Proton conducting gel polyelectrolytes based on 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) copolymers Part II. Hydrogels

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Abstract

Polyelectrolytes of 2-acrylamido-2-methyl-propanesulfonic acid (AMPSA) in the form of crosslinked hydrogels have been obtained. The effect of the amount of crosslinking agent, N,N'-methylene-bis-acrylamide (BAA), and water content on the conductivity and mechanical properties of the gels obtained was studied and the results were compared with those of poly(AMPSA) aqueous solutions. The highest σ values, of the order of $1 \, S \, cm^{-1}$ are reached by systems containing 60–80 wt.% of water and 1–2 wt.% BAA. These systems form flexible and transparent membranes.

Modification of the mechanical properties of hydrogels consisting in the synthesis of structures of mutually interpenetrating polymer networks of poly(vinylidene fluoride) and poly(vinyl alcohol) (PVA) was performed. The thermal properties of these modified gels were studied.
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1. Introduction

Proton conducting polymer electrolytes find numerous applications in many electrochemical devices in which high ionic conductivity is required, such as fuel cells, electrochromic devices or sensors. From among ionic polymers, the greatest attention is paid to systems containing sulfonic acid groups, due to their high conductivity resulting from the high dissociation constant, both in polar organic solvents and in water [1]. In many papers it is stressed that the best properties from the point of view of application in fuel cells are shown by perfluorinated polymer electrolytes, such as Nafion, Aciplex, Flemion and Dow membranes, containing sulfonic groups in the side substituents [2–6]. However, these materials are characterized by some disadvantages, such as crossover problems, loss of hydration above 80 °C, and especially high cost amounting to US$ 700 per square meter [7], which limits their common use. Among the different alternatives, Rikukawa and Sanui suggest the use of hydrocarbon polymers even though they had been previously abandoned due to low thermal and chemical

stability [6]. From among the numerous ranges of materials, a group of 16 membranes was selected as potential candidates for replacing the perfluorinated polymers. This group includes the relatively cheap and commercially available poly(2-acrylamido-2-methyl-propanesulfonic acid) [poly(AMPSA)] [4,5]. There are literature reports on the synthesis of linear and crosslinked copolymers of AMPSA with acrylamide [8,9], *N-tert*-butylacrylamide [10], or 2-hydroxyethyl methacrylate [11,12], considered as membranes for application in fuel cells or electrochromic devices. AMPSA copolymers were studied also in the form of water-soluble complexes with a cationic homopolymer poly(diallyldimethylammonium chloride) [13] or polymers of basic properties, such as poly(vinylpyridine) [14,15].

In reaction with polyfunctional monomers, AMPSA forms crosslinked copolymers, which in the presence of a solvent form gel systems. The gel properties, such as swelling behavior, elasticity, optical properties, and permeability are dependent on the gel network structure resulting from the polymer matrix crosslinking density, presence of polar groups and type of solvent. Studies by means of light scattering were carried out for hydrogels based on AMPSA copolymers with acrylamide crosslinked with N,N'-methylene-bis-acrylamide (BAA), showing non-homogeneity of the gel systems [16].

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In this work we present the results of studies on the structure and conducting properties of AMPSA and BAA copolymers in the form of gels, and compare the features of these gels with those of aqueous solutions.

It is assumed that effective charge transport in membranes based on perfluorinated ionomers proceeds in the micelar structure in which the ion exchange sites are separated from the fluorocarbon backbone, thus forming clusters which are connected by short narrow channels [17–19]. In this work, attempts of obtaining such a structure have been made by the synthesis of an interpenetrating polymer network of the copolymer poly(AMPSA-co-BAA) with hydrophobic poly(vinylidene fluoride) (PVdF). For comparison, the properties of a network formed with a hydrophilic polymer, poly(vinyl alcohol) (PVA) were investigated.

2. Experimental

2.1. Materials

2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) (Aldrich, 99% purity), N,N'-methylene-bis-acrylamide (Merck), poly(vinylidene fluoride) (PVdF) (Aldrich, $M_w = 534$ kDa), poly(vinyl alcohol) (Aldrich) were used without further purification. Water was purified by reverse osmosis and distilled in nitrogen atmosphere.

