97.78                    | 2.22            | 60                                        | 81.84                       | 16.80                     | 1.36 | 17.18 |
| 97.78                    | 2.22            | 80                                        | 46.99                       | 51.39                     | 1.61 | 52.56 |
| 97.78                    | 2.22            | 90                                        | 2.03                        | 95.87                     | 2.10 | 98.05 |
The subsequent elimination of H$_2$O molecule from H$_3$SO$_4^+$, resulting in the HSO$_3^+$ electrophile, requires even greater energy input (121.6 kcal/mol). Thus, the formation of such S-electrophiles as H$_3$SO$_4^+$ and HSO$_3^+$ is almost impossible under sulfonation conditions at temperature below 100 °C in non-polar solvents such as toluene. An alternative pathway involves the formation of S-electrophile SO$_3$ (relative energy 19.9 kcal/mol) through the transition state TS$_{SO3}^+$ corresponding to elimination of H$_2$O from H$_2$SO$_4$. This TS$_{SO3}^+$ is characterised by the imaginary frequency of $\nu$ = 1694 cm$^{-1}$ (B3LYP/CBSB7), and the activation barrier of SO$_3$ formation from H$_2$SO$_4$ through the TS$_{SO3}$ is 37.9 kcal/mol. Another more energetically favourable pathway includes the formation of S-electrophile H$_2$S$_2$O$_7$, the relative energy of which is only 9.8 kcal/mol higher than the original system (two noninteracting molecules H$_2$SO$_4$). H$_2$S$_2$O$_7$ is formed from dimer (H$_2$SO$_4$)$_2$ by elimination of H$_2$O molecule through TS$_{H_2SO_7}$ ($\nu$ = 1749 cm$^{-1}$, B3LYP/CBSB7). The activation barrier for the H$_2$S$_2$O$_7$ formation is 25.2 kcal/mol.

On the basis of the obtained results, it can be concluded that H$_2$S$_2$O$_7$ (associate SO$_3$-H$_2$SO$_4$, fig. 2) turns out to be the true S-electrophile. This S-electrophile was used for further calculations.

In case of reaction between H$_2$S$_2$O$_7$ and ethylbenzene both para- and ortho-position attack of the phenyl ring is possible (see energy profile in Fig. 3). It is due to +I and +M-effects of ethyl substituent at phenyl ring. In both cases, the reaction proceeds through transition states shown in Fig. 4. These transition states (TS4 and TS2, respectively) lie 24.6 and 23.6 kcal/mol above the original non-reacting system ($\nu$ = 1336 and $\nu$ = 1351 cm$^{-1}$, respectively, B3LYP/6-311+G(d,p)). The descent along internal coordinate of the reaction shows these TSs bind pre-reaction complexes (pre-TS4 and pre-TS2) with the corresponding sulfonation products at para- (Et$^t$C$_6$H$_5$SO$_3^+$H$_2$SO$_4$) and ortho-positions (Et$^t$C$_6$H$_5$SO$_3$H$^-$H$_2$SO$_4$) of phenyl ring in ethylbenzene. As can be seen from Figure 3, the energy profiles of their formation are almost the same; ethyl substituent favours the substitution into ortho-position of the phenyl ring with very minor extent. Thus, sulfonation proceeds with equal probability at both ortho- and para-positions of phenyl ring in ethylbenzene.

![Energy profile of generating various S-electrophiles from H$_2$SO$_4$ calculated at the CBS-QB3 level of theory](image1)

**Fig. 1. Energy profile of generating various S-electrophiles from H$_2$SO$_4$ calculated at the CBS-QB3 level of theory**

![Structures of S-electrophiles: H$_3$SO$_4^+$ (1), HSO$_3^+$ (2), SO$_4^-$ (3) and H$_2$S$_2$O$_7$ (4) calculated at B3LYP/CBSB7 level](image2)

**Fig. 2. Structures of S-electrophiles: H$_3$SO$_4^+$ (1), HSO$_3^+$ (2), SO$_4^-$ (3) and H$_2$S$_2$O$_7$ (4) calculated at B3LYP/CBSB7 level (as a part of the CBS-QB3 calculation). The charges on the sulphur atoms according to Mulliken at the level of MP2/CBSB3 are shown in parentheses**

![Structures of S-electrophiles: H$_3$SO$_4^+$ (1), HSO$_3^+$ (2), SO$_4^-$ (3) and H$_2$S$_2$O$_7$ (4), calculated on the level of B3LYP/CBSB7](image2)

