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## **PROTIC POLYMERIC IONIC LIQUID OF A BLOCK OLIGOMERIC STRUCTURE WITH IONIC BONDS IN THE MAIN CHAIN**

*A method for the synthesis of protic polymeric ionic liquid (PIL) of a block oligomeric structure with ionic bonds in the main chain, which turns into a liquid state at temperatures below 50 °C, was developed. Ionic bonding was used to form a polymer chain. It was formed as a result of neutralization reaction between oligomers of telechelic structure with terminal acidic and basic groups. A new linear oligomer containing basic tertiary nitrogen atoms at the ends of the oligoether chain (PEO-2NEt<sub>2</sub>) was obtained by reaction of  $\alpha,\omega$ -diglycidyl ether of polyethylene glycol MW 1000 with N,N-diethylamine. A linear oligomer with terminal sulfonic acid groups (PEO-2SO<sub>3</sub>H), which is a product of the interaction of polyethylene glycol (MW 1000) with the cyclic anhydride of 2-sulfobenzoic acid, was used as an acidic linear oligomer. The synthesis of PIL [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> was carried out by neutralization of basic oligomer PEO-2NEt<sub>2</sub> with the acidic oligomer PEO-2SO<sub>3</sub>H in their molar ratio of 1:1. The structure of the obtained compound was characterized by the methods of FTIR and <sup>1</sup>H NMR spectroscopy. According to the DSC data, the synthesized PIL contains an amorphous phase with a glass transition temperature of -49.7 °C and a crystalline phase with a melting temperature of 34.5 °C. The decomposition onset temperature corresponding to 5% weight loss is 271 °C according to the TGA. The ionic conductivity of PIL studied by dielectric relaxation spectroscopy under anhydrous conditions in the range from 40 °C to 100 °C increases with increase in temperature and reaches 2.7·10<sup>-4</sup> S/cm. The resulting compound is promising as a proton-conducting medium for various electrochemical devices.*

**Keywords:** polymeric ionic liquids, acid-base interaction, proton exchange media, proton conductivity.

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## ПРОТОННА ПОЛІМЕРНА ІОННА РІДИНА БЛОКОЛІГОМЕРНОЇ БУДОВИ З ІОННИМИ ЗВ'ЯЗКАМИ В ГОЛОВНОМУ ЛАНЦЮЗІ

Розроблено спосіб синтезу протонної полімерної іонної рідини (ППР) блоколігомерної будови з іонними зв'язками в головному ланцюзі, яка переходить у рідкий стан за температури нижче 50 °С. Для формування полімерного ланцюга використовували іонне зв'язування, яке реалізувалося в процесі нейтралізації між олігомерами телехелевої будови з кінцевими групами кислотної та основної природи. Новий лінійний олігомер основного типу, який містить на кінцях олігоетерного ланцюга третинні атоми азоту, отримували реакцією  $\alpha,\omega$ -дигліцидилового етеру олігоетиленоксиду ММ 1000 з N,N-діетиламіном (PEO-2NEt<sub>2</sub>). Як лінійний олігомер з кінцевими сульфокислотними групами (PEO-2SO<sub>3</sub>H) використовували продукт взаємодії олігооксіетиленгліколю ММ 1000 з циклічним ангідридом 2-сульфобензойної кислоти. Синтез ППР здійснювали повною нейтралізацією основних центрів олігомеру PEO-2NEt<sub>2</sub> кислотним олігомером PEO-2SO<sub>3</sub>H за мольного співвідношення 1:1. Будову отриманої сполуки охарактеризовано методами ІЧ- та <sup>1</sup>H ЯМР-спектроскопії. Згідно з даними ДСК, синтезована ППР містить аморфну фазу зі значенням температури склування -49,7 °С і кристалічну фазу зі значенням температури плавлення 34,5 °С. Встановлена методом ТГА температура початку розкладання, яка відповідає 5 % втрати маси, становить 271 °С. Провідність ППР, досліджена методом діелектричної релаксаційної спектроскопії за безводних умов у діапазоні від 40 °С до 100 °С, зростає з підвищенням температури і досягає 2,7·10<sup>-4</sup> См/см. Отримана сполука перспективна як протонпровідне середовище для різних електрохімічних пристроїв.

