

Development of Hydrogel Polyelectrolyte Membranes with Fixed Sulpho-Groups via Radical Copolymerization of Acrylic Monomers

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ABSTRACT

Electrolyte hydrogels are perspective materials for applications in electrochemical devices, which work at ambient temperatures. In this work, hydrogel sulpho-modified membranes were formed by radical co-polymerization of sodium styrenesulphonate and potassium sulphopropyl acrylate with acrylamide and acrylonitrile. The hydrogel membranes were obtained in the form of thin films. Properties of the membranes were studied by thermogravimetry, mass-spectrometry and IR-spectrometry. The prepared membranes were thermally stable up to 70°C - 90°C, and showed ion exchange capacity and swelling coefficients sufficient for use as ion-exchange or proton-conducting membranes.

Keywords: Copolymer Hydrogels, Polyelectrolyte Membranes, Acrylamide, Swelling, Ion Exchange Capacity, Thermogravimetry

1. Introduction

Synthetic polymeric membranes continue to be the object of intensive researches because of their important role in separation science and technology [1,2]. Fast growing application of membrane processes in various industrial sectors demands development of synthetic membranes with diversified properties and performance characteristics. Membrane separation properties are governed by methods of membranes preparation and chemico-physical nature of the membrane materials.

Hydrogel membranes have attracted vast attention because of their novel properties and high potential for applications in industry [3], in particular, as electrolyte membranes [4-6]. One of the advantages of hydrogels is that they can be easily transformed into thin films. Several different polymerization techniques have been developed for this purpose. Moreover, such techniques allow introduction of interacting species with active functional groups into a polymeric network. These advantages, alongside with gels good ionic conductivity and ionic exchange property [7,8], have led to their interesting applications in many electrochemical solid state ionic

devices, such as high-energy density batteries, fuel cells, sensors and electrochemical display devices [9,10].

Hydrogels have 3D networks, which contain hydrophilic functional groups. They are insoluble in water but rather swell more than 95% after absorbing water. Hydrogel membranes can essentially be thought of as substances which contain solid skeleton and are composed of polymers or long chain molecules cross-linked to create a tangled network, enclosing a continuous liquid phase. The properties of such gels depend strongly on the interaction of the skeleton and the liquid phase. The liquid phase prevents polymer network from collapsing into compact mass while the skeleton prevents liquid from escaping the network. Macroscopically most gel materials are solid, but exhibit liquid-like characteristics microscopically due to the presence of a large number of liquid-filled micro- and nanopores. Such ultraporous structure of gels provides channels for directed ion migration [11] and allows to synthesize ion conducting materials and membranes.

One of the methods for producing polymeric electrolyte membranes is entrapping of an aqueous solution of strong acid with a polymeric matrix [12,13]. It has been

determined, in particular, that polyacrylamide-based hydrogels after doping with H_3PO_4 exhibit ionic conductivities in the range of 10^{-3} - 10^{-2} $\text{S}\cdot\text{cm}^{-1}$ at room temperature. The observed ionic conductivity increases with the increase in water content up to about 30 mass% - 35 mass%, remaining almost constant for higher water concentrations reaching a conductivity plateau. At this conductivity plateau, ionic conductivity increases with the increase of phosphoric acid/acrylamide molar ratio to a maximum at 1.8 - 2.0 mol of H_3PO_4 to 1 mol of acrylamide [13].

All characteristics of an electrolyte directly depend upon the structure and morphology of the host matrixes of the prepared hydrogels. The electrical conductivity change is most likely related to changes in local viscosity due to H_3PO_4 interactions both with the solvent and the polymer matrix which stiffens the hydrogel [14]. Polar organic or inorganic fillers and additives are known to lower the host polymer's crystallinity and flexibility [15]. For example, addition of alkali salts to a phosphoric acid-polyacrylamide proton conducting hydrogel influences the hydrogel structure and morphology [16]. This effect was examined by measuring changes polyacrylamide chain vibrations, in phosphate group and in interstitial water molecules as a function of concentration and cationic nature of the additive. After addition of H_3PO_4 to the polyacrylamide hydrogel matrix, amide groups become more accessible and the polyacrylamide-phosphoric acid network behaves like structure-maker promoting larger association with the 'bulk' liquid water molecules.

