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ION-CONDUCTING MEMBRANES COMPRISING POLY(ETHYLENE OXIDE) AND POLY(ACRYLIC ACID)

*Ion-conducting membranes based on di- and triblock copolymers of poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA), with varying PEO block lengths, were synthesised and their ionic conductivity at room temperature was investigated. The highest conductivity values for the studied membranes were found to range from $4.2 \cdot 10^{-5}$ — $9.8 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$, depending on the copolymer architecture and environmental conditions. The ionic conductivity of the diblock copolymer membranes was further enhanced by the addition of lithium hexafluorophosphate. Increasing the lithium hexafluorophosphate content from 3 to 9 wt.% was shown to lead to a significant increase in conductivity, from $4.49 \cdot 10^{-6}$ — $1.98 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ due to an increase in the concentration of mobile ions, the plasticisation of the polymer matrix and improved dissociation of the copolymer's carboxyl groups in a saline environment. Additionally, the dielectric properties of the MePEO-*b*-PAA membrane were examined at different ambient humidity levels (33%, 65%, 81% and 98% relative humidity). It was determined that high humidity levels (81% and 98%) are unsuitable for the practical operation of these membranes as excessive water absorption deteriorates their mechanical and physicochemical properties. Conversely, moderate humidity increases ionic conductivity without significantly compromising the membrane's integrity. These results highlight the importance of polymer architecture, salt content and environmental control in developing PEO-based polymer electrolytes, and provide useful guidance for designing ion-conducting membranes for use in fuel cells.*

Keywords: Solid polymer electrolytes, block copolymer, dielectric characteristics, ion conductivity, proton exchange membrane.

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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 high 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 exhibit relatively 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 strategy based on complete replacement of amide groups in polyacrylamide segments by carboxylic acid groups is explored. Accordingly, block copolymers composed of poly(ethylene oxide) and poly(acrylic acid) were selected as model systems for the preparation and investigation of ion-conducting membranes.

Experimental Part

Materials

Methyl ether polyethylene glycol (MePEG) with a number-average molecular weight $M_n = 5.3$ kDa (Fluka, Germany), diammonium hexanitratocerate

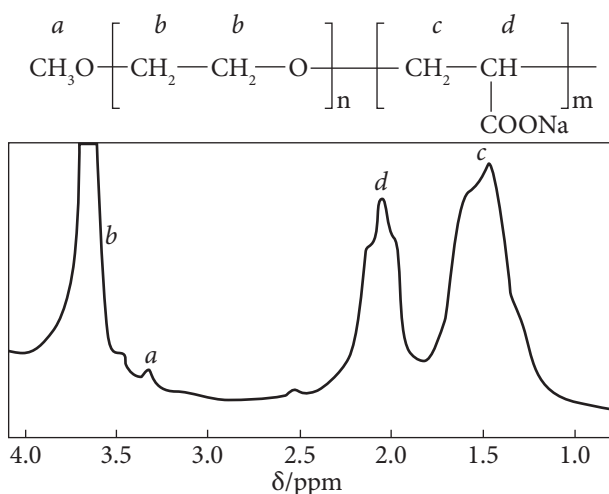


Fig. 1. ^1H NMR spectrum for DBC-PANa in D_2O

Table 1. Molecular parameters of the diblock and triblock copolymers

Copolymer	$M_{n\text{MePEO/PEO}}$, kDa	$M_{n\text{PANa}}$, kDa	$M_{n\text{PAA}}$, kDa	$M_{n\text{DBC/TBC}}^*$, kDa
DBC	5.3	23.1	17.6	22.9
TBC6	6	7.6	5.8	17.6
TBC35	35	36.9	28.3	91.6

$$^* M_{n\text{DBC}} = M_{n\text{MePEO}} + M_{n\text{PAA}}; M_{n\text{TBC}} = M_{n\text{PEO}} + 2 \cdot M_{n\text{PAA}}$$

(IV) (Aldrich, USA), and acrylic acid (Fluka, Germany) were used. Acrylic acid was distilled prior to use.

