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Copolymers of sodium 4-styrene sulphonate and vinyl derivatives of nitrogen-containing heterocycles

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Abstract: The formation of ion-exchange composite materials based on high molecular weight precursors appears to be an intensively developing area in the synthesis of proton-conducting membranes for fuel cells. In such membranes, proton transfer is often provided by functional polymers simultaneously containing sulphonic acid groups in their composition units along with fragments of vinyl derivatives of nitrogen-containing heterocyclic bases. Proton exchange activity in the latter is determined by the possibility of doping with inorganic acids. In the framework of this study, for the further formation of hybrid composite membranes under conditions of radical initiation, copolymers of sodium 4-styrene sulphonate (SSSt) with 4-vinylpyridine (VP) and 1-vinylimidazole (VIM) were obtained. The monomodal nature of the turbidimetric titration curves for solutions of copolymerisation reaction products indicates the presence of true copolymers during the process of formation. The composition and structure of the copolymers were characterised using data from elemental analysis, as well as from IR and ^{13}C NMR spectroscopy. Constants of the relative activity for the monomers and the microstructure parameters of the polymer chains are calculated according to the non-linear least-squares method using the MathCAD package. The calculated copolymerisation constant values indicate a greater reactivity of SSSt in comparison with nitrogen-containing monomers. The lengths of the monomer unit blocks depend on the composition of the initial mixture and vary over a wide range from 1 to 18. The possibility of varying the length of the unit blocks in the composition of the copolymers will affect the ion-conducting properties of hybrid composites formed on their basis. The stability of the copolymers to thermal oxidative degradation by heating in air was studied using the differential scanning calorimetry (DSC) method. The copolymers demonstrated significant thermo-oxidative stability. Decomposition temperatures were 350 °C and 400 °C for SSSt-VIM and SSSt-VP copolymers, respectively.

Keywords: radical copolymerisation, sodium 4-styrene sulphonate, 4-vinylpyridine, 1-vinylimidazole, relative activity constants

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Сополимеры 4-стиролсульфоната натрия и винильных производных азотсодержащих гетероциклов

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Резюме: Формирование ионообменных композиционных материалов на основе высокомолекулярных прекурсоров является интенсивно развивающимся направлением синтеза протонпроводящих мембран для топливных элементов. Протонный перенос в таких мембранах нередко обеспечивается функциональными полимерами, одновременно содержащими в своем составе звенья с сульфокислотными группировками, а также фрагменты винильных производных азотсодержащих гетероциклических оснований. Протонообменная активность последних определяется возможностью их допирования неорганическими кислотами. В рамках данной работы для дальнейшего формирования гибридных композиционных мембран в условиях радикального иницирования получены сополимеры 4-стиролсульфоната натрия (ССст) с 4-винилпиридином (ВП) и 1-винилимидазолом (ВИМ). Мономодальный характер кривых турбидиметрического титрования растворов продуктов реакции сополимеризации свидетельствует об образовании в ходе процесса истинных сополимеров. Состав и строение сополимеров охарактеризованы с помощью данных элементного анализа, ИК-спектроскопии и спектроскопии ЯМР ^{13}C . Нелинейным методом наименьших квадратов в пакете MathCAD рассчитаны константы относительной активности мономеров и параметры микроструктуры полимерных цепей. Значения констант сополимеризации свидетельствуют о большей реакционной способности ССст по сравнению с азотсодержащими мономерами. Длины блоков звеньев мономеров зависят от состава исходной смеси, изменяются в широких пределах и могут составлять от 1 до 18. Возможность варьирования длины блоков звеньев в составе сополимеров позволит влиять на ионопроводящие свойства гибридных композитов, сформированных на их основе. Методом дифференциально сканирующей калориметрии (ДСК) исследована устойчивость сополимеров к термоокислительной деструкции при нагревании на воздухе. При этом показано, что сополимеры обладают значительной термоокислительной устойчивостью. Температуры разложения составляют: 350 °С – для сополимеров ССст-ВИМ, 400 °С – для сополимеров ССст-ВП.

Ключевые слова: радикальная сополимеризация, 4-стиролсульфонат натрия, 4-винилпиридин, 1-винилимидазол, константы относительной активности

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INTRODUCTION

Recently, increased attention has been attracted to polymer composite membrane materials with ion-conducting properties [1–8]. This is mainly due to the widespread possibility of modifying their conductive, mechanical and chemical properties by changing the nature of the components included in their structure. Thus, the modification of organic macromolecules by inorganic components with ionic groups is aimed primarily at increasing water-holding ability and preventing the dehydration of the materials obtained on this basis. Moreover, the introduction of inorganic compounds into the composites often allows the proton conductivity of the final membranes to be increased. Silicon,

zirconium and cerium oxides [9–11], carbon materials formed as nanotubes and fullerenes [12, 13], heteropolyacids, for example, phosphoric tungsten or silicon tungsten, as well as polyantimonic acids, etc. are widely used as inorganic additives [14, 15].

