Research Article

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# Ion-Conducting Membranes Comprising Poly (Ethylene Oxide) and Poly (Acrylic Acid)

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***Abstract***

*Two series of solid solvent-free polymer membranes comprising poly (ethylene oxide) and poly (acrylic acid) were prepared by using casting technique, and their ion conductivity was examined at ambient temperature and in the present of LiPF6. It was established that the best conductivity, which is in the range 4.2·10-5 - 9.8·10-5 S·cm-1, corresponds to the films obtained on the base of triblock copolymer PAA-b-PEO-b-PAA. The membranes obtained from diblock copolymer PAA-b-PEO have a conductivity two orders of magnitude lower, however, the introduction of 3-9 weight % of LiPF6 made it possible to increase conductivity to 4.49·10-6-1.98·10-5 S·cm-1. Thus, obtained results allow to consider PAA-b-PEO-b-PAA and PAA-b-PEO as a possible solid polymer matrix for proton exchange membranes.*

***Keywords***

*Membranes, Ethylene Oxide, Acrylic Acid*

## Introduction

Among the wide variety of fuel cells, solid polymer electrolytes (SPEs) are currently considered the most promising. In these systems, liquid electrolytes are replaced by solid polymers in the form of proton-conducting membranes. The electrolyte is a critically important component of any energy storage or conversion device, as it plays a dual role by ensuring both the physical separation of the electrodes and the medium for ion transport. An ideal proton-conducting membrane should possess several key properties, including minimal thickness, low internal resistance, mechanical flexibility, sufficient thermal and electrochemical stability, as well as mechanical and structural robustness. Achieving an optimal combination of all these properties simultaneously is challenging; however, polyethylene oxide (PEO)-based polymer matrices, owing to the presence of ether groups and a low glass transition temperature, provide one of the most balanced sets of characteristics among known polymers [1–4]. Despite these advantages, the hight crystallinity of PEO significantly restricts segmental mobility and reduces ionic conductivity. Considerable efforts have therefore been devoted to enhancing the conductivity of PEO-containing electrolytes while suppressing or preventing crystallization.

It has been demonstrated that the formation of intramolecular polycomplexes effectively reduces PEO crystallinity in solid polymer electrolytes [5-7]. Previously, we showed that electrolyte membranes based on block copolymers of polyethylene oxide–polyacrylamide block copolymers exibit relatevely high ionic conductivity, and that partial hydrolysis of the polyacrylamide blocks introducing additional -COOH groups further improves charge transport properties [8].

In the present work, a srategy based on complete replacement of amide groups in polyacrylamide segments by carboxylic acid groups is explored. Accordingly, block copolymers composed of poly(ethelene oxide) and poly(acrylic acid) were selected as model systems for the preparation and investigation of ion-conducting membranes.

## Methods

### Synthesis of MePEO-b-PAA Diblock Copolymer

The MePEO-b-PAA diblock copolymer (DBC) was synthesized via radical block copolymerization of acrylic acid (AA) with methyl ether polyethylene glycol (MePEG), using a redox initiation mechanism for the generation of free radicals at the terminal

hydroxyl groups of MePEG, initiated by Ce+4 ions [9]. MePEG with a number-average molecular weight Mn= 5.3 kDa (Fluka, Germany), diammonium hexanitratocerate(IV) (Aldrich, USA), and acrylic acid (Fluka, Germany) were used. Acrylic acid was distilled prior to use. The concentrations of MePEG and Ce4+ salt in the reaction mixture were both 0.004 kg·m$^{-3}$. The final product of the synthesis was obtained in the sodium salt form (MePEO-b-PANa), which was isolated from aqueous solution by freeze-drying. The refined molecular weight of the initial MePEG sample and the main molecular characteristics of the obtained DBC, determined by 1H NMR spectroscopy, are summarized in Table 1.

