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SYNTHESIS AND CHARACTERIZATION OF ORGANIC-INORGANIC MEMBRANES CONTAINING SULPHOGROUPS

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Abstract. Organic-inorganic materials have been synthesized by photoinitiated copolymerization of monomers: acrylonitrile, acrylamide and 3-sulphopropyl acrylate potassium salt in the presence of sol-gel systems based on tetraethoxysilane. Thermal stability, water uptake and ion-exchange capacity of obtained materials have been determined. Undertaken studies may be used for development of protonconductive membrane for fuel cells.

Keywords: organic-inorganic composite, hydrogel, polyelectrolyte, protonconductive membrane, sol-gel method, photoinitiated copolymerization.

1. Introduction

Polymeric electrolyte membranes find growing application in separation processes, ion-exchange processes, in systems of electrochemical generation of energy due to their physical and chemical properties [1]. They consist of cross-linked polymer chains which form a spatial network filled with a liquid phase. Ion transport in membranes takes place due to segmental motion of polymeric chains and causes their ionic conductivity and ionic-exchange property.

Nowadays considerable attention of researchers is attracted to gel polymeric electrolytes [2]. They can be obtained from mixing of polymer with alkaline metal salts, dissolved in organic solvents. Polymeric gel electrolytes display liquid-like ionic conductivity, at the same time they maintain dimensional stability like solid systems. A number of polymers – poly(propylene oxide), poly(vinyl alcohol), poly(ethylene imine) and others – are known to form gel polymeric electrolyte. Their conductivities vary within the limits of 10^{-4} – 10^{-2} Sm/cm.

The low molecular-weight organic solvents with high dielectric constant (tetrahydrofuran, ethylene carbonate, propylene carbonate) are employed in gel polymeric electrolytes as plasticizers. However, organic solvents are environmentally hazardous, therefore it is desirable to substitute them with water which also reduces the process cost.

Water-containing polymeric gels – hydrogels – are insoluble in water; however, they have a very high swelling degree. The porous structure of hydrogels provides channels for ion migration. Hydrogel membranes can be easily transformed into thin films with large surface area. These features of hydrogel membranes allow to create protonconductive materials on their basis.

Polymeric electrolytes are obtained by incorporation the aqueous solution of strong acid into a polymeric matrix. In [3] the protonconductive hydrogel membrane was prepared on the basis of poly(vinyl alcohol) varying concentrations of perchloric acid: the mixture of poly(vinyl alcohol) aqueous solution ($M_w = 125000$) and a proper quantity of glutaraldehyde (25% water solution) were placed into Petri dish and left at ambient conditions for 12 h to allow water to evaporate. After evaporation of water a given concentration of HClO_4 is added to initiate a cross-linking reaction between poly(vinyl alcohol) and glutaraldehyde, then a mixture was kept at 298 K for gelation to take place. The time required for gelation decreases with increasing of perchloric acid concentration. The obtained hydrogel membranes possess satisfactory thermal and electrochemical characteristics.

Similarly the authors [4] have synthesized the hydrogel material *via* reaction of the chemical cross-linking of (poly(vinyl alcohol), chitosan, gelatin) and water-soluble cross-linking agent – glutaraldehyde, which

was catalyzed by protonic acid at ambient conditions (temperature and pressure). Such chemically cross-linked hydrogel material is water-insoluble and can be used in fuel cells, batteries, electrochemical capacitors *etc.*

Ionic conductivity of poly(acrylamide)-based hydrogel after dopping by orthophosphoric acid was found to vary in a range of 10^{-3} – 10^{-2} Sm/cm at the room temperature [5]. Interestingly, with the increase of water content in material up to 30–35 mas % the proton conductivity grows, while at higher water contents it remains almost permanent. In this interval the conductivity grows with the increase of molar ratio of phosphoric acid : acrylamide.

In [6] the method of conductive hydrogel preparation by the mixing of organic polymer and water leading to make a hydrophilic gel, followed by dispergation of conductive powder in a gel and repeating freeze drying and freeze thawing at least twice is reported. Preferably the organic polymers are poly(vinyl alcohol), poly(acrylate), copolymer of poly(vinyl alcohol) and poly(acrylate), polysulfonate. Conductive carbon powder, graphite powder or metal powder are used as a conductive inorganic filler. Preferably the organic polymer is poly(vinyl alcohol) having a molecular weight of 10000 or more and a degree of hydrolysis of 98 mol.