2.2. Preparation of hydrogels

2.2.1. Poly(AMPSA) aqueous solutions

Polyelectrolytes in the form of aqueous solutions were obtained in the radical polymerization of AMPSA carried out in the presence of 1 wt.% of $K_2S_2O_8$ at 65 °C for 6 h. Solutions of low concentration were obtained by dissolution in water of appropriate weighed samples of the homopolymer obtained in methanol at 20 wt.% concentration, then precipitated with acetone, washed three times and dried under vacuum.

2.2.2. Polyelectrolytes in the form of crosslinked AMPSA and BAA hydrogels

Hydrogels of AMPSA crosslinked with BAA copolymer of various water and crosslinking agent content were obtained by radical polymerization initiated thermally in the presence of hydrogen peroxide at 65 °C for 3 h or by irradiation of the solution of monomers and 1 wt.% of photoinitiator (Irgacure 184) in a Teflon® dish with a UV lamp (300 W) for 10–15 min.

The contents of the crosslinked phase and of water-soluble hydrogel phase were determined by precipitation of the polymer with acetone and then extraction with water in a Soxhlet apparatus for 18 h.

2.2.3. Composite membranes of a structure of mutually interpenetrating polymer networks of AMPSA crosslinked with BAA in the presence of PVdF or PVA

The membranes were obtained by photochemical crosslinking of AMPSA with BAA in a colloidal dispersion of PVdF in DMF or DMA, and then the organic solvent was replaced with water. The AMPSA to BAA mole ratio was 9:1, which constitutes 7.6 wt.% of the crosslinking agent with respect to AMPSA. After PVdF dissolution, AMPSA, BAA and 1 wt.% of photoinitiator (Irgacure 184) were added. The homogeneous solution was conditioned at 5 °C for 12 h and then irradiated on a Teflon® dish with UV lamp (300 W) for 5–15 min. Flexible, maintaining their shape and non-transparent membranes were obtained. In order to remove the organic solvent, the membranes were placed in water, which was changed every 24 h, for 5 days. Membranes involving PVA were obtained analogously, but with carrying out the crosslinking in water. In some cases, glycerol was additionally introduced. The electrolytes obtained were colorless and flexible and were characterized by high cohesion and adhesion to glass, polyethylene or metal.

2.3. Techniques of electrolyte studies

2.3.1. Impedance spectroscopy

Ionic conductivity was determined using the complex impedance method in the temperature range from −60 to 70 °C. The samples were sandwiched between stainless steel blocking electrodes and placed in a temperature-controlled oven. The impedance measurements were carried out on a computer-interfaced Solartron-Schlumberger 1255 impedance analyzer over the 1 Hz to 1 MHz frequency range. The reproducibility of impedance spectroscopy results was checked by multiple experiments performed at room temperature. No results for samples of the same composition differ by more than ±5%.

2.3.2. DSC

Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Pyris 1 scanning calorimeter. The sample was placed in a hermetically closed aluminum cell. DSC traces were recorded with heating rate of 10 °C min⁻¹ from 173 to 473 K.

2.3.3. Thermogravimetric analysis—TGA/DTA/DTG

The measurements were carried out with a Derivatograph Q 1500-D apparatus in a 20–700 °C temperature range. The heating rate was 5 °C min⁻¹ and aluminum oxide was used as reference substance.

2.3.4. Swelling in water

Polyelectrolytes of various content of the crosslinking agent, BAA, were precipitated with acetone, dried and then weighed and immersed in water at room temperature. After 48 h, the wetted membranes were blotted dry with absorbent paper before weighing again. The amount of absorbed solvent was calculated on the basis of the difference in mass of the gel before and after immersing in the solvent.

3. Results and discussion

3.1. Synthesis of AMPSA hydrogels crosslinked with BAA

It is known that the gel structure is determined by its reactivity and concentration of monomers forming the polymer network.