**Fig. 2. Структуры S-электрофилов H$_3$SO$_4^+$ (1), HSO$_3^+$ (2), SO$_4^-$ (3) и H$_2$S$_2$O$_7$ (4), рассчитанные на уровне B3LYP/CBSB7 (в рамках расчета CBS-QB3). В скобках приведены заряды на атомах серы по Малликену на уровне MP2/CBSB3/B3LYP/CBSB7**
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Fig. 3. Energy profiles of adducts formation as a result of H$_2$S$_2$O$_7$ attack to ethylbenzene (EB) and 2-(propoxymethyl)oxirane (PO) calculated at the level of MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p). Energy values are given for B3LYP/6-311++G(d,p) level taking into account ZPVE correction.

Рис. 3. Энергетические профили образования аддуктов в результате взаимодействия H$_2$S$_2$O$_7$ с этилбензолом (EB) и 2-(пропоксиметил)оксираном (PO), рассчитанные на уровне MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p). Значения энергий приведены с учетом ZPVE поправки на уровне B3LYP/6-311++G(d,p).

Fig. 4. The structure of transition states of TS4 (1), TS2 (2) and TS$_{PO}$ (3) calculated at B3LYP/6-311++G(d,p) level.

Рис. 4. Структуры переходных состояний ПС4 (1), ПС2 (2) и ПСРО (3), рассчитанные на уровне B3LYP/6-311++G(d,p).

It should be noted the transformation products are presented in fig. 4 as associates with H$_2$SO$_4$ due to strong hydrogen bonds; this is the result of the attack of ethylbenzene (as well as 2-(propoxymethyl)oxirane) by H$_2$S$_2$O$_7$ electrophile. The barrier of H$_2$SO$_4$ elimination from the latter is ca. 18 kcal/mol (omitted from consideration).

In the case of para-position product (Et$_{p}$C$_6$H$_4$SO$_3$H), the mechanism of 4-ethylbenzene-1,3-disulfonic acid formation is also studied. Here, the activation barrier of second H$_2$S$_2$O$_7$ attack to ortho-position of phenyl ring of Et$_{p}$C$_6$H$_4$SO$_3$H turns out to be
slightly higher and is equal to 32.7 kcal/mol (1267 cm⁻¹).

Since the oxirane cycle can also be attacked with H₂S₂O₇, the reaction of 2-(propoxymethyl)oxirane with H₂S₂O₇ was studied. The reaction starts with the formation of the pre-reaction complex pre-TSPO, resulting in a significant decrease in the system's energy (-16.8 kcal/mol; Fig. 3) – two times lower than that of ethylbenzene. It was assumed that the product of electrophilic attack would be 3-propoxypyropane – 1,2-disulfonic acid. However, during the search for TS, only TSPO was found, connecting, in accordance with IRC results, connecting pre-TSPO (Fig. 4) and the product of oxirane ring expansion (4-(propoxymethyl)-1,3,2-dioxathiolane 2,2-dioxide, DTD, Fig. 5), while the activation barrier is 24.5 kcal/mol (526 cm⁻¹).

Ring-opening of 1,3,2-dioxathiolane fragment in DTD by H₂SO₄ or H₂O can lead to the formation of a range of products including 3-propoxypyropane-1,2-disulfonic, 1-hydroxy-3-propoxypyropan-2-sulfonic, 2-hydroxy-3-propoxypyropan-1-sulfonic acids and 3-propoxypyropane-1,2-diol (Fig. 6). The relative energies of formation of these transformation products increase in following sequence: 3-propoxypyropane-1,2-disulfonic acid (-40.6 kcal/mol) < 1-hydroxy-3-propoxypyropane-2-sulfonic acid (-35.3 kcal/mol) = 2-hydroxy-3-propoxypyropan-1-sulfonic acid (-33.7 kcal/mol) < 3-propoxypyropane-1,2-diol (-18.8 kcal/mol).