To provide ion-exchange and protonconductive properties hydrogels are synthesized with the use of monomers containing corresponding functional groups, in particular, sulphogroups [7]. Sulphogroups $-\text{SO}_3\text{H}$ – easily dissociate in water forming proton H^+ , that provides ion-exchanging and conductive properties of material. In [8] the hydrogel polyelectrolyte membrane was synthesized *via* radical copolymerization of sulphopropyl acrylate potassium salt and sodium styrene sulphonate with acrylamide and acrylonitrile in aqueous media. The process of gel formation was induced by potassium persulphate-sodium metabisulphite oxidation-reduction system. The data of thermogravimetric analysis show that these membranes are capable to hold water at temperatures up to 343 K for membranes with sulphopropyl acrylate and up to 363 K for membranes with styrene sulphonate. The ion-exchange capacity of membranes was 1.4 mg-equiv/g and 0.8 mg-equiv/g., respectively.

Recently sol-gel technique has been often used for synthesis of materials of various applications including membranes. Using this method alkoxysilanes are introduced into a polymeric matrix on the stage of synthesis and form inorganic network as a result of sol-gel transformation. Sol-gel method attracts considerable interest due to its simplicity and availability.

In the present work polymeric and organic-inorganic membranes have been obtained by a method of photoinitiated radical copolymerization of monomers polymerizing composition: acrylamide, acrylonitrile,

potassium sulphopropyl acrylate and sol-gel system on the basis of tetraethoxysilane. Their main characteristics – water uptake, thermal stability and ion-exchange capacity – have been studied.

2. Experimental

All chemicals were of reagent analytical grade and were used as received.

Synthesis of polymer membranes was conducted *via* radical photoinitiated polymerization of acrylamide, acrylonitrile and 3-sulphopropylacrylate potassium salt. The reaction was carried out in thin films using UV irradiation of a mercury-quartz lamp. The intensity of irradiation was 14 W/m^2 . Photoinitiator used was 2,2-dimethoxy-1,2-diphenylethane-1-on (IRGACURE 651). Content of comonomer containing sulphogroups varied in the range of 5–20 wt % of total comonomer mixture. Cross-linker *N,N'*-methylenebisacrylamide was used to form cross-linked structure of a copolymer.

The obtained films were washed from unreacted products of the reaction in sufficient amount of distilled water.

Polymer-silica composites were obtained using a sol-gel method of synthesis. Sol-gel system (SGS) tetraethoxysilane-ethanol-water in appropriate proportions was added to the above-mentioned mixture of comonomers. The content of SGS in compositions was 5–20 wt %. The process of photoinitiated copolymerization was carried out similarly.

Thermogravimetric and differential thermal analysis of polymer samples and polymer-silica membranes was conducted on Derivatograph Q-1500D (Paulik-Paulik-Erdey) in the temperature range of 293–723 K. The analysis was carried out in a dynamic mode – heating rate of samples was 5 K/min. Alumina was used as a standard. The samples weight was 300 mg.

Water uptake of membranes was evaluated from the change of a sample mass before and after drying. After membrane swelling in distilled water its surface was carefully dried by a filter paper and the membrane was immediately weighed with accuracy to $\pm 0.00005 \text{ g}$. Then the membrane was dried till constant mass. Water uptake (WU) was calculated from the formula:

$$WU = (m_{wet} - m_{dry}) \cdot 100\% / m_{dry} \quad (1)$$

where m_{wet} and m_{dry} are masses of fully dehydrated membrane and dry membrane, respectively.

Ion-exchange capacity of the synthesized membranes was determined as a number of mg-equiv. of sulphogroups in 1 g of dry polymer. To estimate the ion-exchange capacity first membranes were placed into

0.1 M hydrochloric acid solution, washed with distilled water, and then dipped in 10 ml of 2 M sodium chloride solution for 24 h to complete a substitution of sulphogroups protons with sodium ions. After that the ion-exchange capacity was determined by carrying out a back titration of solution with 0.1 M NaOH to evaluate the released amount of protons using phenolphthalein as an indicator. The value of ion-exchange capacity is calculated by using the following equation:

$$IEC = M_{E\ NaOH} / m \quad (2)$$

where $M_{E\ NaOH}$ is an amount of NaOH, expended for titration, mg-equiv.; m is a weight of a dry sample, g.