Another way of producing polymeric hydrogel electrolyte membranes is introduction of copolymers based on highly conducting monomers [17]. In the present study we have prepared hydrogel electrolyte membranes containing highly conducting sulpho-group by radical copolymerization of sodium styrenesulphonate or potassium sulphopropyl acrylate with acrylamide and acrylonitrile. The most important parameters for the prepared polyelectrolyte hydrogels (e.g. thermostability, ion exchange capacity and swelling) were also studied.

2. Experimental

Hydrogels with potassium sulphopropyl acrylate (SpA) and sodium styrene sulphonate (SS) were prepared by radical copolymerization with acrylamide (AA) and acrylonitrile (AN) in aqueous media at room temperature. Cross-linking was accomplished by $\text{N,N}'$ -methylenebisacrylamide (BIS). The process of gel formation was induced using potassium persulfate-sodium metabisulphite oxidation-reduction system. Scheme of polymerization is presented on **Figure 1**.

Potassium sulphopropylacrylate concentration varied

from 0 to 25 wt% of the total co-monomers content, styrene sulphonate concentration-from 0 to 14 wt%, limited by the solubility of the respective monomers. Total content of monomers was 50 wt% of polymerization mixture. Concentration of BIS was equal to 0.4 wt%. The ratio of AA to AN was 1:1 (wt).

All chemicals were purchased from Sigma-Aldrich and used as received except AN, which was washed from the polymerization inhibitor and then distilled.

Hydrogel membranes were obtained in the form of films (plates) with thickness of about 500 μm . In order to separate non-reacted monomers and initiators after the synthesis, hydrogel samples were washed with significant amount of distilled water at 45°C. Water was changed once per day, and the ratio between mass of gel and mass of water was always 1:4 [18].

FT-IR spectra of the synthesized hydrogel films were obtained using a FT-IR spectrometer TENSOR 37 BRUKER to a depth of about 2 - 3 μm into the sample.

The dynamic weight loss tests were conducted on thermogravimetric analyzer (TGA) Derivatograph Q-1500D for 50 mg samples with heating rate 10 °C/min in the 20°C - 900°C temperature range. Measurements were performed under nitrogen atmosphere. This analysis produced differential curves of mass loss, allowing for evaluation of thermal degradation.

Hydrogel mass-spectrometry was carried out at 30 to 800°C and for molecular weights ranging from 10 to 200 Daltons. Hydrogel samples were placed in a quartz-molibdenum cell and evacuated at 5×10^{-1} Pa, then system was connected to the admission system of MI-1201 mass-spectrometer (Ukraine). Rate of samples heating was 10°C per minute.

Water uptake (WU) of the membranes was evaluated from the mass change of membrane before and after drying. The dry membrane swelled in de-ionized water for a day, then the surface water was wiped carefully with a filter paper, and it was immediately weighed. After drying the sample overnight in a vacuum oven at 60°C, the water uptake (WU), was calculated using the formula:

$$\text{WU} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} * 100$$

where m_{wet} and m_{dry} are mass of fully hydrated membrane, and that of the dry membrane, respectively.

The ion exchange capacity (IEC, mequiv/g) of the membranes was found titrimetrically. To determine the membranes' IEC, the membranes were placed in 0.1M hydrochloric acid solution, washed with distilled water and immersed in 10 ml of 2 M NaCl solution for 1 day to

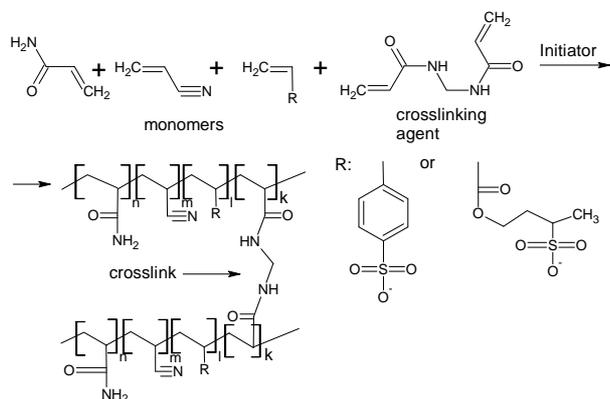


Figure 1. Scheme of hydrogels formation.

fully replace hydrogen of the sulphogroups with sodium. After this, H^+ ions in solution were titrated with 0.01 M NaOH. IEC is defined as mequiv of sulphonic groups per gram of a dried sample.