Fig. 5. Structure of 4-(propoxymethyl)-1,3,2-dioxathiolane 2,2-dioxide (DTD) calculated at B3LYP/6-311++G(d,p)
Рис. 5. Структура 4-(пропоксиметил)-1,3,2-диоксатиолан 2,2-диоксида (ДТД) рассчитанная на уровне B3LYP/6-311++G(d,p)

Fig. 6. Structure of 3-propoxypyropane-1,2-disulfonic (1), 1-hydroxy-3-propoxypyropan-2-sulfonic (2), 2-hydroxy-3-propoxypyropan-1-sulfonic acids (3) and 3-propoxypyropane-1,2-diol (4) calculated at B3LYP/6-311++G(d,p)
Рис. 6. Структуры 3-пропоксипропан-1,2-дисульфоновой (1), 1-гидрокси-3-пропоксипропан-2-сульфоновой (2), 2-гидрокси-3-пропоксипропан-1-сульфоновой кислот (3) и 3-пропоксипропан-1,2-диола (4), рассчитанные на уровне B3LYP/6-311++G(d,p)
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REFERENCES

1. Yaroslavtsev A.B. Perfluorinated ion-exchange membranes. Polymer Science. Series A. 2013, vol. 55, no. 11, pp. 674-698. DOI: 10.1134/S0965545X13110060
2. Yaroslavtsev A.B., Dobrovol'sky A.Y., Frolova L.A., Gerasimova E.V., Sanginov E.A., Shaglaeva N.S. Nanostructured materials for low-temperature fuel cells. Russian Chemical Reviews. 2013, vol. 81, no. 3, pp. 191-200. DOI: 10.1070/RC2012v081n03
3. Wang F., Roovers J. Functionalization of poly(aryl ether ketone) (PEEK): synthesis and properties of aldehyde and carboxylic acid substituted PEE. Macromolecules. 1993, vol. 26, pp. 5295-5302. DOI: 10.1021/ma940321302
4. Devaux J., Delimoy D., Dauost D., Legras R., Mercier J.P., Strazielle C., Nield E. On the molecular weight determination of a poly(aryl-ether-ether-ketone). Polymer. 1985, vol. 26, no. 13, pp. 2994-2000. DOI: 10.1016/0032-3861(85)90179-X
5. Gaur S.S., Dhar P., Kumar A., Katiyar V. Prospects of poly (vinyl alcohol)/Chitosan/poly (styrene sulfonic acid) and montmorillonite Cloisite (R) (30B) clay composite membrane for direct methanol fuel cells. Journal of renewable and sustainable energy. 2014, vol. 6, No. 5, p. 053135. DOI: 10.1002/14899192
6. Pedroza O.J.O., Oscar J. O., Dutra J.C., Picciani P.H.S., Dias M.L. Morphology and proton conductivity of composite membranes based on poly(styrene sulfonic acid-maleic anhydride) nanofibers prepared by electrospinning. IONICS. 2015, vol. 21, no. 3, pp. 755-764. DOI: 10.1007/s11581-014-1212-2
7. Sochilin V.A., Pebalk A.V., Semeniv V.I., Kardash I.E. Sulphonated poly-p-xylene. Vysokomolekulyarnye soedineniya. Seriya A [Higher molecular compounds. Series A]. 1991, vol. 33, no 7, pp. 1536-1542. (in Russian)
8. Sochilin V.A., Pebalk A.V., Semeniv V.I., Sevast'yanov M.A., Kardash I.E. Permeability and structure of poly-p-xylene. Vysokomolekulyarnye soedineniya [Higher molecular compounds]. 1993, vol. 35, no. 9, pp. 1480-1485. (in Russian)
9. Bredas J.L., Chance R.R., Silbey R. Comparative theoretical study of the doping conjugated polymers; Polaron in polyacetylene and polypropyphenylene. Physical Review B. 1982, vol. 26, no. 10, pp. 5843-5854. DOI: 10.1103/PhysRevB.26.5843
10. Bailly C., Williams D.J., Karasz F.F., MacKnight W.J. The sodium salts of sulphonatedpoly (aryl-ether-ether-ketone) (PEEEK): preparation and characterization. Polymer. 1987, vol. 28, no. 6, pp. 1009-1016. DOI: 10.1016/0032-3861(87)90179-9
11. Jin X., Bishop M.T., Ellis T.S., Karasz F.E. A sulphonated poly(aryl ether ketone). Polymer International Journal. 1985, vol. 17, no. 1. pp. 4-10. DOI: 10.1002/pi.4980170102
12. Litter M.I., Marvel C.S. Polymaromatic ether-ketones and polynaromatic ether-ketone sulphonamides from 4-phenoxybenzoyl chloride and from 4,4'dichloroformyldiphenyl ether. J. Polymer Sci., Polymer Chem. Edd. 1985, vol. 23, no. 8, pp.2205-2223. DOI: 10.1002/poi.1985.170230811
13. Ogawa T., Marvel C.S. Polynaromatic ether-ketones and ether-keto-sulphones having various hydrophilic groups. Journal of Polymer Science., Polymer Chemistry. 1985, vol. 23, no. 4, pp. 1231-1241. DOI: 10.1002/poi.1985.170230426
14. Nolte R., Ledjeff K., Bauer M., Mulhaupt R. Partially sulphonated poly(arylene ether sulfone) - a versatile proton conducting membrane material for modern energy-conversion technologies. J. Membr. Sci. 1993, vol. 83, no. 2, pp. 211-220. DOI: 10.1016/0376-7388(93)85268-2
15. Johnson B.C., Yilgor I., Tran C., Iqbal M., Wightman J.P., Lloyd D.R., McGrath J.E. Synthesis and characterization of sulphonated poly(arylene ether sulphones). J. Polym. Sci, Part A: Polym. Chem. 1984, vol. 22, pp. 721-737. DOI: 10.1002/pol.1984.170220320
16. Mottet C., Revillon A., Perchec P.L., Lauro M.E., Guyot A. Analogous reaction for maximum sulfonation of polysulfones. Polym. Bull. 1982, vol. 8, no. 11-12, pp. 511-517. DOI: 10.1007/BF00262929
17. Qi Z., Lefebvre M.C., Pickup P.G. Electron and proton transport in gas diffusion electrodes containing electronically conductive proton-exchange polymers. J. Electroanalytical Chemistry. 1998, vol. 459, no. 1, pp. 9-14. DOI: 10.1016/S0022-0728(98)00241-1