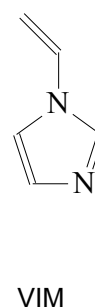
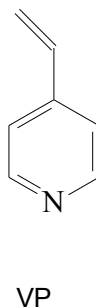
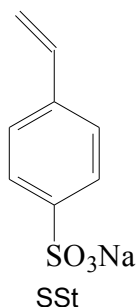
A new direction, which has recently been under intensive development, relates to the direct synthesis of inorganic fragments in the structure of the formed organic polymer by the sol-gel synthesis method. In this case, the inorganic component is most often formed by hydrolytic polycondensation of alkoxysilanes resulting in the formation of polysiloxane blocks formed in the composite structure with the study of latter being the subject of a significant number of works, for example [16–18].

This approach to the formation of composite membranes seems to be the most successful, since it leads to the formation of materials with a high degree of homogeneity and excludes the possibility of phase separation of components. The introduction of silicon-containing fragments into the structure of composites provides the increase in their thermal stability and proton conductivity [17–19]. During the formation of membranes by such methods, proton transfer is supplied mainly by functional groups included in the structure of the organic polymer: sulfo groups or nitrogen-containing organic

bases capable of doping with phosphoric acid.

Earlier, the authors of this article obtained sulphonated copolymers of styrene and allyl glycidyl ether, on the basis of which hybrid membranes with high proton conductivity were formed by sol-gel synthesis with the participation of tetraethoxysilane [20].

The aim of this work involves the synthesis and study of the properties of copolymers of sodium 4-styrene sulphonate (SSt) and nitrogen-containing heterocyclic monomers: 4-vinylpyridine (VP) and 1-vinylimidazole (VIM):



The use of SSt as a monomer will eliminate the stage of sulphonation of organic copolymers during the formation of composite membranes.

EXPERIMENTAL PART

Synthesis of copolymers. The copolymerisation of SSt and vinyl derivatives of nitrogen-containing heterocyclic compounds was carried out in a DMF solution at a temperature of 70 °C for 6 hours in the presence of azobisisobutyronitrile (1% wt.). During the process, the ratio of monomers in the initial mixture was varied. The copolymers were isolated by precipitation from DMF into isopropyl alcohol, washed with DMF and dried in vacuum to a constant weight.

Elemental analysis of the copolymers was carried out by the Thermo Finnigan Flash EA 1112 Series gas analyser.

Turbidimetric titration was carried out at a temperature of 25 °C, the initial concentration of copolymer solutions in DMF equalled 0.96 g/100 mL, toluene was applied as a precipitant. The optical density of the solutions was determined using a PE-5400V photoelectric colorimeter at a wavelength of 325–1000 nm.

IR spectra of the copolymers were obtained on a Bruker IFS-25 spectrometer both in tablets with potassium bromide and in the microlayer.

Copolymer ¹³C NMR spectra were recorded using Varian VXR-500S spectrometer (operating frequency 125.5 MHz) with noise isolation from protons and relaxation delay of 2.5 s. Impulse comprised 90°. D₂O was applied as a solvent.

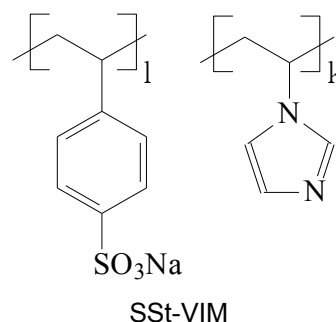
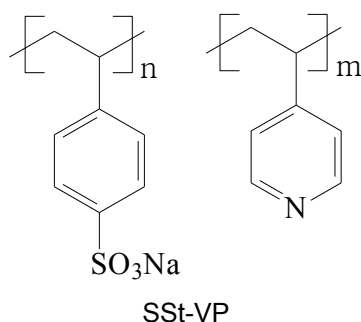
The calculation of the constants of the relative activity of monomers for the studied systems was carried out by the nonlinear least squares method in the MathCAD package [17].

Thermal analysis was performed using a Q-derivatograph instrument (MOM, Hungary).

RESULTS AND DISCUSSION

The monomodal nature of the turbidimetric titration curves for solutions of copolymerisation reaction products indicates the formation of true copolymers during the process.

The IR and ¹³C NMR spectroscopy data indicate the course of the copolymerisation reaction on the vinyl groups of the starting monomers with the formation of the SSt-VP and SSt-VIM copolymers:



Although the vibration bands of pyridine (1600, 1580, 1490, 1020 cm⁻¹) and imidazole (1500, 1220, 1080 cm⁻¹) rings are preserved, the IR spectra of the SSt-VP and SSt-VIM copolymers demonstrate no absorption bands characteristic of the vinyl group (960, 1680 cm⁻¹). The observation of absorption bands in the regions of 1260-1150, 1080-1010 and 700-600 cm⁻¹ in the IR spectra of sulphonated copolymers can be attributed to asymmetric and symmetric stretching vibrations of the sulphogroup.

In the ¹³C NMR copolymer spectrum, resonance signals corresponding to the carbon atoms of pyri-

dine (153.5; 152.5; 149.5; 136.2; 135.1; 122.8 ppm for SSt-VP) or imidazole (130.34; 100.83 ppm for SSt-VIM) cycles are observed. Bands belonging to the sulphogroup (24.1 ppm) are also presented.