3. Results and Discussion

3.1. IR-Spectroscopy

IR spectra (Figure 2) showed absorption bands in 4000 - 1500 cm^{-1} range corresponding to $\nu(XH)$ (stretching vibrations of the X-H bonds), $\nu(CX)$ (stretching vibrations of the C-X bonds) and $\delta(XH)$ (bending vibrations of the X-H bonds) vibrations (where X = O, N, C). 3426 and 3346 cm^{-1} bands were produced by amino groups without hydrogen bonds, 3200 cm^{-1} bands—by amino groups with hydrogen bonds. 2243 cm^{-1} band corresponded to the nitrile group. Carbonyl group was characterized by an intensive band $\nu(CO) = 1662$ cm^{-1} and a “shoulder” at 1618 cm^{-1} . Bending vibrations $\delta(XH)$, (X = N, O) were ob-

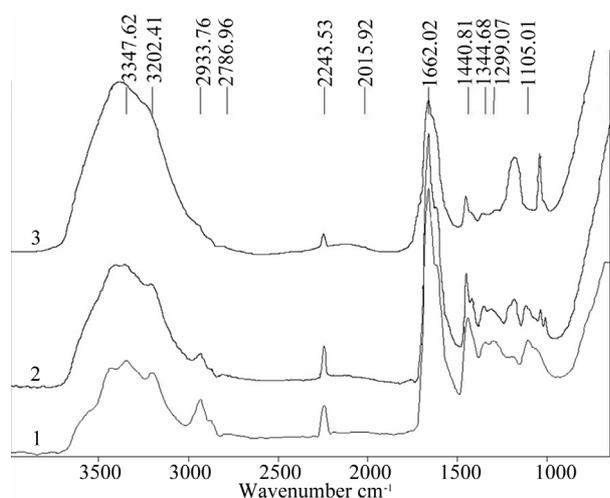


Figure 2. IR-spectra of copolymer hydrogels: curve 1 - AA-AN hydrogel; curve 2 - AA-AN-SpA hydrogel; curve 3 - AA-AN-SS hydrogel.

served at 1400 cm^{-1} . C-C bond vibrations were observed in the 1400 - 1200 cm^{-1} range. When sulphogroup was introduced into hydrogels (curves 2 and 3), 3380 cm^{-1} band was intensified due to hydrophilisation of hydrogels. Spectra 2 and 3 showed new bands at 1180 and 1040 cm^{-1} , which correspond to $\nu(SO)$ vibrations.

3.2. Thermal Analysis

To determine membranes' thermal stability and rate of water loss upon heating, we conducted thermo-gravimetric analysis (TGA). TGA curves (Figure 3) showed that cross-linked membranes based on acrylamide and acrylonitrile have 5 stages of mass loss. Percentage of weight loss for each stage and temperature of maximum weight loss for each stage are listed for convenience in Table 1. The first temperature range (25°C to 120°C) with maximum weight loss rate at 90°C corresponds to the loss of lightly bound water. DTG curve shape in this region depended on sample composition. As data in Table 1 for the 25°C - 120°C temperature range show, membranes with sulphopropyl acrylate lost the most water in this temperature range because of high concentration of sulfogroups with weakly bound water. Acrylamide-acrylonitrile membranes have proven to be thermally stable up to 90°C with overall mass loss under 6%. Membranes with sodium styrene sulphonate were just as stable. Membranes with sulphopropyl acrylate lost up to 20% of their mass at 70°C.

Temperature range of 120°C to 195°C was the most interesting for our studies. The mass loss at this stage was attributed to the evaporation of bound water, which

Table 1. Membrane thermooxidative destruction.