**Synthesis of PAA-b-PEO-b-PAA Triblock Copolymer**

PAA-b-PEO-b-PAA triblock copolymers (TBCs) with different lengths of the central PEO block were synthesized via radical block copolymerization of acrylic acid with polyethylene glycol (PEG) having Mn= 6 kDa and 35 kDa. The synthesis was carried out according to previously reported procedures [10], employing a redox initiation system. The chemical structure and molecular parameters of the obtained TBCs were determined by 1H NMR spectroscopy and potentiometric titration of water–ethanol solutions ($C_2H_5OH/H_2O$ = 5/95 vol%) [11]. 1H NMR spectrum of TBC– PANa recorded in $D_2O$ exhibits characteristic signals corresponding to the –$CH_2$– protons of the PEO block and the –$CH_2$– and >CH– groups of the PANa blocks at δ = 3.60, 1.399, and 1.987 ppm, respectively.

**Table 1:** Molecular parameters of the diblock and triblock copolymers

| Polymer | MnPEO, kDa | MnPAA, kDa | MnDBC(TBC) |
|---|---|---|---|
| DBC | 5.3 | 17.6 | 22.9 |
| TBC6 | 6 | 5.8 | 17.6 |
| TBC35 | 35 | 28.3 | 91.6 |

**Potentiometric Titration Procedure**

The molecular weights of the ionogenic blocks and the overall macromolecules in the synthesized TBC–PANa samples were determined by potentiometric titration. Considering that the samples were in the sodium salt form, reverse titration of the copolymer solution and the solvent blank was performed using 0.2 N HCl. The titration results, presented as proton uptake curves (dependence of proton uptake σH$^+$ vs pH), are shown in Figure 1. As demonstrated previously, the plateau value σlim on the proton uptake curve corresponds to the concentration of –COO-Na groups in the DBC–PANa or TBC–PANa samples, allowing calculation of the molecular weights of the PANa blocks and the macromolecules as a whole [12]. Accurate determination of σlim in aqueous solutions of block copolymers is hindered by the formation and precipitation of intramolecular polycomplexes (IntraPCs) on the electrodes at pH < 4. These complexes arise from strong interactions between chemically complementary PAA and PEO blocks and are accompanied by micellization. The addition of ethanol significantly reduces hydrophobic interactions in such systems. Therefore, reverse titration of TBC–PANa samples was carried out in a water–ethanol mixture ($C_2H_5OH/H_2O$ = 5/95 vol%), which prevented IntraPC precipitation on the electrodes and enabled determination of σlim = 6.8 mg-eq·g$^{-1}$.

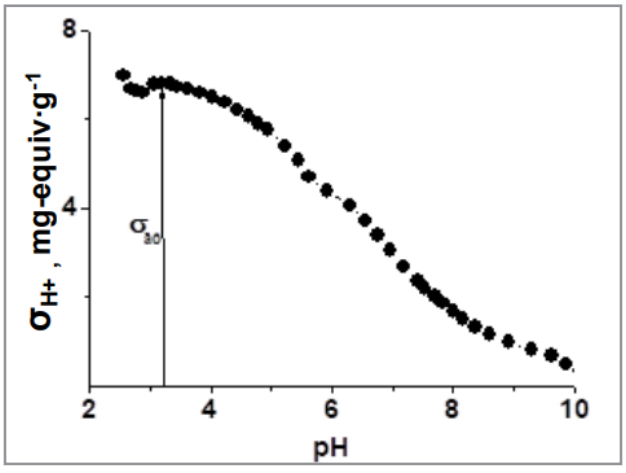


**Figure 1:** Proton absorption curves of TBC–PANa in an aqueous-alcohol solution

**Ionic Conductivity Measurements**

Dielectric properties were measured in the frequency range of 102-105 Hz using a dielectric spectrometer based on an R5083 AC bridge and a three-electrode measurement cell. The sample temperature was monitored using a chromel–copel thermocouple introduced through an opening in the shielding electrode. After temperature stabilization (10–15 min), the dielectric loss tangent (tan δ) and capacitance (C) were recorded over the working frequency range. The capacitance of the empty cell C0 was calculated according to Equation 1:

$C_0=S_{\varepsilon o}/d$, (1)

where $\varepsilon_0 = 8.85 \cdot 10^{-14}$ F·cm$^{-1}$ is the permittivity of free space, S is the sample surface area, and d is the sample thickness (cm). The dielectric response of the materials was characterized by the dielectric loss tangent tan δ, the real part of the complex dielectric permittivity ε′, and the real part of the complex conductivity σ′. For all samples, these values were analysed at a frequency of 1 kHzis.