**Ключові слова:** полімерні іонні рідини, кислотно-основна взаємодія, протоннообмінні середовища, протонна провідність.

## Introduction

Polymer ionic liquids (PILs), which combine the properties of polymers and ionic liquids, have attracted considerable interest in many applications [1, 2]. They are used to develop nanofibers, membranes for gas capture, transport, and storage, biosensors, antimicrobial coatings, and catalysts [1]. One of the promising areas for the use of PILs is the development of electrolytes for lithium batteries, supercapacitors, dye-sensitized solar cells, and fuel cells [2]. Of particular interest are proton PILs, which are used as a proton exchange media for fuel cells that can operate in the temperature range of 100-200 °C in the absence of moisture [3–5]. They are mainly prepared by the polymerization reaction of low molecular weight protic ionic liquids. In this case, the ionic groups are located in the side branches of the main polymer chain of the synthesized PILs. However, it should be noted that the proton conductivity of the resulting PILs is signi-

ficantly reduced compared to the initial monomers [5] due to the transition to a solid aggregate state and the retarded movement of charge carriers.

Recently, a new direction of research related to the synthesis of PILs, which are characterized by low T<sub>g</sub> values and a wide temperature range of existence in the liquid aggregate state has emerged [6–9]. To obtain such compounds with ionic groups in side branches, the chain polymerization of monomers containing ionic groups with bulky counterions including oligoester fragments is used [6, 7]. Another way is the block copolymerization of two types of monomers, especially one of them contains ionic groups, and the other oligoether fragments [8, 9]. The significant size of counterions and the asymmetry of the structure of the obtained PILs weaken the ability of opposite charges to attract and minimize intermolecular interactions, which leads to a decrease in T<sub>g</sub> values [6]. The resulting compounds are considered not only as ion-conducting media, but also as solvents for

substance dissolution and separation, and as reaction medium for catalysis and colloidal synthesis [6].

A significantly different approach to obtaining PILs with a wide temperature interval of existence in a liquid aggregate state is proposed by us in works [10, 11]. It consists in the synthesis of PILs of block oligomeric structure using ionic bonds to build a polymer chain. For this purpose, a neutralization reaction between telechelic oligomers with acidic and basic end groups was used. It should be noted that polymers containing covalently bonded cations in the main polymer chain are currently known in the literature [12]. They are also known as polyiones [13]. In contrast to polyiones, the structural element of the polymer chains in the PILs developed by us is ionic groups [10, 11]. Due to the formation of these groups, the oligomeric blocks are linked to form a polymer chain. Functionalized poly (ethylene oxide) containing two types of basic centers in the composition of the end fragments, namely secondary amino groups and nitrogen atoms of imidazole heterocycles, was used as an oligomer with basic properties [14]. The protonation of these basic centers leads to the formation of two types of ionic groups. By partial (50%) or complete (100%) neutralization of the basic centers of this compound with an acid-type telechelic oligomer [15], polymers of block oligomeric ion-extended [10] or ion-crosslinked [11] structure have been obtained. An increase in the content of ionic groups with an increase in the degree of neutralization of the basic centers leads to an increase in the electrical conductivity in anhydrous conditions, which reaches the value of  $3.1 \cdot 10^{-4}$  S/cm at 100 °C. At the same time, the migration of protons between different types of basic centers during their partial neutralization allows to increase the conductivity of block-oligomeric ion-extended PIL, similar to what was previously found for low-molecular ILs [16] and oligomeric ionic liquids [14, 17] with two types of ionic groups. It should be noted that for low-molecular protic ILs with two types of ionic groups, the presence of such migration was confirmed by comparing their conductivity with the conductivity of ILs with one type of ionic groups [16]. A protic PIL with one type of ionic groups in the main chain of polymer can be obtained by using of a telechelic oligomer with one type of basic centers at the chain ends as a starting compound for neutraliza-

tion by the above-mentioned acid-type telechelic oligomer. The purpose of this work is to develop a method for synthesizing protic PILs of a block oligomeric structure with ionic bonds in the main chain containing single type ionic groups and to establish the features of their structure and proton conductivity in comparison with analogous PILs containing ionic groups of two types obtained by us previously.

## Experimental

**Materials.** Diethylamine (Sigma-Aldrich,  $\geq 99.5\%$ ), epichlorohydrin (Sigma-Aldrich,  $\geq 99.0\%$ ), 2-sulfobenzoic anhydride (Sigma-Aldrich,  $\geq 96.0\%$ ) were used without further purification. Polyethylene glycol with MW 1000 (PEO-1000) (Sigma-Aldrich, 1000, for synthesis) was dried under reduced pressure. Ethanol was distilled before use.

**Synthesis of PEO-2Ep.** PEO-2Ep was prepared by the reaction of PEO-1000 and epichlorohydrin according to the method described in [18].

**Synthesis of PEO-2NEt<sub>2</sub>.** 0.46 g (0.00626 mol) of diethylamine was added to a solution of 4.03 g (0.00313 mol) PEO-2Ep in 6 ml of ethanol. The reaction was held at 50 °C and stirred until the absorption band of epoxy groups in the FTIR spectrum disappeared. The solvent was removed under reduced pressure. The obtained PEO-2NEt<sub>2</sub> was dried in a vacuum at 60 °C. Yield was 4.31 g (96 %). The product was a viscous colorless liquid, soluble in DMF, DMSO, acetone, ethanol, and water. Content of tertiary amino groups: calculated 1.95 %, found 1.92 %.