In the case of the AMPSA and BAA monomer system, the reactivity ratios are not known, but it can be assumed that, similarly as for the AMPSA and acrylamide (AA) copolymerization ($r_{AMPSA} = 0.42$ and $r_{AA} = 1.05$) [9], BAA is completely consumed in the first reaction stage. Such a reaction course is the reason for the non-uniformity of the gel formed and some thought should be given to whether a fully crosslinked form or mixture of a network and AMPSA homopolymer are present in systems in which small concentrations of the difunctional monomer are applied. The synthesis of gels comprising from 5 to 25 mol% of BAA was carried out in order to explain the structure of AMPSA and BAA hydrogels. It was found that after 6 h the monomer conversion is close to 100%. The gels obtained were precipitated with acetone and then extracted with water in a Soxhlet apparatus for 18 h. Leaching resulted in fractionation of the polymer matrix to water-soluble and insoluble fractions. The composition of the insoluble copolymer was determined based on elemental analysis. For the water insoluble fraction after removal of the solvent FTIR spectra were recorded (KBr pellets). In these spectra no vibrations of the unsaturated C=C bonds were observed, which means that the washed out fraction contains only the AMPSA homopolymer, without monomers and linear copolymers. Water-soluble, linear copolymers would contain unreacted unsaturated bonds originating from BAA. Table 1 shows the compositions of the isolated fractions of copolymerization products.

As seen from the data presented, the share of AMPSA homopolymer increases with a decrease in the BAA concentration in the monomer mixture, and at 5 mol% content of the crosslinking monomer about 50 wt.% of AMPSA forms the homopolymer. The copolymerization is terminated at a certain stage of reaction, due to which the AMPSA content in the copolymer is lower than that in the initial monomer feed and a certain amount of the AMPSA monomer is unable anymore to link to the crosslinked structure and forms a homopolymer. Thus, when considering the hydrogel properties it is assumed that it constitutes a mixture of a crosslinked copolymer and interpenetrating it AMPSA homopolymer. Moreover, a rise in the ability of water embedding by the gel along with a decrease in the degree of crosslinking of the polymer can be observed (Table 1). At a BAA content of about 5 mol%, the degree of swelling is very high, 2400%. In the case of practical applications, the ability to water embedding should be limited, and therefore the synthesis of membranes in the presence of also PVdF was carried out; the results are presented further.

3.2. Characterization of AMPSA and BAA hydrogels

Gel electrolytes were synthesized in the radical copolymerization of AMPSA and BAA in an aqueous medium at various concentrations of the crosslinking medium and water content in the system. The polymerization can be initiated using both standard initiators of radical polymerization in aqueous media ($K_2S_2O_8$, H_2O_2) as well as photoinitiators (Irgacure 184, room temperature). This is of practical importance, since it permits to produce a conducting membrane directly between the electrodes. In Table 2, the properties of the obtained hydrogels containing 80 wt.% of water are collected.

The electrolyte comprising 1 wt.% of BAA is characterized by good flexibility and good adhesion to materials such as glass and metal. The membrane at this BAA content does not retain its shape due to considerable cohesion forces. When increasing the share of the crosslinking agent to 1.5 wt.%, the membrane shows high flexibility and retains its dimensions. A further increase in the BAA concentration causes a decrease in the membrane flexibility.

The conductivity values of crosslinked hydrogels containing a constant amount of water of 80 wt.% and from 1 to 2 wt.% of BAA in the polymer matrix are similar, of the order of $1 \, S \, cm^{-1}$ at room temperature. At a higher content of the crosslinking monomer, above 7 wt.%, the conductivity undergoes a two-fold decrease, which is connected with a decrease in the concentration of acidic groups in the system. Fig. 1 shows the course of conductivity changes of poly(AMPSA) aqueous solutions as a function of polyelectrolyte concentration. Exact data concerning the properties of poly(AMPSA) solutions in different solvents can be found in our earlier paper [20]. The conductivity of poly(AMPSA) solution of 80 wt.% water content was $1.2 \, S \, cm^{-1}$, which indicates that at a not too high degree of crosslinking of the gel a polyelectrolyte of analogous conductivity as the solution is obtained.