**Water Uptake Measurements of MePEO-b-PAA**

To investigate water absorption, MePEO-b-PAA (DBC) films were thorouly dried in a desiccator over freshly calcined CaCl2 until constant weight wasreached. The samples were than equilibrated for five days in atmosphere with different relative humidities at 20 oC . The relative humidity was controlled using saturated salt solutions of $MgCl_2$ (33%), $NH_4NO_3$ (65%), $(NH_4)_2SO_4$ (81%), and $CuSO_4 \cdot 5H_2O$ (98%). After equilibration, the samples were weighed using an analytical balance, then dried again over $CaCl_2$ under vacuum and reweighed. Water uptake was calculated according to Equation (2):

$WH2O = ((W_{dry} - W_{wet})/ W_{dry}) \cdot 100\%$ (2)

where Wwet and Wdry are the masses of the wet and dry polymer samples, respectively.

## Results

**Formation of Polymer Electrolyte Membranes and Conductivity of Dry Films**

Free-standing ion-conducting membranes with a thickness of approximately 100-150 µm were prepared by casting aqueous polymer solutions onto polystyrene substrates, followed by drying anhydrous $CaCl_2$ for 24 h. Membranes prepared from the triblock copolymer with a 6 kDa central PEO block were extremely brittle and unstable for measutements. Therefore, only DBC and TBC with a 35 kDa central PEO block (TBC35) were further investigated.

Even thoroughly dried exhibited measurable ionic conductivity, indicating intrinsic charge transport enabled by polar polymer segments (Figure 2, Table 2). This observation indicates the presence of intrinsic charge transport mechanisms in the polymer matrices, which can be attributed to the polar nature of the polymer chains and the presence of ionogenic groups. In particular, the ether oxygen atoms in the PEO segments are capable of coordinating esidual ionic species, thereby enabling limited ion mobility even under nominally anhydrous conditions.

A comparison between DBC and TBC35 reveals that triblock copolymer membranes consistently exhibit higher conductivity values under identical conditions. This behaviour correlates well with the increased length of the PEO block in TBC35, which provides a higher density of ether oxygen atoms along the polymer backbone. Repeating $–CH_2–CH_2–O–$ units create favourable pathways for ion coordination and transport, facilitating more efficient ion migration through the membrane. Similar trends were previously observed for triblock copolymers of polyethylene oxide and polyacrylamide, confirming that elongation of the polyether block is a key structural parameter governing ionic conductivity in such systems [13].

**Table 2:** Dielectric characteristics of dehydrated membranes based on diblock- and triblock copolymers

| Polymer | ε′ | σ′ |
|---|---|---|
| DBC | 5.10 | 6.47·10-9 |
| TBC35 | 6.93 | 3.64·10-9 |

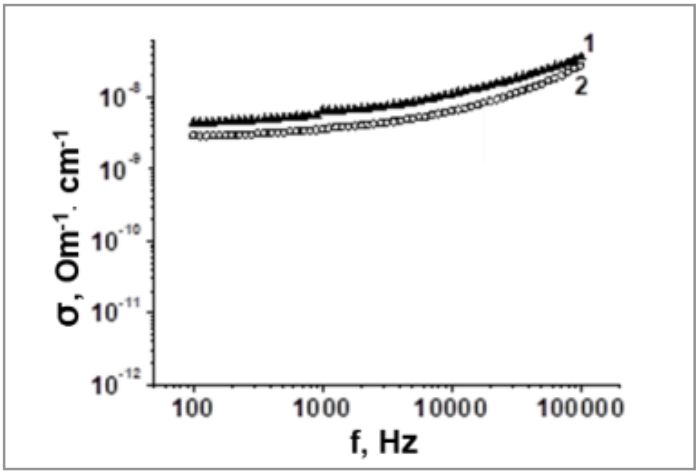


**Figure 2:** Conductivity vs frequency for dehydrated membranes on the base of TBC35 - 1, and DBC - 2

**Effect of Ambient Humidity on Ionic Conductivity**

Iincrease in ionic conductivity was observed upon exposure of the membranes to ambient air. After only 1 h of storage at 16 °C and relative humidity of approximately 70%, the real part of the complex conductivity σ′ increased by nearly two orders of magnitude for the DBC-based membranes and by almost four