Methods

^1H NMR spectrum of copolymers was recorded with a 400 MHz Mercury-400 spectrometer from “Varian” (USA) at $T = 20^\circ\text{C}$ in D_2O .

The potentiometric titration was performed in an inert (argon) atmosphere at $T = 25 \pm 0.1^\circ\text{C}$ using a 1–160M ionomer (Belarus) calibrated with five standard buffer solutions.

Dielectric properties were measured in the frequency range of 10^2 – 10^5 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 ($\tan \delta$) and capacitance (C) were recorded over the working frequency range. The capacitance

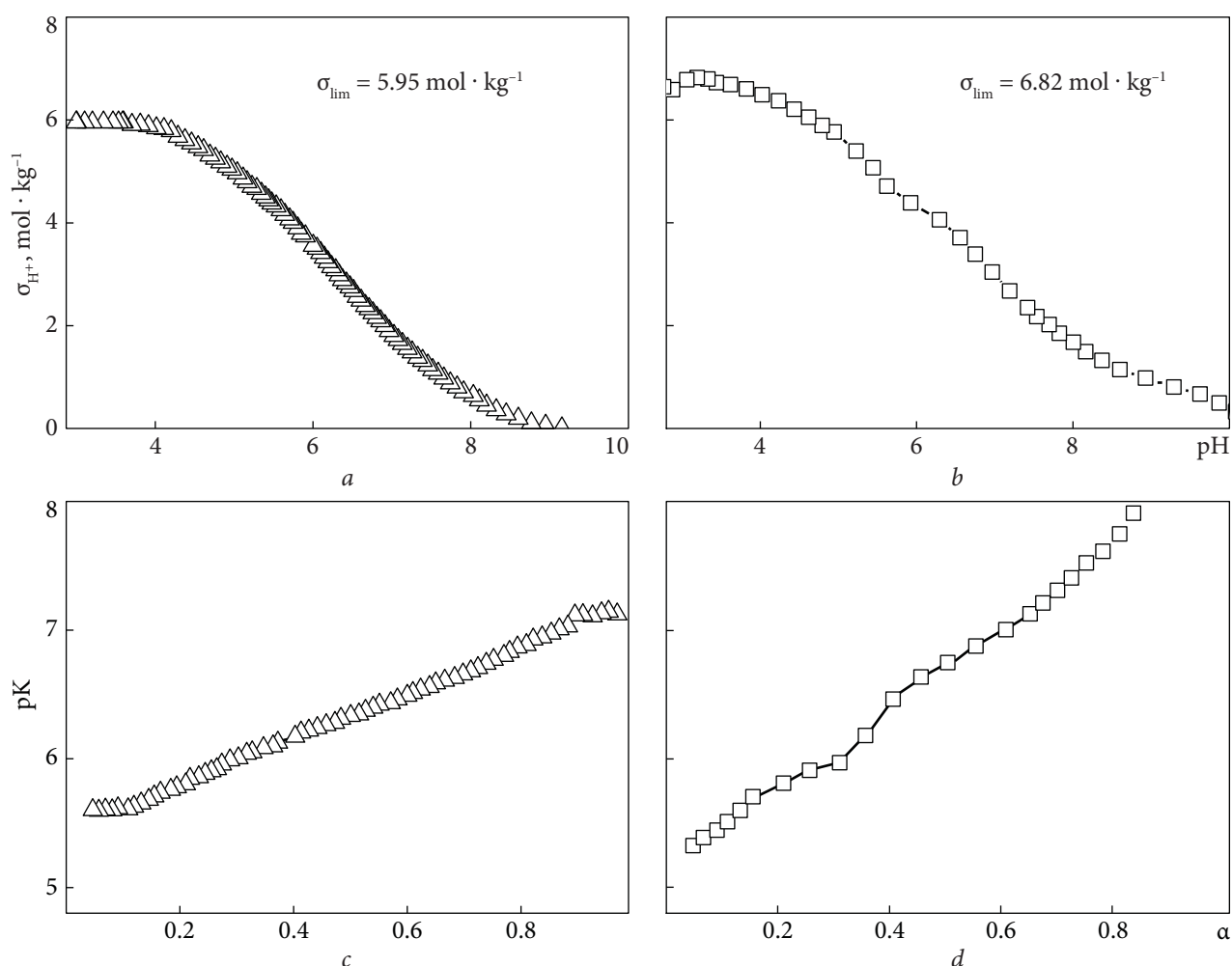


Fig. 2. The proton absorption curves (*a*, *b*) and the dependences of pK_a vs α (*c*, *d*) for DBC and TBC35 solutions. Solvent: water/ethanol (95/5v/v) mixture. $C_{\text{DBC/TBC}} = 1 \text{ kg} \cdot \text{m}^{-3}$, $T = 25^\circ \text{C}$

of the empty cell C_0 was calculated according to Equation 1:

$$C_0 = S\varepsilon_0/d, \quad (1)$$

where $\varepsilon_0 = 8.85 \cdot 10^{-14} \text{ F} \cdot \text{cm}^{-1}$ 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 $\tan \delta$, 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 1 kHz.