The SSt-VP and SSt-VIM copolymers appears as powdery substances of white or light brown colour, having good and limited solubility in water and in DMF and DMSO, respectively.

The results of elemental analysis, the calculated compositions of the copolymers, as well as some characteristics of the obtained products are presented in Table 1.

Results of SSt and nitrogen-containing heterocyclic monomers copolymerisation

Результаты сополимеризации ССт с азотсодержащими гетероциклическими мономерами

| M ₁ , % mol | Elemental analysis data, % wt. | | m ₁ , % mol* | Yield, % | Relative viscosity | Monomer Relative Activity Constants | Average block lengths in copolymer | |
|---------------------------|-----------------------------------|-------|----------------------------|----------|-----------------------|--|---------------------------------------|----------------|
| | S | N | | | | | L ₁ | L ₂ |
| SSt - VIM system (1) | | | | | | | | |
| 0.25 | 7.00 | 10.98 | 0.676 | 83 | 1.82 | $r_1 = 0.262 \pm 0.03$ $r_2 = 0.765 \pm 0.09$ | 6 | 1 |
| 0.50 | 11.46 | 5.49 | 0.422 | 78 | 1.68 | | 3 | 1 |
| 0.75 | 8.38 | 14.53 | 0.561 | 77 | 2.33 | | 2 | 2 |
| 0.80 | 7.05 | 12.10 | 0.591 | 95 | 2.00 | | 1 | 3 |
| 0.90 | 5.91 | 16.41 | 0.728 | 96 | 1.46 | | 1 | 8 |
| SSt - VP system (1) | | | | | | | | |
| 0.05 | 15.01 | 0.81 | 0.112 | 21 | 1.15 | $r_1 = 0.171 \pm 0.02$ $r_2 = 0.875 \pm 0.08$ | 1 | 18 |
| 0.25 | 15.53 | 0.78 | 0.108 | 24 | 1.19 | | 1 | 12 |
| 0.50 | 14.52 | 1.33 | 0.216 | 57 | 1.27 | | 2 | 10 |
| 0.75 | 11.44 | 3.25 | 0.388 | 71 | 1.32 | | 4 | 3 |
| 0.95 | 11.82 | 5.67 | 0.592 | 80 | 1.43 | | 7 | 2 |

* Calculation is based on nitrogen concentration.

The copolymerisation in the studied systems is characterised by the presence of azeotropic compositions. Moreover, with an increase in the content of units of heterocyclic monomers, the copolymer yield generally increases along with the relative viscosity of their 1% solutions in DMF. The copolymerisation constant values indicate a greater reactivity of SSt in comparison with nitrogen-containing monomers.

The microstructure parameters of the copolymers were characterised on the basis of the calculated copolymerisation constants. The lengths of the monomer unit blocks depend on the composition of the initial mixture and vary over a wide range from 1 to 18.

Using differential scanning calorimetry (DSC), the resistance of the copolymers to thermal oxidative degradation by heating in air was studied. The copolymers demonstrated significant thermo-oxidative stability with decomposition temperatures of

350 °C and 400 °C for SSt-VIM and SSt-VP copolymers, respectively.

CONCLUSION

New copolymers of sodium 4-styrene sulphonate with 4-vinylpyridine and 1-vinylimidazole, characterised by high thermal stability, were synthesised in terms of radical copolymerisation in the presence of azobisisobutyronitrile. The calculated values of the copolymerisation constants indicate a greater reactivity of sodium 4-styrenesulphonate in radical copolymerisation compared with nitrogen-containing heterocyclic monomers.

The possibility of varying the length of the unit blocks in the composition of the copolymers provides a means to affect the ion-conducting properties of hybrid composites formed on their basis. Therefore, the obtained copolymers can be considered as promising materials for the further formation of hybrid composite membranes.

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Contribution

Ekaterina A. Malakhova, Oksana V. Lebedeva, Tatiana V. Raskulova, Artem I. Emelyanov, Vaibhav Kulshrestha, Yuriy N. Pozhidaev carried out the experimental work, on the basis of the results summarized the material and wrote the manuscript. Ekaterina A. Malakhova, Oksana V. Lebedeva, Tatiana V. Raskulova, Artem I. Emelyanov, Vaibhav Kulshrestha, Yuriy N. Pozhidaev have equal author's rights and bear equal responsibility for plagiarism.

Кратерии авторства

Малахова Е.А., Лебедева О.В., Раскулова Т.В., Емельянов А.И., Кулшреста В., Пожидаев Ю.Н. выполнили экспериментальную работу, на основании полученных результатов провели обобщение и написали рукопись. Малахова Е.А., Лебедева О.В., Раскулова Т.В., Емельянов А.И., Кулшреста В., Пожидаев Ю.Н. имеют на статью равные авторские права и несут равную ответственность за плагиат.

Conflict of interests

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

Конфликт интересов

Авторы заявляют об отсутствии конфликта интересов.

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