orders of magnitude for the TBC35-based membranes (Table 3, Figure 3). The pronounced sensitivity of the ionic conductivity to ambient humidity prompted a more detailed investigation of membrane behaviour under controlled atmospheric conditions. Membranes based on both DBC and TBC35 copolymers were exposed to air for extended periods, and their dielectric response was monitored as a function of frequency. It was found out that prolonged exposure to ambient air leads to a further increase in ionic conductivity across the entire investigated frequency range. This effect is considerably more pronounced for TBC35-based membranes, confirming the synergistic influence of polymer architecture and environmental moisture. The continuous rise in σ′ with exposure time suggests gradual water uptake by the membranes, resulting in enhanced polymer chain mobility and more efficient ion transport pathways.

The dependence of conductivity on humidity can be rationalized by considering the dual role of water in PEO-containing polymer electrolytes. First, absorbed water acts as a plasticizer, reducing intermolecular interactions and increasing the flexibility of the polymer chains. This facilitates segmental motion, which is a prerequisite for ion hopping and migration. Second, water promotes partial dissociation of carboxylic acid groups, thereby increasing the concentration of mobile charge carriers. Both effects contribute to the observed increase in ionic conductivity. Notably, despite the beneficial effect of moderate moisture uptake on conductivity, excessive humidity leads to pronounced swelling of the membranes and deterioration of their mechanical integrity. This indicates the existence of an optimal humidity range in which enhanced ionic conductivity can be achieved without compromising membrane stability. The triblock copolymer membranes, owing to their longer PEO segments, demonstrate a higher tolerance toward moisture-induced plasticization, which explains their superior performance compared to diblock copolymer- based membranes under identical conditions.

**Table 3:** Dielectric characteristics of DBC and TBC35 membranes under ambient humidity conditions

| Polymer | ε′ | σ′ |
|---|---|---|
| DBC | 6.93 | 5.51·10-7 |
| TBC35 | 1587.03 | 4.19·10-5 |

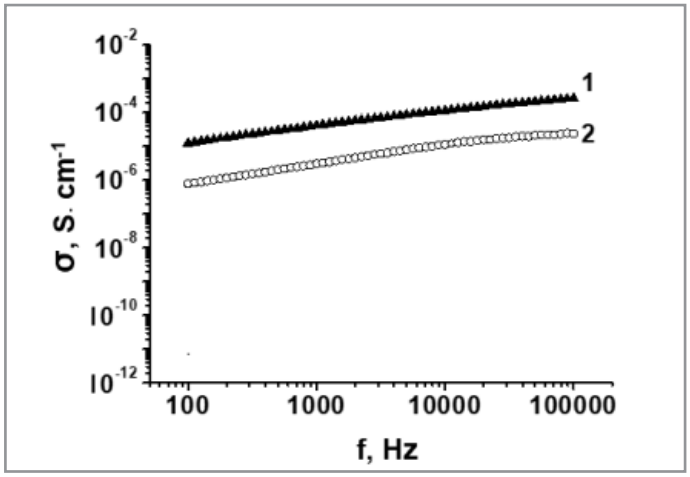


**Figure 3:** Conductivity vs frequency for membranes on the base of DBC - 1, and TBC35 - 2 under ambient humidity conditions