FTIR:  $\nu$  OH (3074 – 3699 cm<sup>-1</sup>),  $\nu$  C-H bonds of CH, CH<sub>2</sub> and CH<sub>3</sub> groups (2871 cm<sup>-1</sup>),  $\delta$  C-H bonds of CH, CH<sub>2</sub> and CH<sub>3</sub> groups (1460 cm<sup>-1</sup>),  $\nu$  C-O-C (1109 cm<sup>-1</sup>).

**Synthesis of PEO-2SO<sub>3</sub>H.** PEO-2SO<sub>3</sub>H was synthesized by the reaction of PEO-1000 with 2-sulfobenzoic anhydride in a molar ratio of 1:2 according to the method described in [15].

**Synthesis of [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup>.** A solution of 1.59 g (0.00111 mol) PEO-2SO<sub>3</sub>H in 3 ml of ethanol was added to a solution of 1.62 g (0.00111 mol) PEO-2NEt<sub>2</sub> in 3 ml of ethanol. The synthesis was carried out for 6 hours at room temperature. The solvent was partially removed under reduced pressure. The product was then precipitated and washed twice with ethyl acetate. The obtained [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> was

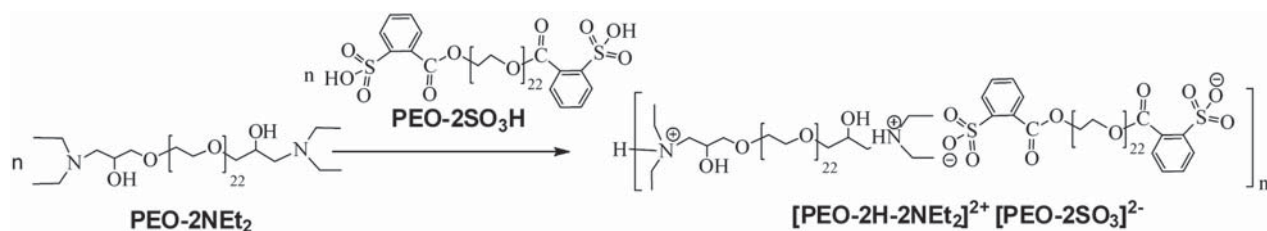


Fig. 1. Scheme for synthesis of the protic PIL of block oligomer structure with ionic bonds in the main chain

dried under vacuum at 60 °C. The product was a clear, light brown viscous liquid, soluble in DMF, DMSO, acetone, ethanol, and water.

FTIR:  $\nu$  OH,  $\nu$  NH<sup>+</sup> (3105 – 3703 cm<sup>-1</sup>),  $\nu$  ar C-H (3060 cm<sup>-1</sup>),  $\nu$  C-H bonds of CH, CH<sub>2</sub>, CH<sub>3</sub> (2871 cm<sup>-1</sup>),  $\nu$  C=O (1730 cm<sup>-1</sup>),  $\delta$  NH<sup>+</sup> (1645 cm<sup>-1</sup>),  $\nu$  ar C-C (1593 cm<sup>-1</sup>),  $\delta$  C-H bonds of CH<sub>2</sub>, (1460 cm<sup>-1</sup>),  $\nu$  C-O-C (1108 cm<sup>-1</sup>),  $\nu_{\text{sym}}$  SO<sub>2</sub> (1020 cm<sup>-1</sup>),  $\delta_{\text{oop}}$  ar C-H (761 cm<sup>-1</sup>).

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  1.18 (CH<sub>3</sub>-CH<sub>2</sub>-N<sup>+</sup>, 12H), 3.01-3.14 (CH<sub>3</sub>-CH<sub>2</sub>-N<sup>+</sup>, NH<sup>+</sup>-CH<sub>2</sub>-CH(OH)-, 12H), 3.42, 3.50 (-O-CH<sub>2</sub>-CH(OH)-, 4H), -(O-CH<sub>2</sub>-CH<sub>2</sub>)<sub>n</sub>-, 3.68 (-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-Ar-SO<sub>3</sub>-, 4H), 3.99 (-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-, 2H), 4.23 (-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-Ar-SO<sub>3</sub>-, 4H), 7.26, 7.36, 7.43, 7.71 (CH(Ar), 8H), 8.86 (NH<sup>+</sup>, 2H) ppm