3. Results and Discussion

As a result of radical photoinitiated copolymerization of acrylonitrile, acrylamide and 3-sulfopropyl acrylate in the presence of a cross-linker N,N' -methylenebisacrylamide copolymer with the cross-linked structure is formed. Due to the structure containing nano- and micropores the copolymer may retain a large volume of water.

At photoinitiated polymerization of the monomer mixture in the presence of SGS (tetraethoxysilane-

ethanol-water) sol-gel conversion (hydrolysis of tetraethoxysilane followed by condensation of silanol groups) takes place simultaneously with the process of polymer chains formation. As the result a common organic-inorganic composite structure is formed in which organic and inorganic components are combined at nanoscale.

In Fig. 1 integral (a) and differential (b) kinetic curves of photoinitiated copolymerization of polymerizing composition (PC) and the same mixture with different content of sol-gel system (PC:SGS) are presented. The kinetic curves of polymerization process have the characteristic S-like form in both cases. Maximal rate of polymerization and conversion of the system at the maximal rate decrease with the increase of SGS content and the time of achievement of maximal rate increases (Table 1).

In the case of membranes application at high temperatures (for example, in fuel cells), they must possess a sufficient thermal stability. To determine the thermal stability of polymer and organic-inorganic membranes (PM and OIM, respectively) and water loss rate under heating complex thermogravimetric and differential thermal analyses of samples have been conducted. The results are presented in Fig. 2.

Table 1

Kinetic parameters of the process of photoinitiated polymerization of the system PC:SGS

PC:SGS, vol %	Time of w_{max} achievement (t), s	Conversion at w_{max} (P)	Max. rate (w_{max}), s^{-1}
100:0	22	0.51	0.034
90:10	25	0.43	0.033
80:20	27	0.42	0.031

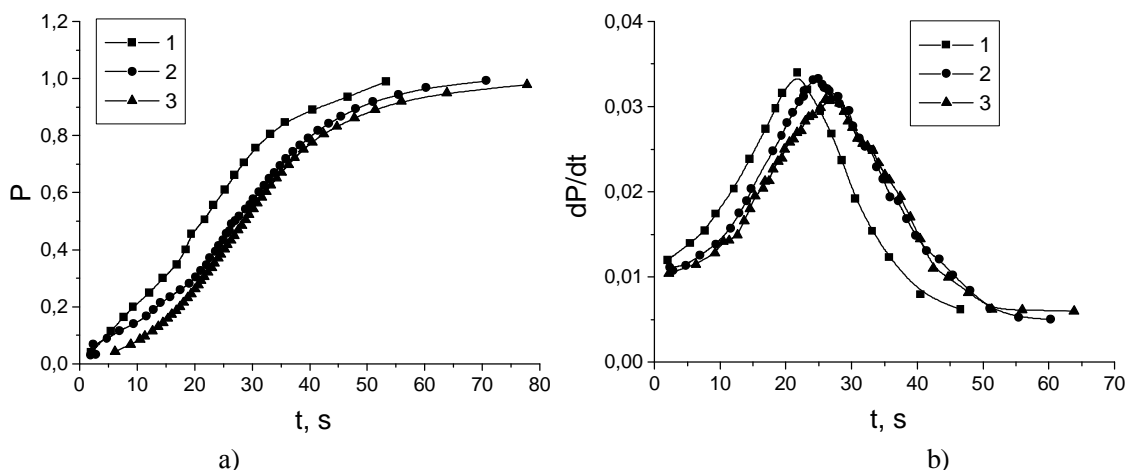


Fig. 1. Integral (a) and differential (b) kinetic curves of photoinitiated polymerization: PC (1); PC:SGS = 90:10 w/w % (2) and PC:SGS = 90:20 w/w % (3)

As it is shown in Fig. 2a, in the temperature range of 293–408 K the weight loss of the samples of sulphogroup-containing copolymer (~ 6 %) with a maximal weight loss rate at 338 K may be attributed to evaporation of physically adsorbed and chemically bound water. In the same range the endothermic effect is observed in DTA curve. Next interval 408–583 K is characterized by the significant weight loss of the samples – 16.5 % (maximal weight loss takes place at 513 K). Obviously, it is caused by destruction of sulphogroups in the polymer. At higher temperatures (583–723 K) the weight loss corresponds to the destruction of cross-links and at temperatures above 723 K deep destruction of polymer chains takes place.