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18. Belomoina N.M., Rusanov A.L., Yanul’ N.A., Kirsch Yu. Ye. Thermoreactive sulfur containing polyphenyleinquinolines. Vysokomolekulanye soedineniya. Seriya B [Higher molecular compounds. Series B]. 1996, vol. 38, pp. 355-358. (in Russian)

19. Kirsch Yu. Ye., Yanul’ N.A., Belomoina N.M., Rusanov A.L. Electrochemical properties of cation-exchange membranes from sulfonate-containing polyphenyleinquinolines. Elektrokhimiya [Electrochemistry]. 1996, vol. 35, no. 2, pp. 169. (in Russian)

20. Srarkov V.V. Silicon-based monolithic fuel elements. Nano-i mikroisistemnaya tekhnika [Nano and microsystem technique]. 2006, vol. 3, pp. 26-30. (in Russian)

21. Schwaben H.D. Polystyrene (PS). Kunststoffe - Plast Europe. 1999, vol. 89, no. 10, pp. 52-56.

22. Dobrovolsky Yu.A., Volkov E.V., Pisareva A.V., Fedotov Yu.A., Lihachev D.Yu., Rusanov A.L. Proton-exchange membranes for hydrogen-air fuel cells. Rossiiskij khimicheskij zhurnal [Russian chemical bulletin]. 2006, no. 6, pp. 95-104. (in Russian)

23. Lebedeva O.V., Sipkina E.I., Chesnkova A.N., Maksimenko S.D., Pozhidaev Y.N., Rzhechitskiy A.E., Ivanov N.A., Malahova E.A., Raskulova T.V., Kuzmin A.V. Ion exchange membranes based on silica and sulfonated copolymers of styrene with allyl glycidyl ether. Petroleum chemistry. 2017, vol. 57, no. 9, pp. 763-769. DOI: 10.1134/S0965554417090067

24. Kreuer K.D. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. Journal of Membrane Science. 2001, vol. 185, pp. 29-39. DOI: 10.1016/S0376-7388(00)00632-3

25. Malakhova E., Chernigovskaya M., Raskulova T. New proton-conductive membranes for fuel cells based on hybrid composites. Procedia Engineering. 2015, vol. 113, pp. 441-445. DOI: 10.1016/j.proeng.2015.07.328

26. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas O., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J. Gaussian, Inc., Wallingford CT, 2009.

27. OBecke A.D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, vol. 98, no. 7, pp. 5648-5652. DOI: 10.1063/1.464913

28. McLean A.D., Chandler G.S. Contracted Gaussian-basis sets for molecular calculations. 1. 2nd row atoms, Z=11-18. J. Chem. Phys. 1980, vol. 72, pp. 5639-5648. DOI: 10.1063/1.438980

29. Head-Gordon M., Pople J.A., Frisch M.J. MP2 energy evaluation by direct methods. Chem. Phys. Lett. 1980, vol. 153, pp. 503–506. DOI: 10.1016/0009-2614(88)85250-3

30. Miertuš S., Scrocco E., Tomasi J. Electrostatic interaction of a solute with a continuum. A Direct Utilization of AB initio molecular potentials for the prevision of solvent effects. Chem. Phys. 1981, vol. 55, no. 1, pp. 117-129. DOI: 10.1016/01-0104(81)85090-2

31. Fukui K. The path of chemical-reactions - The IRC approach. Acc. Chem. Res. 1981, vol. 14, pp. 363-368. DOI: 10.1021/ar00072a001

32. Bamford C.H., Tipper C.F.H. Comprehensive chemical kinetics. New York. Elsevier Scientific Publishing Company,1972. Vol. 13. 508 p.