**Characterization.** FTIR spectra were recorded using a TENSOR 37 FT-IR spectrophotometer operated in the 6004000 cm<sup>-1</sup> range. <sup>1</sup>H NMR spectra were recorded with a Varian VXR-400 MHz spectrometer using DMSO-d<sub>6</sub> (Cambridge Isotope Laboratories, Inc.) as a solvent. The temperature dependence of the heat flow of the obtained compounds was studied using Q2000 (TA Instruments, USA) in the temperature range of -80 to 100 °C at a heating rate of 20 °C/min under a nitrogen atmosphere. The heating and cooling cycle was repeated twice and the data obtained during the second cycle were used to characterize the structure of the compound. The onset temperature of thermal oxidative degradation, which was taken as the temperature of 5% weight loss of the sample, was determined using Q50 (TA Instruments) in the temperature range of 20 to 700 °C at a heating rate of 20 °C/min in air. The ionic conductivity ( $\sigma_{\text{dc}}$ ) was measured by dielectric relaxation spectroscopy using a dielectric spectrometer based on a P5083 AC bridge scheme (0.1–100 kHz) and a two-electrode stainless steel cell (measurement accuracy of 0.03%). Samples were dried at 100 °C under a nitrogen flow for 30 min prior to measu-

rements. Measurements were performed in a dry nitrogen atmosphere at a temperature of 40 to 100 °C.

## Results and Discussion

**Synthesis and Characterizations of PIL.** In order to obtain PIL of a block oligomer structure with ionic bonds in the main chain and one type of ionic groups, the telechelic oligomer containing functional fragments with tertiary amino groups (PEO-2NEt<sub>2</sub>) at the ends of ethylene oxide chains was used as the initial oligomer with basic properties (Fig. 1). It was synthesized by the reaction of  $\alpha,\omega$ -diglycidyl ether of polyethylene glycol (MW 1000) (PEO-1000) with diethylamine in a molar ratio of 1:2. As acidic telechelic oligomer, a product of the interaction of polyethylene glycol (MW 1000) with the cyclic anhydride of 2-sulfobenzonic acid with terminal sulfonic acid groups (PEO-2SO<sub>3</sub>H) was used, as in our previous works [10, 11]. Neutralization of basic oligomer PEO-2NEt<sub>2</sub>

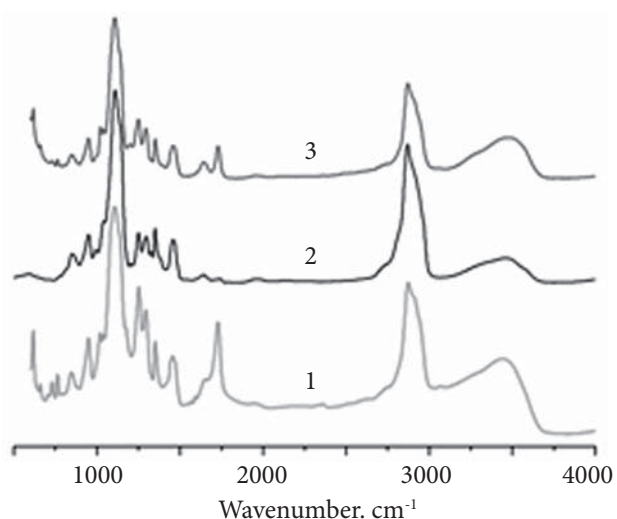


Fig. 2. FTIR spectra: PEO-2SO<sub>3</sub>H (1), PEO-2NEt<sub>2</sub> (2) and PIL [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (3)

with acidic oligomer PEO-2SO<sub>3</sub>H was performed at a molar ratio of 1:1 (Fig. 1).

According to the simulation data from ACD/Laboratories [19], the pK<sub>a</sub> value of the conjugate acid for the tertiary amino group of PEO-2NEt<sub>2</sub> is 9.96, and the pK<sub>a</sub> value of the sulfonic acid group of the PEO-2SO<sub>3</sub>H oligomer is -0.74. The value of ΔpK<sub>a</sub>, which is equal to the difference between the pK<sub>a</sub> values of the conjugate acid for the base and the pK<sub>a</sub> of the acid [20], was 10.70. Since, according to [20], proton transfer from acid to base is nearly complete in systems with ΔpK<sub>a</sub> > 8, it can be assumed that the tertiary amino groups of the PEO-2NEt<sub>2</sub> are completely protonated during its neutralization with PEO-2SO<sub>3</sub>H. The synthesized [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> was a clear, light brown viscous liquid at ambient temperature, soluble in DMF, DMSO, acetone, ethanol, and water.