Thus, data of poly(AMPSA) aqueous solutions can be taken advantage off when analyzing the effect of the acidic groups concentration on hydrogel conductivity. Fig. 2 shows the ambient temperature ionic conductivity of poly(AMPSA) aqueous solutions as a function of the number of moles of water molecules falling per 1 mol of AMPSA monomeric units (m.u.). As can be

Table 1
Composition of products formed in the copolymerization of AMPSA and BAA

AMPSA content in monomer feed (mol%)	AMPSA content in copolymer (mol%)	Amount of washed-out homopolymer (wt.%)	Degree of swelling (%)
75.0	63.3	31.9	106
82.3	74.0	35.7	140
88.9	78.6	44.4	217
94.7	89.8	48.2	2400

Table 2
Properties of hydrogels of AMPSA crosslinked with various amounts of BAA[a]

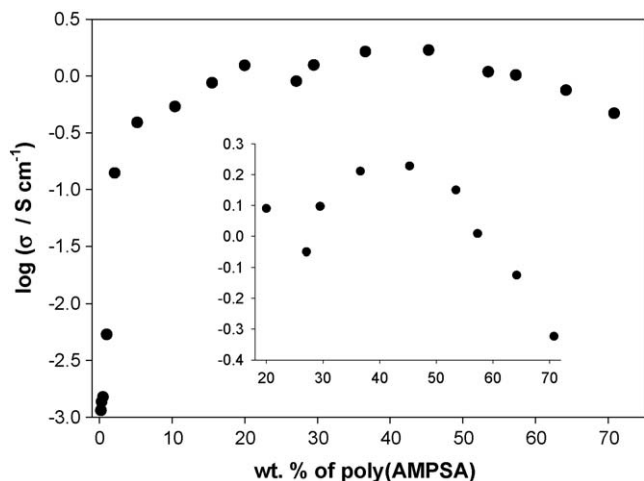| BAA content in polymer matrix (wt.%)	$\sigma_{20\,°C}$ ($S \, cm^{-1}$)	Hydrogel features
0	1.24	Very viscous solution
1	1.07	Flexible, good adhesion, membrane does not maintain shape
1.5	1.15	Flexible, good adhesion, membrane maintains shape
2	0.93	Less flexible, good adhesion, membrane maintains shape
7.6	0.57	Brittle, weaker adhesion, membrane maintains shape

[a] Water content 80 wt.%.

Fig. 1. Conductivity of aqueous poly(AMPSA) solutions as a function of polymer concentration.

Fig. 3. Comparison of conductivity of the crosslinked form of AMPSA hydrogel containing 7.6 wt.% of BAA and of AMPSA homopolymer solution, both containing 20 wt.% of polymer matrix and 80 wt.% of water.

noticed, the maximum of conductivity of the solutions occurs at ca. 20 mol of H_2O molecules falling per 1 mol of $-SO_3H$ acidic groups.

When comparing the temperature changes of conductivity of the gel composed of the matrix of 7.6 wt.% (10 mol%) of BAA and of 80 wt.% of water with the values obtained for the AMPSA homopolymer solution of similar concentration (Fig. 3), it appears that the character of conductivity is very similar over the whole temperature range, and the differences in ionic conductivity are below one order of magnitude.

Fig. 4 shows the changes of ionic conductivity as a function of temperature for gels in which the AMPSA m.u. to BAA m.u. mole ratio is 9:1 (which corresponds to 7.6 wt.% BAA content in the polymer matrix). As can be noticed the effect of water content in the gel on conductivity is most evident at low temperature.