In the case of organic-inorganic composite (the content of sol-gel system in the initial mixture for polymerization was 30 wt %) the weight loss of the sample, observed in the temperature range of 293–429 K due to evaporation of physically and chemically bound water, is ~ 7 % (Fig. 2b). Like in the previous case, a maxi-

mum of DTG curve corresponds to the endothermic effect in DTA curve. In the temperature range of 429–590 K the sulphogroups destruct, followed by destruction of the cross-links and dehydration of functional groups. Mass loss of the samples in this temperature range is ~ 13 %. Heating of the samples above 723 K leads to complete destruction of membranes.

Thus, for organic-inorganic composites the temperature shift of the beginning of sulphogroups destruction from 408 to 429 K is observed. The temperature of the beginning of cross-linking sections destruction is shifted insignificantly – from 583 to 590 K. These effects may be attributed to formation of common organic-inorganic net in the process of photoinitiated polymerization of monomer mixture in the presence of sol-gel system.

Thus, polymer membrane can be operated without destructive changes at temperatures till 408 K. Organic-inorganic structure of polymer-silica membranes allows to use them till slightly higher temperatures – up to 429 K.

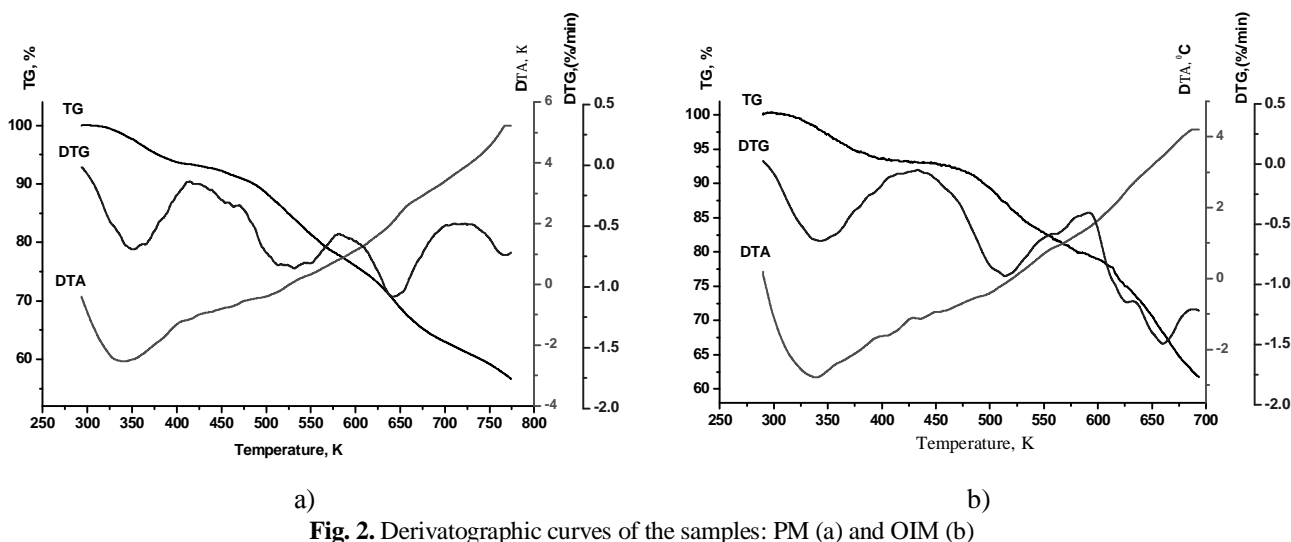


Fig. 2. Derivatographic curves of the samples: PM (a) and OIM (b)