The structure of the initial telechelic oligomers and the protic PIL based on them were studied by FTIR (Fig. 2) and <sup>1</sup>H NMR (Fig. 3) spectroscopy. In the FTIR spectrum of PEO-2SO<sub>3</sub>H (curve 1 in Fig. 2) [15], absorption bands of stretching (2873 cm<sup>-1</sup>) and deformation (1452 cm<sup>-1</sup>) vibrations of C-H bonds of CH<sub>2</sub> groups, as well as stretching vibrations of C-O-C bonds (1107 cm<sup>-1</sup>) of ethylene oxide fragments are observed. Absorption bands of stretching vibrations of C=O bonds of ester groups (1726 cm<sup>-1</sup>), C-H bonds of aromatic rings (3072 cm<sup>-1</sup>), out-of-plane deformation vibrations of C-H bonds of aromatic rings (ar C-H δ<sub>oop</sub>) with substituents (763 cm<sup>-1</sup>), symmetric and asymmetric stretching vibrations of SO<sub>2</sub> groups of sulfonate anion (maximums at 1020 cm<sup>-1</sup> and 1174 cm<sup>-1</sup>), and stretching vibrations of O-H bonds of sulfonic acid groups (a broad absorption band in the range of 3681–3135 cm<sup>-1</sup>) characterize the structure of terminal fragments of PEO-2SO<sub>3</sub>H.

In the FTIR spectrum of the oligomer PEO-2NEt<sub>2</sub> (curve 2 in Fig. 2), absorption bands of stretching vibrations of C-H bonds of CH<sub>2</sub> groups (2871 cm<sup>-1</sup>), deformation vibrations of these groups (1460 cm<sup>-1</sup>) and stretching vibrations of C-O-C bonds (at 1109 cm<sup>-1</sup>) in the composition of oligoether fragments are observed, as well as absorption bands of stretching vibrations of O-H bonds of secondary hydroxyl groups (in the range of 3699–3074 cm<sup>-1</sup>) of terminal fragments [21].

Neutralization of the basic centers of PEO-2NEt<sub>2</sub> by oligomer PEO-2SO<sub>3</sub>H leads to the appearance of absorption bands of stretching vibrations

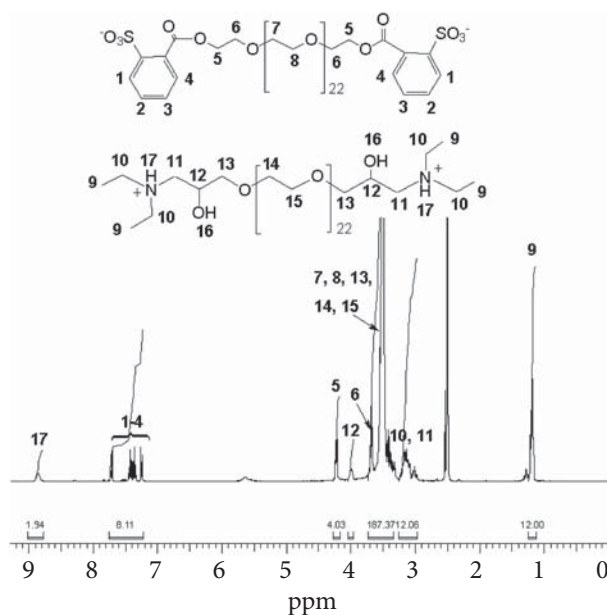
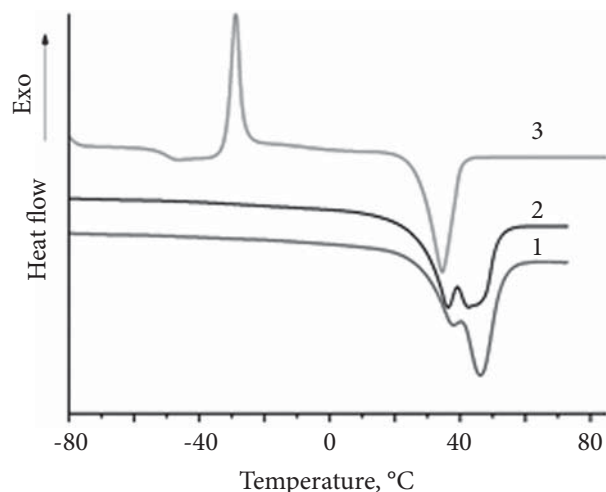


Fig. 3. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) spectrum of [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup>

of C=O bonds of ester groups (1730 cm<sup>-1</sup>), C-H bonds of aromatic rings (3060 cm<sup>-1</sup>), out-of-plane deformation vibrations of C-H bonds of aromatic rings (ar C-H δ<sub>oop</sub>) with substituents (761 cm<sup>-1</sup>) in the spectrum of the compound [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (curve 3 in Fig. 2). The positions of these bands are close to those in the spectrum of PEO-2SO<sub>3</sub>H (curve 1 in Fig. 2). The absorption band at 1020 cm<sup>-1</sup> corresponds to symmetric stretching vibrations of SO<sub>2</sub> groups of sulfonate anion, while the absorption band of stretching vibrations of N<sup>+</sup>-H bonds of protonated tertiary amino groups overlaps with the absorption band of valence vibrations of O-H bonds of secondary hydroxyl groups.