At above 0 °C the conductivities are high and reach values of the order of 0.1–1 S cm^{-1}, rising with an increase in the water content. The highest ionic conductivity values are reached by systems containing 60–80 wt.% of water. At such a composi-
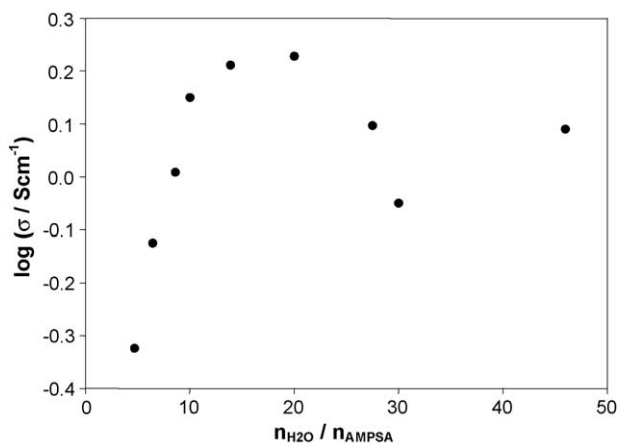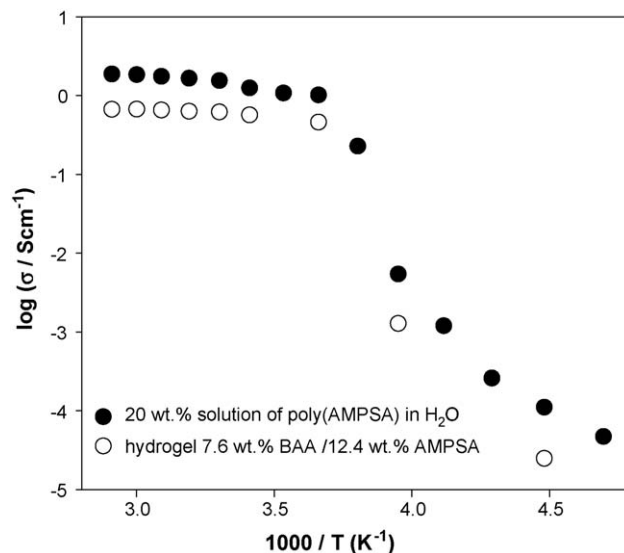
tion, 20–50 molecules of water fall at an average per one acidic group. In the range of low temperatures a rapid decrease in conductivity occurs. In the range below the freezing point of water the conductivity is the lower, the more water is embedded by the gel.

In hydrogels based on polyelectrolytes, part of water strongly interacts with the polar or ionic groups present in the polymer and as results from calorimetric studies, such bound water does not undergo freezing. The amount of water which interacts much weaker with the polymer chains, as the structural water, freezes most often at a temperature lower than that of bulk water, present

Fig. 2. Conductivity of poly(AMPSA) aqueous solutions as a function of the number of water molecules per 1 mol of AMPSA monomeric units.
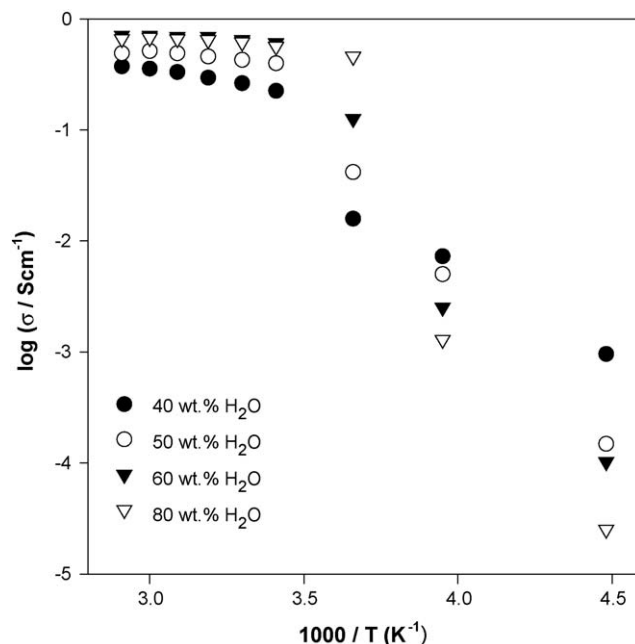

Fig. 4. Conductivity of the hydrogels of AMPSA crosslinked with 7.6 wt.% of BAA, of various water content.

Fig. 5. DSC traces of the hydrogel containing 95 mol% of AMPSA, 5 mol% of BAA and 65 wt.% of water.