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 (IV) ions [9]. The DBC synthesis was carried out at a molar ratio $[\text{CeIV}]/[\text{MePEG}] = 1.1$ and a ratio of $[\text{CeIV}]/[\text{AA}] = 4.8 \cdot 10^{-3}$. The final product was obtained as the sodium salt (MePEO-*b*-PANa) and isolated from aqueous solution by freeze-drying. The chemical structure and molecular parameters of the DBC were characterized by ^1H NMR spectroscopy. ^1H NMR spectrum of DBC—PANa showed characteristic signals corresponding to the CH_3 — (*a*) and — CH_2 — (*b*) protons of the MePEO block at $\delta = 3.37$ and 3.66 ppm, respectively, as well as — CH_2 — (*c*) and $>\text{CH}$ — (*d*) protons of the PANa block at 1.44 and 2.05 ppm, respectively (Fig. 1). The number average molecular weight of the PANa block in DBC—PANa was

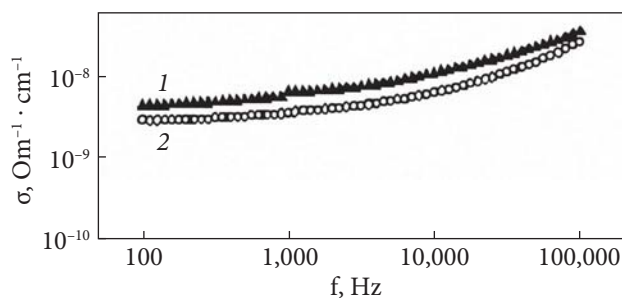


Fig. 3. Conductivity vs frequency for dehydrated membranes on the base of TBC35 — 1, and DBC — 2

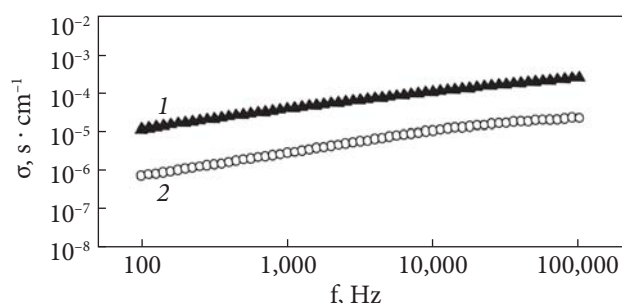


Fig. 4. Frequency dependence of the conductivity of membranes based on DBC — 1, and TBC35 — 2 under ambient humidity conditions

Table 2. Dielectric characteristics of dehydrated membranes based on DBC and TBC

Polymer	ϵ'	σ'
DBC	5.10	$6.47 \cdot 10^{-9}$
TBC35	6.93	$3.64 \cdot 10^{-9}$

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

Polymer	ϵ'	σ'
DBC	6.93	$5.51 \cdot 10^{-7}$
TBC35	1587.03	$4.19 \cdot 10^{-5}$

calculated according to the ratio of the integral intensities of corresponding proton signals as in the studies [10].