33. Montgomery Jr. J. A., Frisch M. J., Ochterski J. W., Petersson G. A. A complete basis set model chemistry. VII. Use of the minimum population localization method. J. Chem. Phys. 2000, vol. 112, pp. 6532-6542. DOI: 10.1063/1.481224
Sulfonation of styrene – allyl glycidyl ether copolymers

6. Pedroza O.J.O., Oscar J. O., Dutra J.C., Picciani P.H.S., Dias M.L. Morphology and proton conductivity of composite membranes based on poly(styrene sulfonic acid-maleic anhydride) nanofibers prepared by electrospinning. IONICS. 2015, vol. 21, no. 3, pp. 755-764. DOI: 10.1007/s11581-014-1212-2

7. Сочилин В.А., Пебалк А.В., Семенов В.И., Кардаш И.Е. Сульфанированный поли-п-ксиллен // Высокомолекулярные соединения. Серия А. 1991. Т. 33, N 7. C. 1536-1542.

8. Сочилин В.А., Пебалк А.В., Семенов В.И., Севастьянов М.А., Кардаш И.Е. Проницаемость и структура сульфанированного поли-п-ксиллена // Высокомолекулярные соединения. 1993. Т. 35, N 9. С. 1480-1485.

9. Bredas J.L., Chance R.R., Slibey R. Comparative theoretical study of the doping conjugated polymers; Polaron in polycatenylene and polyarylene. Physical Review B. 1982, vol. 26, no. 10, pp. 5843-5854. DOI: 10.1103/PhysRevB.26.5843

10. Bailly C., Williams D.J., Karasz F.F., MacKnight W.J. The sodium salts of sulphonated poly(aryl-ether-ether-ketone) (PEEK): preparation and characterization. Polymer. 1987, vol. 28, no. 6, pp. 1009-1016. DOI: 10.1016/0032-3861(87)90178-9

11. Jin X., Bishop M.T., Ellis T.S., Karasz F.E. A sulphonated poly(aryl ether ketone). Polymer International Journal. 1985, vol. 17, no. 1. pp. 4-10. DOI: 10.1002/pi.4980170102

12. Litter M.I., Marvel C.S. Polyaromatic ether ketones and polyaromatic ether-ketone sulphonamides from 4-phenoxycarbonyl chloride and from 4,4’dichloroformylidiphenyl ether. J. Polymer Sci., Polymer Chem. Edd. 1985, vol. 23, no. 8, pp.2205-2223. DOI: 10.1002/pol.1985.170230811

13. Ogawa T., Marvel C.S. Polyaromatic ether ketones and ether-keto-sulfones having various hydrophilic groups. Journal of Polymer Science., Polymer Chemistry. 1985, vol. 23, no. 4, pp. 1231-1241. DOI: 10.1002/pol.1985.170230426

14. Nolte R., Ledjef K., Bauer M., Mulhaupt R. Partially sulphonated poly(arylene ether sulfone) - a versatile proton conducting membrane material for modern energy-conversion technologies. J. Membr. Sci. 1993, vol. 83, no. 2, pp. 211-220. DOI: 10.1016/0376-7388(93)85268-2

15. Johnson B.C., Yilgor I., Tran C., Iqbal M., Wightman J.P., Lloyd D.R., McGrath J.E. Synthesis and characterization of sulphonated poly(acrylene ether sulfones). J. Polym. Sci, Part A: Polym. Chem. 1984, vol. 22, pp. 721-737. DOI: 10.1002/pol.1984.170220320

16. Mottet C., Reivill A., Perchec P.L., Lauro M.E., Guyot A. Analogous reaction for maximum sulphonation of polysulphones. Polym. Bull. 1982, vol. 8, no. 11-12, pp. 511-517. DOI: 10.1007/BF00262929

17. Qi Z., Lefebvre M.C., Pickup P.G. Electron and proton transport in gas diffusion electrodes containing electronically conductive proton-exchange polymers. J. Electroanalytical Chemistry. 1998, vol. 459, no. 1, pp. 9-14. DOI: 10.1016/S0022-0728(98)00241-1

18. Беломоина Н.М., Русланов А.Л., Януль Н.А., Кирил Ю.Э. Термореактивные серосодержащие полифенилхиноксалины // Высокомолекулярные соединения. Серия Б. 1996. Т. 38. С. 355-358.