Membrane	Stage temperature range, $T_{start} - T_{final}$, °C	Temperature of maximum destruction rate, °C	Mass loss on the stage, %
AA-AN	25 - 120	90	15.3
	120 - 195	175	2.1
	195 - 290	235	7.6
	290 - 450	375	18.7
	450 - 800	695	52
AA-AN-SpA	25 - 120	80	43.1
	120 - 195	175	6.8
	195 - 295	250	4.1
	290 - 450	375	10.5
	450 - 800	620	27.8
AA-AN-SS	25 - 120	95	14
	120 - 195	160	6.9
	195 - 290	250	8.2
	290 - 450	390	14
	450 - 800	665	46.8

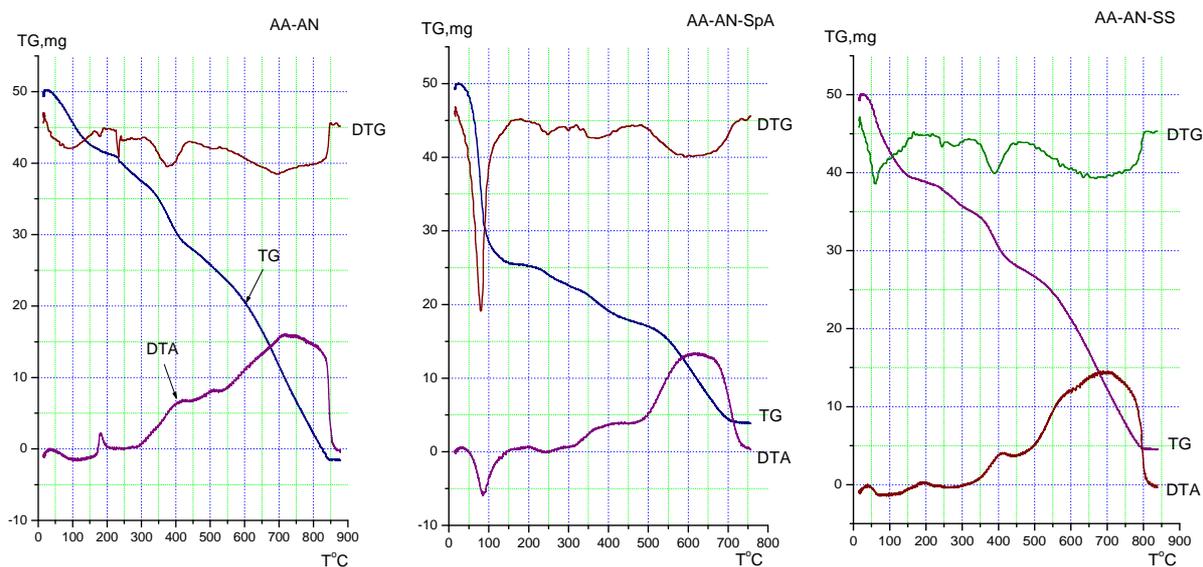


Figure 3. TGA curves of membranes without sulphogroups (AA-AN), with sulphopropyl acrylate (AA-AN-SpA), with styrene sulphonate (AA-AN-SS).

greatly influenced proton-conductive properties of membranes. In this range we have observed a peak in mass loss rate with the maximum at 175°C. The presence of sulphogroups in the polymer matrix increased bound water content in the hydrogel. This was indicated by 6.9% loss for membranes with sulphogroups and 2.9% loss for membranes without them, as shown by the data for 120°C - 195°C range in **Table 1**. The mass loss was still relatively low, indicating that membranes will withstand steam sterilization, if necessary. Differential curves for membranes with styrene sulphonate showed a band between 180°C and 350°C with a peak at 250°C, when the sulphogroups started to destruct. All membranes lost high percentage of their mass in 290 to 450°C range. At this stage the mass lost corresponds to the destruction of cross-links, followed by dehydration of functional groups. Further heating to 800°C leads to total destruction of membranes, as seen by large loss of weight in **Table 1**.