Synthesis of PAA-*b*-PEO-*b*-PAA triblock copolymers

PAA-*b*-PEO-*b*-PAA triblock copolymers (TBCs) with different lengths of the central PEO block were synthesized via radical block copolymeriza-

tion of acrylic acid with polyethylene glycol (PEG) having $M_n = 6$ kDa and 35 kDa. The synthesis was carried out according to previously reported procedures [9, 11], employing a redox initiation system. The ratios of reagents were equal to $[\text{CeIV}]/[\text{PEG}] = 2.2$ and $[\text{CeIV}]/[\text{AAc}] = 2.8 \cdot 10^{-2} - 4.0 \times 10^{-3}$. The chemical structure and molecular parameters of the obtained TBCs were determined by ^1H NMR spectroscopy as described above. In particular, the ^1H NMR spectrum of TBC35—PAA recorded in D_2O exhibits characteristic signals corresponding to the $-\text{CH}_2-$ protons of the PEO block and the $-\text{CH}_2-$ and $>\text{CH}-$ groups of the PAA blocks at $\delta = 3.60, 1.399$, and 1.987 ppm, respectively. The obtained molecular characteristics of DBC and TBCs are represented in Table 1.

Potentiometric titration measurements

The existence of the ionogenic blocks in the copolymer structures was additionally confirmed by potentiometric titration. The reverse potentiometric titration of the block copolymers in the Na form ($C = 1 \text{ kg} \cdot \text{m}^{-3}$) in deionized water and water/ethanol solutions (95/5 v/v) was performed with 0.2 N HCl to pH ~ 2 . Potentiometric titrations of a copolymer-free deionized water and a water/ethanol mixture (95/5 v/v) were carried out under the same experimental conditions. The proton absorption curves $\sigma_{\text{H}^+} = f(\text{pH})$ and the dependences of the negative logarithm of the effective dissociation constant (pK) of the copolymer carboxylic groups on the degree of dissociation (α) of these groups were calculated using the well-known methodology [12] according to Equation 2:

$$\sigma_{\text{H}^+} = \frac{C_{\text{HCl}}}{g} \cdot (1 - 10^{\text{pH}_0 - \text{pH}}),$$

$$\text{pK}_a = \text{pH} - \lg\left(\frac{\alpha}{1 - \alpha}\right) \quad (2)$$

Here σ_{H^+} is the value of proton absorption ($\text{mol} \cdot \text{kg}^{-1}$), C_{HCl} is the concentration of HCl ($\text{mol} \cdot \text{m}^{-3}$), g is the mass (kg) of the copolymer in m^3 of solution, pH and pH_0 are the negative logarithms of the concentration of hydrogen ions in the copolymer solution and pure water, respectively.

The proton absorption curves for DBC and TBC35 solutions are shown in Fig. 2 *a, b*. According to these curves, the process of protonation of carboxyl groups in macromolecules of block copolymers

was completed at pH ~ 3.0 . The limit absorption values (σ_{lim}) at pH ~ 3 correspond to the total concentration of $-\text{COONa}$ groups in the copolymer. The curves $\text{pK}_a = f(\alpha)$, which were calculated from these data, demonstrate a gradual increase in pK_a versus α that is typical for weak polyacids (Fig. 2 c, d).

To characterize the acidic properties of the $-\text{COOH}$ groups in the DBC and TBC structures, we extrapolated the initial linear parts of the curves $\text{pK}_a = f(\alpha)$ to $\alpha = 0$ and found the intrinsic pK_0 values, which were 5.4 for DBC and TBC6 as well as 5.2 for TBC35 samples. These values turned out to be close to each other, but differed significantly from the analogous parameter for pure PAA in aqueous solution ($\text{pK}_0 = 4.5$) [13].

Water uptake measurements of MePEO-b-PAA

To investigate water absorption, MePEO-b-PAA (DBC) films were thoroughly dried in a desiccator over freshly calcined CaCl_2 until constant weight was reached. The samples were then equilibrated for five days in atmosphere with different relative humidities at 20 °C. The relative humidity was controlled using saturated salt solutions of MgCl_2 (33%), NH_4NO_3 (65%), $(\text{NH}_4)_2\text{SO}_4$ (81%), and $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ (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 3:

$$W_{\text{H}_2\text{O}} = \frac{W_{\text{dry}} - W_{\text{wet}}}{W_{\text{dry}}} \cdot 100\% \quad (3)$$

where W_{wet} and W_{dry} are the masses of the wet and dry polymer samples, respectively.