19. Кирил Ю.Э., Януль Н.А., Беломоина Н.М., Русланов А.Л. Электрохимические свойства кационобменных мембран из сульфонатосодержащих полиарилэфирхиноксалинов // Электрохимия. 1996. Т. 35. N 2. С. 169.

20. Старков В.В. Монолитные топливные элементы на основе кремния // Нано- и микросистемная техника. 2006. N 3. C. 26-30.

21. Schwaben H.D. Polystyrene (PS). Kunststoffe - Plast Europe. 1999, vol. 89, no. 10, pp. 52-56.

22. Добровольский Ю.А., Волков Е.В., Писарева А.В., Федотов Ю.А., Лихачев Д.Ю., Русланов А.Л. Протонообменные мембраны для водородо-воздушных топливных элементов // Рос. хим. журнал. 2006. N 6. C. 95-104.

23. Lebedeva O.V., Sipkina E.I., Chenskova A.N., Maksimenko S.D., Pozhidaev Y.N., Rzhechitsky A.E., Ivanov N.A., Mahalova E.A., Raskulova T.V., Kuzmin A.V. Ion exchange membranes based on silica and sulfonated copolymers of styrene with allyl glycidyl ether. Petroleum chemistry. 2017, vol. 57, no. 9, pp. 763-769. DOI: 10.1134/S0965544117090067

24. Kreuer K.D. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. Journal of Membrane Science. 2001, vol. 185, pp. 29-39. DOI: 10.1016/S0376-7388(00)00632-3

25. Malakhova E., Chernigovskaya M., Raskulova T. New proton-conductive membranes for fuel cells based on hybrid composites. Procedia Engineering. 2015, vol. 113, pp. 441-445. DOI: 10.1016/j.proeng.2015.07.328

26. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas O., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J. Gaussian, Inc., Wallingford CT, 2009.
27. Becke A.D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, vol. 98, no. 7, pp. 5648–5652. DOI: 10.1063/1.464913

28. McLean A.D., Chandler G.S. Contracted Gaussian-basis sets for molecular calculations. 1. 2nd row atoms, Z = 11–18. J. Chem. Phys. 1980, vol. 72, pp. 5639–5648. DOI: 10.1063/1.438980

29. Head-Gordon M., Pople J.A., Frisch M.J. MP2 energy evaluation by direct methods. Chem. Phys. Lett. 1980, vol. 153, pp. 503–506. DOI: 10.1016/0009-2614(88)85250-3

30. Miertuš S., Scrocco E., Tomasi J. Electronic interaction of a solute with a continuum. A Direct Utilization of AB initio molecular potentials for the prevision of solvent effects. Chem. Phys. 1981, vol. 55, no. 1, pp. 117–129. DOI: 10.1016/0009-2614(81)85090-2

31. Fukui K. The path of chemical-reactions - The IRC approach. Acc. Chem. Res. 1981, vol. 14, pp. 363–368. DOI: 10.1021/ar00072a001

32. Bamford C.H., Tipper C.F.H. Comprehensive chemical kinetics. New York. Elsevier Scientific Publishing Company, 1972. Vol. 13. 508 p.

33. Montgomery Jr. J.A., Frisch M.J., Ochterski J.W., Petersson G.A. A complete basis set model chemistry. VII. Use of the minimum population localization method. J. Chem. Phys. 2000, vol. 112, pp. 6532–6542. DOI: 10.1063/1.481224

**Contribution**

Lebedeva O.V., Malakhova A.V., Kuzmin A.V., Chesnokova A.N., Sipkina E.I., Raskulova T.V., Pozhidaev Yu.N., Kulshrestha V. carried out the experimental work, on the basis of the results summarized the material and wrote the manuscript. Lebedeva O.V., Malakhova A.V., Kuzmin A.V., Chesnokova A.N., Sipkina E.I., Raskulova T.V., Pozhidaev Yu.N., Kulshrestha V. have equal author’s rights and bear equal responsibility for plagiarism.

**Conflict of interests**

The authors declare no conflict of interests regarding the publication of this article.

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