Table 3
Composition of hydrogel polymer matrixes of a structure of interpenetrating networks of poly(AMPSA-co-BAA) with PVdF

Gel	PVdF (wt.%)	AMPSA (wt.%)	BAA (wt.%)
I	15	78.5	6.5
II	20	73.8	6.2
III	20	75.3	4.7
IV	25	69.3	5.7
V	30	64.6	5.4

3.3. Hydrogels of a structure of mutually interpenetrating polymer networks (IPN) of AMPSA crosslinked with BAA and of PVdF

The synthesis of polymer membranes of a structure of mutually interpenetrating polymer networks IPN containing a polyelectrolyte, predicted for a fuel cell, in the form of an AMPSA and BAA copolymer and PVdF was carried out. PVdF was used as the hydrophobic component, of which it is known that it forms physical networks in which the polymer crystalline phase plays the role of the nodes. Improvement of the mechanical properties and limitation of the swelling degree of the electrolyte was the purpose for providing the membranes with such a structure. Thus, it was expected to achieve an effect close to that of Nafion membranes, i.e. consisting in a molecule of hydrophobic domains and hydrophilic conducting channels.

The synthesis was performed by means of photochemical crosslinking of AMPSA and BAA in a colloidal PVdF dispersion in an organic solvent, such as DMF or DMA. Then, the membranes obtained were subjected to an exchange of the organic solvent for water. After the introduction of water, the organic segment clearly stiffened and the flexibility of the membrane decreased. It was observed that PVdF causes a loss of transparency of the system. Membranes of PVdF content of 15, 20, 25 and 30 wt.% were made (Table 3).

The results of conductivity determinations as a function of temperature are presented in Fig. 7. The measurements were carried out at maximal water content. As expected, the lowest conductivity was shown by the membranes containing the most, 30 wt.%, of the hybrophobic component. However, it appeared unexpectedly that membranes containing 20 wt.% of PVdF clearly reached higher conductivity values in comparison with that of membranes of the least amount of hydrophobic agent (15 wt.%). Thermogravimetric analysis of the membranes studied was carried out to explain these results. Thermograms of the hydrogel containing AMPSA crosslinked with BAA and 15 wt.% of PVdF are presented in Fig. 8.

Based on DTG, it was determined that 1 g of the membrane sample containing 15 wt.% of PVdF takes up about 5 mol of water. This indicates that over 1000 water molecules fall per 1 mol of acidic groups. Therefore, a decrease in conductivity results from the low concentration of charge carriers at such a high dilution of the system. Gels showing the highest con-

in the system in a neat form forming a separate phase [10,21]. DSC studies carried out by us for hydrogels containing 95 and 67 mol% of AMPSA and 64 and 74 wt.%, respectively of water (Figs. 5 and 6) indicate that part of water in these systems occurs in a form not bound with the polyelectrolyte matrix. Assuming that the melting heat of ice is 6.007 kJ mol^{-1}, it can be calculated that 72% of water molecules undergoes crystallization in the hydrogel of 95 mol% of AMPSA, 5 mol% of BAA and 64 wt.% of water content (Fig. 5). The share of this form of water is higher, since at −40 to −50 °C the region of "cold after-crystallization" of water can be observed in the thermogram. The main melting peak occurs at −4.1 °C and no clear glass transition temperature of the gel is observed. In the case of a gel of greater degree of crosslinking (23 mol% of BAA) and 74 wt.% of water (Fig. 6) the content of water undergoing crystallization calculated based on the melting heat at −0.79 °C is 56%. In the case of this gel, a second melting maximum at −7.6 °C occurs in the thermogram, which indicates the presence of freezing water interacting with the matrix polar groups. The results presented indicate that a greater degree of crosslinking favors stronger interactions of the matrix ionic groups with the solvent. However, full interpretation will be possible after gaining a greater number of data.
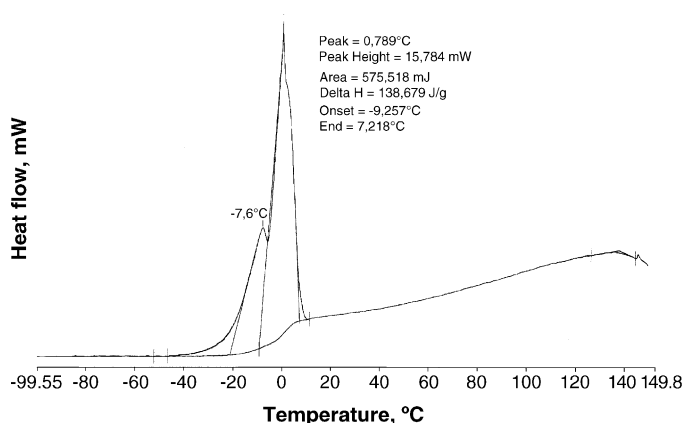