Results and Discussion

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 measurements. Therefore, only DBC and TBC with a 35 kDa central PEO block (TBC35) were further investigated.

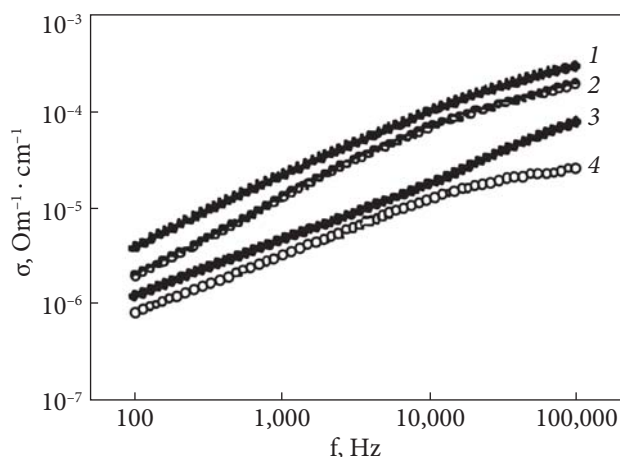


Fig. 5. Frequency dependence of the conductivity of DBC (1), and its compositions with LiPF_6 at ratio $[\text{DBC}]/[\text{LiPF}_6]$: 2 — 0.5; 3 — 0.09; 4 — 0.06

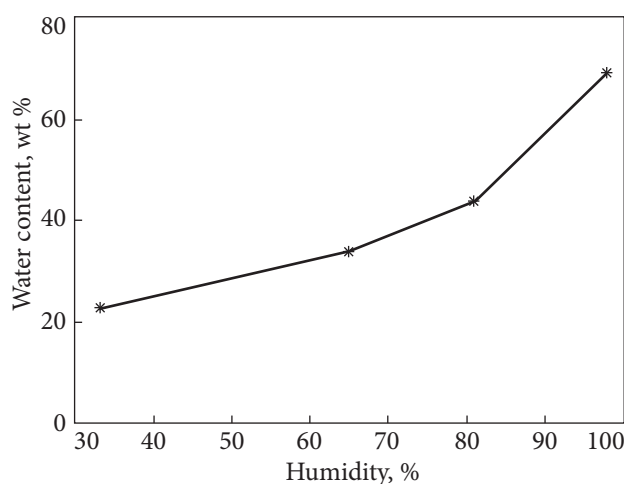


Fig. 6. Dependence of water uptake on relative humidity for DBC-based membranes

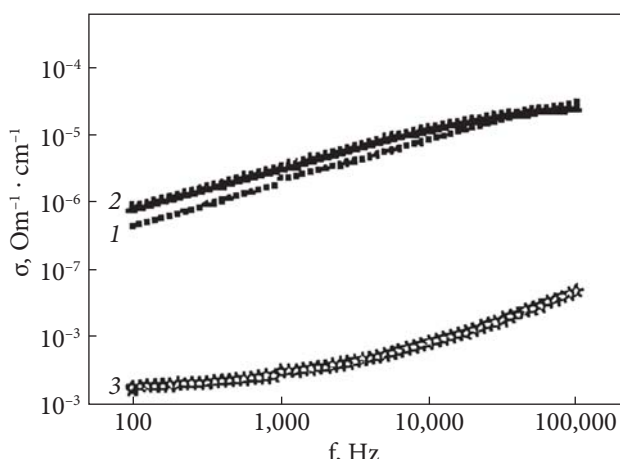


Fig. 7. Frequency dependence of conductivity for humidified and dried DBC membranes: 1 — stored in air for 48 h; 2 — conditioned at 33% relative humidity for 120 h; 3 — dehydrated membranes

Table 4. Dielectric characteristics of DBC membranes doped with lithium hexafluorophosphate