In the <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) spectrum of the compound [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (Fig. 3), similar to the spectra of the compounds [PEO-2H-2Im]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> [10] and [PEO-4H-2Im]<sup>4+</sup> 2[PEO-2SO<sub>3</sub>]<sup>2-</sup> [11], there is an intense signal of protons of ethylene oxide fragments (3.50 ppm, -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>O-).

Signals of protons of methylene groups at α-(-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-ArSO<sub>3</sub>-) and β-(-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-ArSO<sub>3</sub>-) positions to the ester bonds of PEO-2SO<sub>3</sub>H fragments are observed at 4.23 ppm and 3.68 ppm, respectively. The signals of protons of benzene rings (CH(Ar)) of the PEO-2SO<sub>3</sub>H fragment are at 7.26 ppm, 7.36 ppm, 7.43 ppm, and 7.71 ppm.

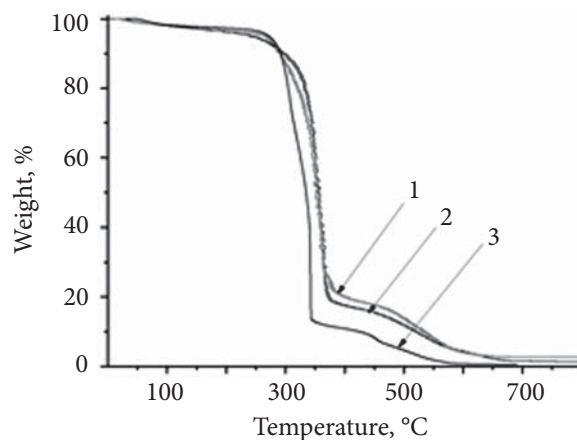


**Fig. 4.** Temperature dependence of the heat flow of block-oligomeric PILs [PEO-2H-2Im]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (1), [PEO-4H-2Im]<sup>4+</sup> 2[PEO-2SO<sub>3</sub>]<sup>2-</sup> (2), [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (3)

The presence of PEO-2NEt<sub>2</sub> fragments in the composition of PIL is evidenced by the signals of protons of methyl groups in the β-position to ammonium ions at 1.18 ppm (CH<sub>3</sub>-CH<sub>2</sub>-NH<sup>+</sup>), methylene groups in α-position to ammonium ions (NH<sup>+</sup>-CH<sub>2</sub>-CH(OH)-, CH<sub>3</sub>-CH<sub>2</sub>-N<sup>+</sup>) in the range of 3.01-3.14 ppm, and CH groups in α-position to secondary hydroxyl groups (-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-) at 3.99 ppm. The spectrum of [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> also shows a signal appears at 8.85 ppm corresponding to protons involved in the protonation of tertiary amino groups appears.

**Thermal Properties.** The currently known protic [6] and aprotic [7, 8] room temperature PILs contain ethylene oxide fragments and ionic groups in side chains. The ethylene oxide fragments are either part of the counterions of anionic [6] or cationic [7] PILs or are side branches of block copolymers [8]. The latter were obtained by copolymerization of a methacrylate-type monomer containing ethylene oxide fragments (*n* = 8–9) and a low molecular weight ionic liquid with double bonds [8]. Such PILs are characterized by an amorphous structure and low T<sub>g</sub> values of the amorphous phase, caused by a decrease in intermolecular interactions in the system due to the introduction of bulky fragments [6].

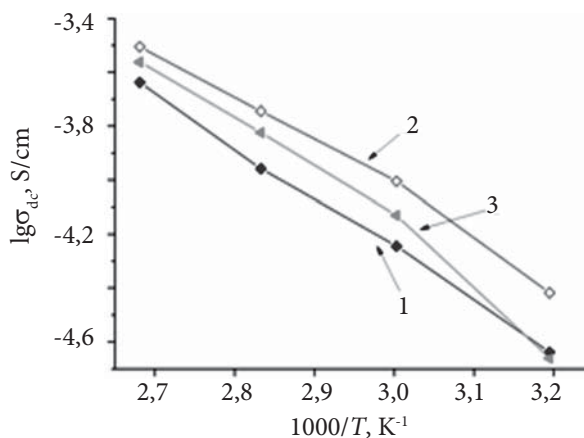
A different behavior is characteristic for the PILs of block oligomer structure described by us in previous works [10, 11]. Both ion-extended [PEO-2H-2Im]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> [10] and ion-crosslinked