Fig. 6. DSC traces of the hydrogel containing 67 mol% of AMPSA, 23 mol% of BAA and 74 wt.% of water.
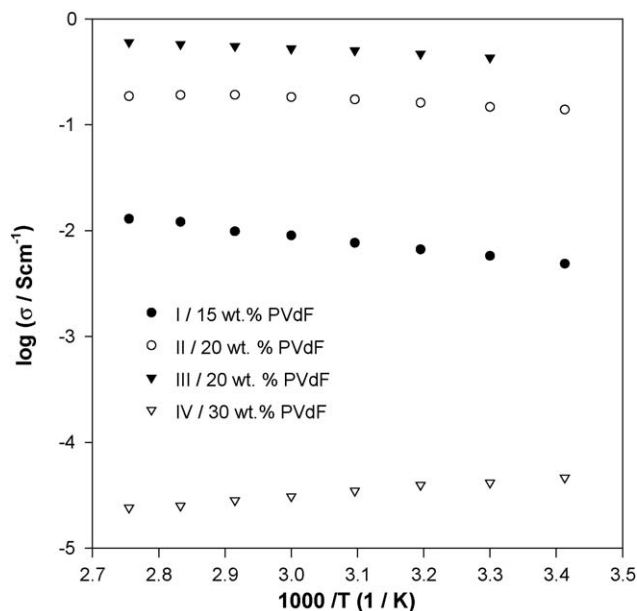
Fig. 7. Conductivity of hydrogels comprising a copolymer of AMPSA crosslinked with BAA of a structure of mutually interpenetrating networks with PVdF. The measurements were carried out at maximum water content.
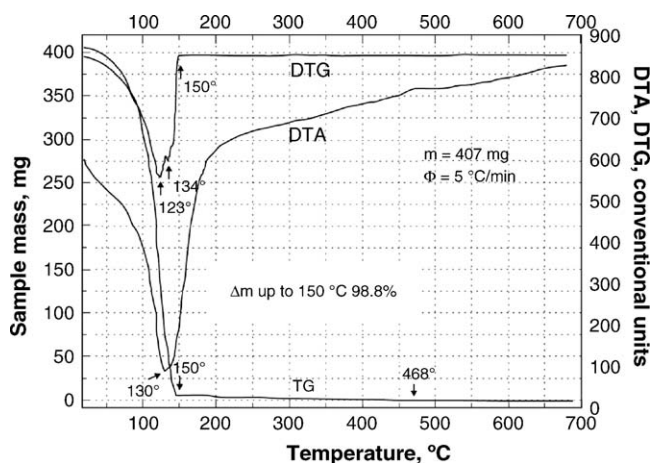

Fig. 8. Thermal analysis of a hydrogel containing an AMPSA crosslinked with BAA copolymer and 15 wt.% of PVdF.