3.3. Mass-Spectrometry

As shown by mass-spectrometry, AA-AN copolymers produce small amount of monomer acrylamide with m/z (mass to charge ration) 71 and acrylonitrile (m/z 53) in this temperature range with a maximum around 350°C. At temperatures over 440°C copolymer chain itself starts to destruct. Hydrogels with sulphogroup additives appear more stable in this temperature range (see also **Table 1**).

With the rise of temperature AA-AN hydrogels lose two kinds of fragments with $m/z = 28$ as well as water bound with different strength (**Figure 4**). The first frag-

ment appears at 350°C - 400°C and may be attributed to CO molecules from amide groups. The second fragment appears at temperatures over 600°C and may be attributed to $\text{CH}_2=\text{CH}_2$, which forms with the hydrocarbon chain destruction.

AA-AN hydrogels also tend to lose numerous small fragments near 350°C (**Figure 5**). $m/z = 44$, $m/z = 43$ and $m/z = 45$ bands may be attributed to amide group and CONH^+ and CONH_3^+ fragments, $m/z = 57$ band being most likely due to the loss of CHCONH_2 .

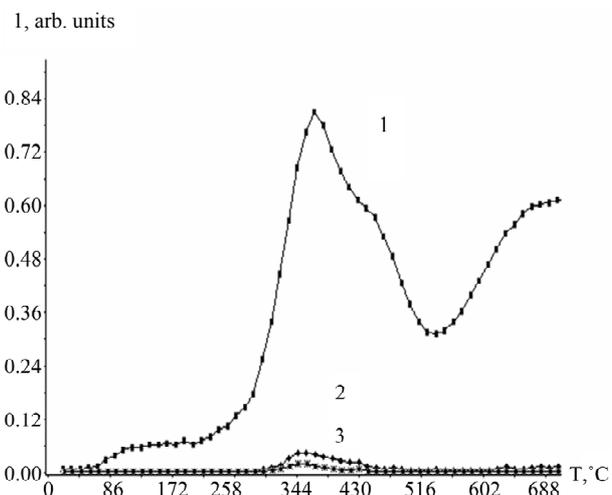


Figure 4. Thermograms for molecular ions m/z 28 ($[\text{M}]^+$ for CO^+ and $\text{CH}_2=\text{CH}_2^+$, line 1), m/z 53 ($[\text{M}]^+$ for AN, line 2) and m/z 71 ($[\text{M}]^+$ AA, line 3) for the hydrogel AA-AN with 50% AN content.

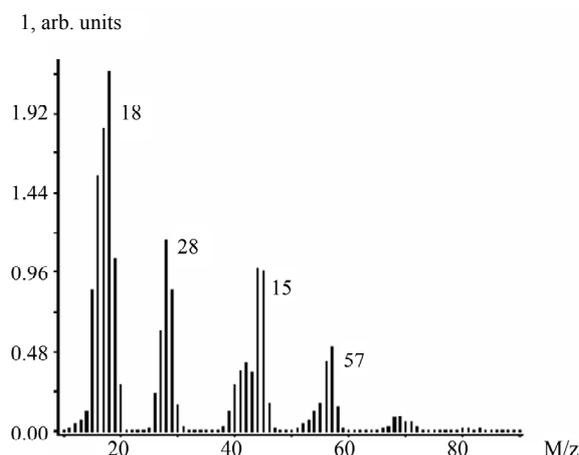


Figure 5. Mass-spectrum of AA-AN hydrogel with 50% AN content at 3500°C.