**Fig. 5.** Temperature dependence of weight loss of block-oligomeric PILs [PEO-2H-2Im]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (1), [PEO-4H-2Im]<sup>4+</sup> 2[PEO-2SO<sub>3</sub>]<sup>2-</sup> (2), [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (3)

[PEO-4H-2Im]<sup>4+</sup> 2[PEO-2SO<sub>3</sub>]<sup>2-</sup> [11] block oligomeric PILs are characterized by the absence of glass transition and the presence of two types of crystalline formations formed by poly (ethylene oxide) units with melting points ranging from 36.3 to 46.2 °C (Fig. 4).

The introduction of one type of ionic group into the protic block oligomeric PIL [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> obtained in this work, according to the DSC data, causes significant changes in the structure compared to the PIL with two types of ionic groups (Fig. 4). Thus, a type of crystalline phase with a T<sub>m</sub> value of 34.5 °C (Fig. 4) is formed in the synthesized PIL, while another type of crystalline phase charac-



**Fig. 6.** Temperature dependence of the conductivity of block-oligomeric PILs [PEO-2H-2Im]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (1), [PEO-4H-2Im]<sup>4+</sup> 2[PEO-2SO<sub>3</sub>]<sup>2-</sup> (2) and [PEO-2H-2NEt<sub>2</sub>]<sup>2+</sup> [PEO-2SO<sub>3</sub>]<sup>2-</sup> (3)

teristic of the PILs with two types of ionic groups disappears. In addition, an amorphous phase with a glass transition temperature of  $-49.7\text{ }^{\circ}\text{C}$  appears in the synthesized PIL. It is probably formed by poly (ethylene oxide) units that have lost their ability to crystallize. Such structural changes may be associated with a decrease in the intensity of intermolecular interactions during the transition from PILs with two types of ionic groups to PILs with one type of ionic group. The content of ionic groups is probably not a determining factor in this case, since, on the contrary, it is slightly higher for the block oligomeric PIL with one type of ionic groups  $[\text{PEO-2H-2NEt}_2]^{2+} [\text{PEO-2SO}_3]^{2-}$  than for ion-extended block oligomeric PIL with two types of ionic groups (0.69 meq/g and 0.65 meq/g, respectively). For ion-crosslinked PIL  $[\text{PEO-4H-2Im}]^{4+} 2[\text{PEO-2SO}_3]^{2-}$ , the content of ionic groups is higher and amounts to 0.88 meq/g.

As follows from the analysis of the TGA curves (Fig. 5), the  $T_d 5\%$  value of the resulting PILs is in the temperature range from 242 to 271  $^{\circ}\text{C}$  and increases slightly when moving from PILs with two types of ionic groups to PILs with one type of ionic group.

**Ionic Conductivity.** The conductivity ( $\sigma_{dc}$ ) of the protic block oligomeric PIL with one type of ionic groups in the main polymer chain obtained in this work was studied under anhydrous conditions at a temperature from 40 to 100  $^{\circ}\text{C}$  (Fig. 6). It was found that the  $\sigma_{dc}$  values of this compound increase with increasing temperature from  $2.2 \cdot 10^{-5}$  S/cm to  $2.7 \cdot 10^{-4}$  S/cm, which indicates the ionic nature of the conductivity [22], while a non-Arrhenius dependence of the conductivity on temperature is observed.

It should be noted that at a temperature of 40  $^{\circ}\text{C}$ , the conductivity value of the PIL with one type of ionic groups  $[\text{PEO-2H-2NEt}_2]^{2+} [\text{PEO-2SO}_3]^{2-}$  obtained in this work ( $2.2 \cdot 10^{-5}$  S/cm) is close to that of the ion-extended PIL with two types of ionic groups  $[\text{PEO-2H-2Im}]^{2+} [\text{PEO-2SO}_3]^{2-}$  ( $2.3 \cdot 10^{-5}$  S/cm) described by us earlier [10], although the content of ionic groups in PIL  $[\text{PEO-2H-2NEt}_2]^{2+} [\text{PEO-2SO}_3]^{2-}$  is slightly higher (0.69 meq/g compared to 0.65 meq/g). This may be due to the contribution of proton migration between different types of basic centers to the increase in the conductivity of PIL  $[\text{PEO-2H-2Im}]^{2+} [\text{PEO-2SO}_3]^{2-}$ . This phenomenon was discovered by us earlier when studying the conductivity of protic ionic liquids with partially neutralized two types of basic

centers, both in the composition of low-molecular ionic liquids [16], and oligomeric linear [14] and star-shaped [17] ionic liquids.