**Effect of $LiPF_6$ Doping on Ionic Conductivity of DBC-Based Membranes**

In the next series of experiments, the ionic conductivity of diblock copolymer (DBC) membranes doped with lithium hexafluorophosphate (LiPF6) was investigated (Table 4, Figure 4). The incorporation of $LiPF_6$ resulted in a pronounced enhancement of ionic conductivity over the entire frequency range studied, clearly demonstrating the effectiveness of salt doping in improving charge transport in MePEO-b-PAA-based polymer electrolytes. As shown in Figure 4, a systematic increase in conductivity was observed with increasing $LiPF_6$content. An increase in the dopant concentration from 3 to 9 wt% led to an increase in the real part of the complex conductivity σ′ from $3.07\cdot 410^{-6}$ to $1.97 \cdot 10^{-5}$ $S\cdot cm^{-1}$. This behavior can be attributed primarily to an increase in the concentration of mobile charge carriers introduced by the lithium salt, as well as to the plasticizing effect of $LiPF_6$ on the polymer matrix. In addition to increasing the number of charge carriers, $LiPF_6$ affects the polymer structure by reducing intermolecular interactions and enhancing segmental mobility of the PEO chains. This plasticization facilitates ion transport by lowering the energetic barriers for ion hopping along the polymer backbone. Furthermore, the presence of carboxylic acid groups in the PAA blocks plays a crucial role in salt dissociation. The high polarity of the –COOH groups promotes lithium salt dissociation through donor–acceptor interactions between the carboxylate groups of the macromolecule and lithium cations, thereby further enhancing ionic conductivity. Overall, the combined effect of increased charge carrier concentration, enhanced polymer chain mobility, and favorable coordination interactions between lithium ions and functional groups of the copolymer accounts for the significant improvement in ionic conductivity observed upon $LiPF_6$ doping.

**Table 4:** Molecular parameters of the diblock and triblock copolymers

| Composition | [PEO]/[LiPF6], base-mol·mol-1 | [DBC]/[LiPF6], base-mol·mol-1 | ε | σ′ |
|---|---|---|---|---|
| DBC | - | - | 15178.15 | 3.07·10-6 |
| DBC+ LiPF6 | 0.15 | 0.3 | 9389.67 | 4.48·10-6 |
| DBC+ LiPF6 | 0.09 | 0.18 | 33153.34 | 1.17·10-5 |
| DBC+ LiPF6 | 0.06 | 0.12 | 47538.14 | 1.97·10-5 |

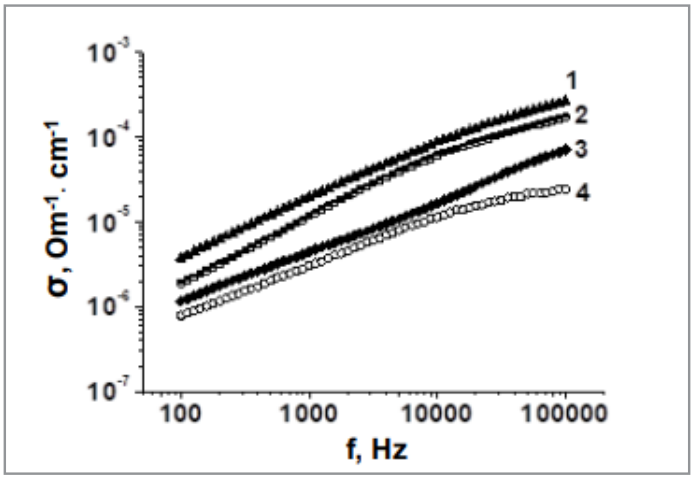


**Figure 4:** Conductivity vs frequency for membranes of 1 – DBC, and its compositions with LiPF6 at ratio [DBC]/[LiPF6]: 2 – 0.5; 3 – 0.09; 4 – 0.06

**Characterisation of Water Absorption in MePEO-b-PAA Membraines**

The fact that with increasing relative humidity the amount of water adsorbed by the copolymer films gradually increases can be considered natural and entirely expected, since it is known that each oxyethylene unit of PEO binds two water molecules. It is interesting that two adsorption regimes exist. Up to 65% relative humidity, adsorption proceeds relatively slowly and reaches an average of 34%, whereas at higher humidity levels water uptake increases significantly (Table 5, Figure 5).