3.4. Ion Exchange Capacity and Water Swelling

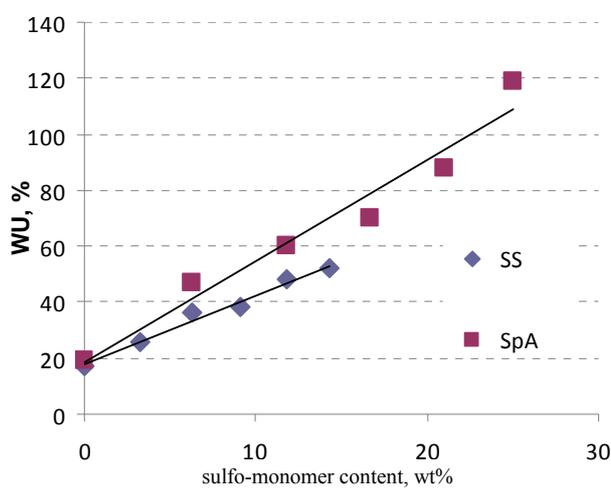
IEC and water swelling are among the most important parameters for any polyelectrolyte hydrogel. They are determined by nature of polymer matrix, number of charged groups, density of cross-links and external parameters (e.g. temperature, pH). An increase in ionogenic group content facilitates better proton exchange and makes a membrane more proton conductive. On the other hand, an increase in the number of polar groups makes the membrane more swellable, which also leads to increased mobility of ions in the membrane, but greatly decreases its mechanical strength.

IEC and swelling were measured as a function of sulfo-monomer content in the initial mixture. Both IEC and water swelling grew almost linearly with the increase in the number of sulphogroups (**Figure 6**). Both IEC and water swelling coefficient were slightly larger for hydrogels with sulphopropyl acrylate. This is probably due to the sulfo-group of styrene sulphonate being attached directly to a benzene ring, thus increasing hydrophobicity and decreasing mobility.

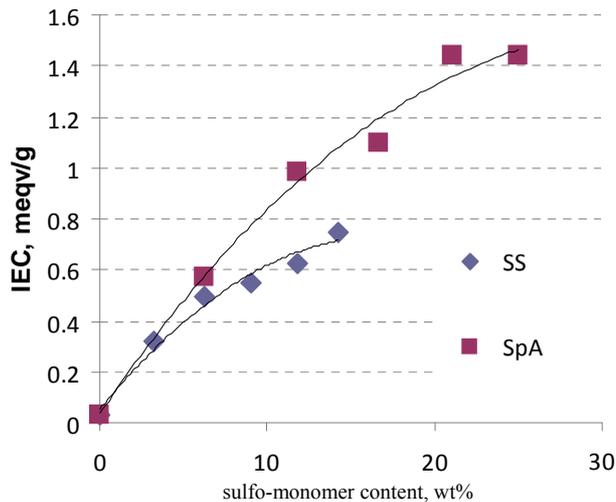
The best IEC of 1.4 mg-equiv/g was shown by membranes formed with 21% of sulphopropyl acrylate. Further increase in sulphomonomer concentration brought very little change in the IEC and caused them to swell excessively (up to 120%). Styrene sulphonate content was limited by its solubility in the initial mixture, but membranes formed with 16% of styrene sulphonate showed high IEC values (0.8 mg-equiv/g) and low swelling (50%) combined with elasticity and mechanical strength.

4. Conclusions

Most polymer electrolyte systems are based on linear or



(a)



(b)

Figure 6. Water swelling (a) and IEC (b) vs sulfo-monomer content in the membrane.

branched polymers having basic sites in the main chain or side chain and doped with strong acids such as H_3PO_4 or H_2SO_4 [13,14]. These electrolytes exhibit high ionic conductivity but suffer from a propensity for attack of acid even in the presence of traces of moisture which limits their application. Therefore, introduction of proton-conductive groups such as sulfo- and phosphorus groups in the polymer skeleton is more advantageous method for polymer electrolyte formation.

In this work hydrogel membranes with fixed high-conducting sulfo-groups have been formed by radical copolymerization of various monomers (potassium sulphopropyl acrylate and sodium styrene sulphonate with acrylamide and acrylonitrile). TGA results indicate that membranes are capable of holding water at temperatures

up to 70°C for membranes with sulphopropyl acrylate and up to 90°C for membranes with styrene sulphonate. Water swelling coefficient was shown to increase linearly with the increase of sulphomonomer content. We were able to obtain membranes with IEC up to 1.4 mg-equiv/g for membranes with sulphopropyl acrylate and up to 0.8 mg-equiv/g for membranes with styrene sulphonate. This makes the membranes viable for further research both as ion-exchange membranes or proton-conducting membranes.

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