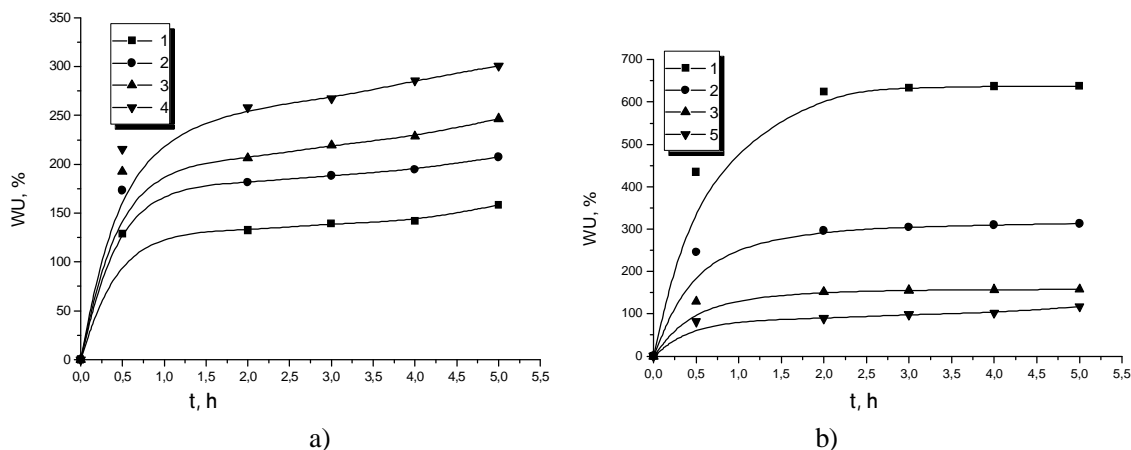


Fig. 3. Water uptake of PM and OIM at different content of SGS (a): 100 % PM (1); 90 % PM + 10 % SGS (2); 85 % PM + 15 % SGS (3) and 80 % PM + 20 % SGS (4) and at different content (wt %) of cross-linker (b): 1 (1); 2 (2); 3 (3) and 5 (4)

An important property of the membrane is its water uptake, because a high degree of water uptake is necessary for proton conductivity of membranes. Water causes dissociation of protons from SO_3H - groups and serves as the “transport vehicle” for transference of them from anode to cathode. At the same time, superfluous swelling of membranes worsens their mechanical durability. The results of water uptake measuring of synthesized PM and OIM are presented in Fig. 3.

As one can see, water uptake of all samples is very high depending on SGS content in the polymerizing mixture and also on the content of cross-linking agent (Fig. 3).

The presence of sulphogroups in the copolymer chain has been confirmed by the quantitative determination of ion-exchange capacity of membranes using the method of titration. An increase of ionogenic group content provides better proton exchange and proton conductivity of membranes. However, it must be mentioned, that an increase of polar group number in the membrane structure leads to its higher swelling, which significantly decreases its mechanical strength. The experimental value of ion-exchange capacity of the copolymer (sulphogroup-containing monomer – potassium sulphopropyl acrylate – content in initial polymerizing mixture was 10 wt %) was 0.4 mg-equiv/g, which is consistent with the data of [8]. For organic-inorganic copolymer with 20 wt % SGS in the initial mixture the experimental value of ion-exchange capacity was slightly lower – 0.38 mg-equiv/g.

4. Conclusions

Sulphocontaining hydrogel membrane has been prepared *via* photoinitiated copolymerization of the monomer mixture. The organic-inorganic sulphocontaining membrane has been prepared *via* simultaneous processes: photoinitiated copolymerization and sol-gel transformation of tetraethoxysilane system. The synthesized membranes can be characterized by a high thermostability – they can be operated at temperatures up to 408 K in the case of PM and up to 428 K in the case of OIM. These temperatures are higher compared to

temperatures usually used in fuel cells (363–393 K). Ion-exchange capacity of copolymer sulphocontaining membrane has been found to be 0.4 mg-equiv/g and of organic-inorganic one – 0.38 mg-equiv/g, that is consistent with the results in [8]. However, both types of membranes have too high degree of water uptake, which leads to the superfluous swelling and loss of mechanical strength. The received materials may be recommended for further research for the purpose of development of ion-exchange and protonconductive membranes.

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СИНТЕЗ І ХАРАКТЕРИСТИКА ОРГАНО-НЕОРГАНІЧНИХ СУЛЬФОВМІСНИХ МЕМБРАН

Анотація. Синтезовано органо-неорганічні сульфоновмісні мембрани методом фотоініційованої кополімеризації мономерів акрилонітрилу, акриламіді і сульфопропілакрилату в присутності золь-гель систем на основі тетраетоксисилану. Визначено термічну стабільність, водопоглинання і іонообмінну ємність одержаних матеріалів. Проведені дослідження можуть бути використані при розробленні протонпровідних мембран для паливних елементів.

Ключові слова: органо-неорганічний композит, протон-провідна мембрана, іонообмінна ємність, золь-гель метод, фотоініційована кополімеризація.