Composition	[PEO]/[LiPF ₆], base-mol · mol ⁻¹	[DBC]/[LiPF ₆], base-mol · mol ⁻¹	ϵ	σ'
DBC	—	—	15178.15	$3.07 \cdot 10^{-6}$
DBC + LiPF ₆	0.15	0.3	9389.67	$4.48 \cdot 10^{-6}$
DBC + LiPF ₆	0.09	0.18	33153.34	$1.17 \cdot 10^{-5}$
DBC + LiPF ₆	0.06	0.12	47538.14	$1.97 \cdot 10^{-5}$

Table 5. Water adsorption by DBC membranes

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

Even thoroughly dried exhibited measurable ionic conductivity, indicating intrinsic charge transport enabled by polar polymer segments (Table 2, Fig. 3). 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 residual 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 —CH₂—CH₂—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 [14].

Effect of ambient humidity on ionic conductivity

An increase 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, Fig. 4). 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 plas-

ticization, which explains their superior performance compared to diblock copolymer-based membranes under identical 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 (LiPF_6) was investigated (Table 4, Fig. 5).

Incorporating LiPF_6 markedly enhanced ionic conductivity across the entire frequency range studied, demonstrating the effectiveness of salt doping in improving charge transport in MePEO-*b*-PAA-based polymer electrolytes. As shown in Fig. 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 $3.07 \cdot 10^{-6}$ to $1.97 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$. 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 $-\text{COOH}$ 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.

Characterisation of water absorption in MePEO-*b*-PAA membranes

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 oxy-

ethylene 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, Fig. 6).

Presumably, the water already present in the polymer acts as a plasticizer, i.e., lowers the polymer's glass transition temperature 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 (Fig. 7).

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 ranged from $4.2 \cdot 10^{-5}$ to $9.8 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$, 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 $1.98 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$, 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 membrane 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 elec-

trolites and provide useful guidelines for the development of ion-conducting membranes for electrochemical energy applications.

Authors Contributions

This article was written with the contribution of all authors. All authors approved the final version of the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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ЩО МІСТЯТЬ ПОЛІ(ЕТИЛЕНОКСИД)
І ПОЛІ(АКРИЛОВУ КИСЛОТУ)

Отримано іон-провідні мембрани на основі ди- та триблок-кополімерів полі(етиленоксиду) (ПЕО) та полі(акрилової кислоти) (ПАК) з різною довжиною блоків ПЕО та досліджено їх іонну провідність за кімнатної температури. Встановлено, що найвищі значення електропровідності досліджених мембран знаходяться в діапазоні від $4,2 \cdot 10^{-5}$ до $9,8 \cdot 10^{-5} \text{ С} \cdot \text{см}^{-1}$ залежно від архітектури кополімеру та умов навколишнього середовища. Іонна провідність диблок-кополімерних мембран була додатково посилена додаванням гексафторфосфату літію. Показано, що збільшення вмісту гексафторфосфату літію з 3 до 9 мас.% призводить до значного підвищення провідності з $4,49 \cdot 10^{-6}$ до $1,98 \cdot 10^{-5} \text{ С} \cdot \text{см}^{-1}$, що пояснюється підвищенням концентрації рухомих іонів, пластифікацією полімерної матриці та покращенням дисоціації карбоксильних груп кополімеру у сольовому середовищі. Крім того, діелектричні властивості мембрани MePEO-b-PAK було досліджено за різних умов вологості навколишнього середовища (відносна вологість 33, 65, 81 і 98 %). Визначено, що високі рівні вологості (81 і 98 %) непридатні для практичної експлуатації цих мембран, оскільки надмірне водопоглинання призводить до погіршення їх механічних і фізико-хімічних властивостей. Навпаки, помірна вологість підвищує іонну провідність без серйозного порушення цілісності мембрани. Отримані результати підкреслюють важливість полімерної архітектури, сольового вмісту та контролю навколишнього середовища при розробленні полімерних електролітів на основі ПЕО та корисні для розроблення іон-провідних мембран при їх застосуванні в паливних елементах.

Ключові слова: тверді полімерні електроліти, блок-кополімер, діелектричні характеристики, іонна провідність, протон-обмінна мембрана.