ductivity values absorbed much less water, about 2 mol per 1 g of the sample. In this case, 275 mol of water fall per 1 mol of AMPSA m.u. This is still a too large amount with respect to the optimal water content in the conducting channels, which is from 20 to 50 water molecules per AMPSA m.u. in hydrogels crosslinked with BAA (60–80 wt.% of water) (Fig. 4) and ca. 20 water molecules in the case of poly(AMPSA) solutions. The small concentration of charge carriers in these systems is probably the reason for the lower conductivity with respect to that of solutions. It is worth noting that the conductivity of systems comprising 20 wt.% of PVdF is higher, over a wide temperature range, than that of Nafion® 117 membranes, for which σ values in the 0.08–0.1 S cm^{-1} range are reported. The ambient temperature conductivity of electrolyte II (20 wt.% of PVdF) is 0.5 S cm^{-1}. These systems quickly lose water at elevated temperature, similarly as Nafion. The equilibrium water content for Nafion is 5 wt.%, whereas for membranes containing 20 wt.% of PVdF it is 10 wt.%. With a rise of temperature they slowly lose water, and the greatest mass loss occurs at 123 °C. A practically complete water loss is observed at 130 °C. It was also noticed that the thermal decomposition of hydrogels proceeds at a lower temperature than that of dry membranes. During heating of hydrated membranes containing 15 wt.% of PVdF, their complete decomposition occurs at 150 °C, whereas a dry membrane is stable up to 173 °C. The data presented show that these systems are suitable electrolytes for electrochemical devices operating at relatively low temperatures.

3.4. Hydrogels of AMPSA crosslinked with BAA and modified with PVA

The AMPSA crosslinked with BAA hydrogels can be additionally modified by introducing polymers of hydrophilic properties to the system. PVA was used as the hydrophilic monomer in the present studies. Table 4 shows the composition and conductivity of the obtained hydrogels. The membranes formed are characterized by high ionic conductivity, high adhesion to the surface and complete transparency.

The ambient temperature conductivity of PVA containing hydrogels ranges from 10^{-2} to 10^{-1} S cm^{-1}, depending on the amount of water. The mechanical strength of these electrolytes is not satisfactory. Additional replacement of water with glycerol did not affect favorably the mechanical properties and caused a considerable decrease in the proton conductivity. However, the high adhesion to materials, such as glass, polyethylene or metal, at simultaneous high cohesion forces provides a possibility for potential application of these systems as ion conducting glues.

Table 4
Conductivity of AMPSA gels crosslinked with BAA with the addition of poly(vinyl alcohol) (PVA)

Electrolyte composition				Proton conductivity (S cm^{-1})				
Matrix				H$_2$O (wt.%)	$\sigma_{5\,°C}$	$\sigma_{20\,°C}$	$\sigma_{50\,°C}$	$\sigma_{70\,°C}$
AMPSA (wt.%)	BAA (wt.%)	PVA (wt.%)	Glycerol (wt.%)					
85.2	6.0	8.8	–	47	2×10^{-2}	3×10^{-2}	5×10^{-2}	6×10^{-2}
83.0	7.0	10	–	67	2×10^{-2}	8×10^{-1}	1.1	1.5
41.6	3.1	4.8	50.5	27	2×10^{-3}	3×10^{-3}	7×10^{-3}	1×10^{-2}
40.7	3.4	5.1	50.8	34	1×10^{-3}	2×10^{-1}	4×10^{-1}	5×10^{-1}

4. Conclusions

The copolymerization of AMPSA and BAA in an aqueous medium affords gel polyelectrolytes of a non-uniform structure resulting from the reactivity of comonomers and their concentration. In such systems, the polymer matrix contains a crosslinked fraction and a water-soluble fraction of AMPSA homopolymer, the mutual share of which depends on the monomers concentration.

The proton conductivity of crosslinked hydrogels reaches high values of the order of 0.1–$1\,\mathrm{S\,cm^{-1}}$, comparable with the conductivity of poly(AMPSA) aqueous solutions. The most effective charge transport in solutions is assured by the water content, at which ca. 20 water molecules fall per one acidic group, and in the case of the crosslinked structure from 20 to 50 water molecules per one AMPSA monomeric unit (60–80 wt.% of water). Aqueous gels, due to their high conductivity, may be considered as electrolytes in low-temperature sources of energy.

Preliminary results of studies on the synthesis of gels of a structure of mutually interpenetrating polymer networks with hydrophilic PVA or hydrophilic PVdF show great possibilities for the modification of mechanical and thermal properties of these systems. The conductivity of systems comprising 20 wt.% of PVdF is higher over a wide temperature range than that of membranes from Nafion® 117.

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