**Table 5:** Water adsorption by DBC membranes

| Sample | Amount of adsorbed water at the corresponding ambient humidity, %: | | | |
|---|---|---|---|---|
| | 33% | 65% | 81% | 98% |
| DBC | 22.9 | 33.8 | 44.0 | 68.8 |

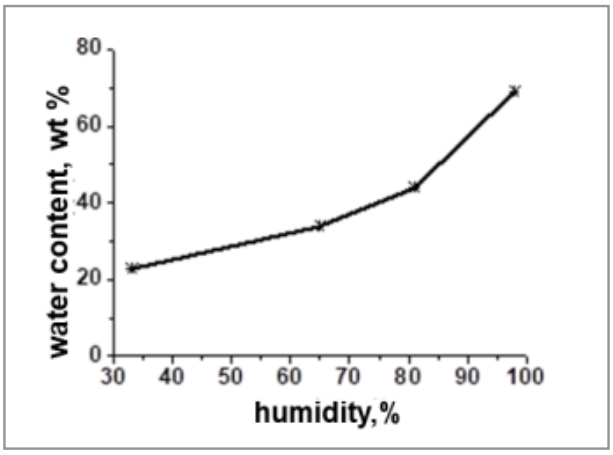


**Figure 5:** Dependence of water uptake on relative humidity for DBC-based membranes

Presumably, the water already present in the polymer acts as a plasticizer, i.e., lowers the glass transition temperature of the polymer and promotes further water absorption. Unfortunately, the water adsorbed by the membranes negatively affects the mechanical properties of the films, causes excessive swelling, increases their tendency to stick together, and makes further

handling impossible. Since the DBC membranes proved to be unsuitable for operation at humidity levels above 65%, the data presented below include only samples conditioned at 33% relative humidity and dehydrated samples (Figure 6).

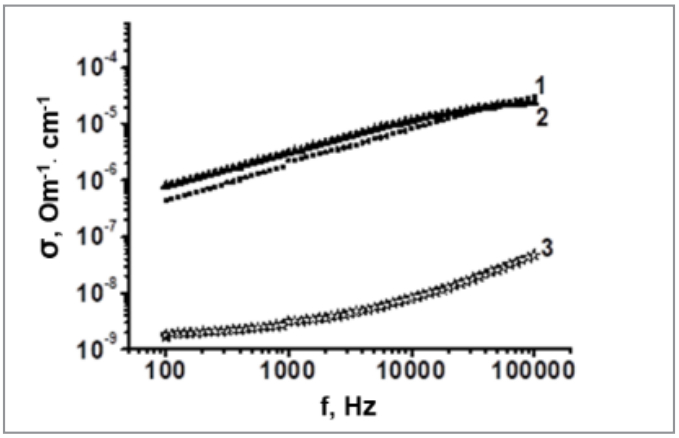


**Figure 6:** Frequency dependence of conductivity for humidified and dried DBC membranes:
1 – stored in air for 48 h; 2 – conditioned at 33% relative humidity for 120 h; 3 – dehydrated membranes.

## Conclusions

The ionic conducting membranes comprising di- and triblock copolymers of poly (acrylic acid) and poly(ethylene oxide) with varying PEO block lengths were successfully prepared, and their ionic conductivity properties were systematically investigated at room temperature. It was established that the highest conductivity values fall within the range of $4.2 \cdot 10^{-5}$ to $9.8 \cdot 10^{-5}$ S·cm-, depending on polymer architecture and environmental conditions.

The ionic conductivity of diblock copolymer membranes was further enhanced by doping with lithium hexafluorophosphate. Increasing the dopant content from 3 to 9 wt% resulted in a significant rise in conductivity from $4.49 \cdot 10^{-6}$ to $1.98 \cdot 10^{-5}$ S·cm-1 which was attributed to the increased concentration of mobile ions, plasticization of the polymer matrix, and improved salt dissociation facilitated by carboxylic acid groups.

The dielectric properties of MePEO-b-PAA membraine were also examined under different ambient humidity conditions (33%, 65%, 81%, and 98% relative humidity). It was demonstrated that high humidity levels (81% and 98%) are unsuitable for practical operation of these membranes, as excessive water uptake leads to deterioration of their mechanical and physicochemical properties. In contrast, moderate humidity enhances ionic conductivity without critically compromising membrane integrity.

These results highlight the importance of polymer architecture, salt doping, and environmental control in the design of PEO-based polymer electrolytes and provide useful guadelines for the development of ion-conducting membranes for electrochemical energy application.

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