However, with increasing temperature, the conductivity of protic block-oligomeric PIL with one type of ionic groups  $[\text{PEO-2H-2NEt}_2]^{2+} [\text{PEO-2SO}_3]^{2-}$  increases more intensively than the conductivity of ion-extended PIL with two types of ionic groups  $[\text{PEO-2H-2Im}]^{2+} [\text{PEO-2SO}_3]^{2-}$  (Fig. 6). In the temperature range 60–100  $^{\circ}\text{C}$ , the conductivity of PIL  $[\text{PEO-2H-2NEt}_2]^{2+} [\text{PEO-2SO}_3]^{2-}$  is higher than the conductivity of  $[\text{PEO-2H-2Im}]^{2+} [\text{PEO-2SO}_3]^{2-}$ , but lower than the conductivity of ion-crosslinked PIL with two types of ionic groups  $[\text{PEO-4H-2Im}]^{4+} 2[\text{PEO-2SO}_3]^{2-}$ , which correlates with the content of ionic groups in the composition of these PILs. At the same time, for PIL  $[\text{PEO-2H-2NEt}_2]^{2+} [\text{PEO-2SO}_3]^{2-}$ , as well as for PILs with two types of ionic groups, the non-Arrhenius dependence of conductivity on temperature is preserved (Fig. 6).

## Conclusion

A method for the synthesis of a protic polymeric ionic liquid (PIL) of a block oligomeric structure with ionic bonds in the main chain by ionic bonding using linear oligomers of the basic and acidic types has been developed. It was found that the synthesized PIL transforms into a liquid state at temperatures below 50  $^{\circ}\text{C}$ . It contains both a crystalline phase with a melting point of 34.5  $^{\circ}\text{C}$ , formed by poly (ethylene oxide) fragments, and an amorphous phase with a glass transition temperature of  $-49.7\text{ }^{\circ}\text{C}$ . The conductivity of PIL under anhydrous conditions in the range of 40  $^{\circ}\text{C}$  to 100  $^{\circ}\text{C}$  increases with increasing temperature and reaches  $2.7 \cdot 10^{-4}$  S/cm.

Compared to the PILs with two types of ionic groups we described earlier, the introduction of one type of ionic groups into the PIL of block oligomeric structure is accompanied by a decrease in the intensity of intermolecular interactions and the disappearance of one of the two types of crystalline phases. The conductivity of the resulting compound is of the same order as that of PILs with two types of ionic groups. The resulting compound is promising as a proton-conducting medium for various electrochemical devices.

## REFERENCES

1. *Mecerreyes D.* Polymeric ionic liquids: broadening the properties and applications of polyelectrolytes. *Progress in Polymer Science*, 2011, **36**, 12: 1629-1648. <https://doi.org/10.1016/j.progpolymsci.2011.05.007>.
2. *Shaplov A.S., Marcilla R., Mecerreyes D.* Recent advances in innovative polymer electrolytes based on poly (ionic liquid)s. *Electrochimica Acta*, 2015, **175**: 18-34. <https://doi.org/10.1016/j.electacta.2015.03.038>.
3. *Shevchenko V.V., Stryutskii A.V., Klimenko N.S.* Polymeric organic-inorganic proton-exchange membranes for fuel cells produced by the sol-gel method. *Theoretical and Experimental Chemistry*, 2011, **47**: 67-91. <https://doi.org/10.1007/s11237-011-9187-9>.
4. *Amarasekara A.S.* Acidic ionic liquids. *Chemical Reviews*, 2016, **116**: 6133-6183. <https://doi.org/10.1021/acs.chemrev.5b00763>.
5. *Díaz M., Ortiz A., Ortiz I.* Progress in the use of ionic liquids as electrolyte membranes in fuel cells. *Journal of Membrane Science*, 2014, **469**: 379-396. <https://doi.org/10.1016/j.memsci.2014.06.033>.
6. *Prescher S., Polzer F., Yang Y., Siebenbürger M., Ballauff M., Yuan J.* Polyelectrolyte as solvent and reaction medium. *Journal of the American Chemical Society*, 2014, **136**, no. 1: 12-15. <https://doi.org/10.1021/ja409395y>.
7. *Ke Y., Zhang W., Suo X., Ren Q., Xing H., Yuan J.*  $\beta$ -Cyclodextrin-derived room temperature macromolecular ionic liquids by PEGylated anions. *Macromolecular Rapid Communications*, 2020, **41**, no. 8: e1900576. <https://doi.org/10.1002/marc.201900576>.
8. *Porcarelli L., Shaplov A.S., Salsamendi M., Nair J.R., Vygodskii Y.S., Mecerreyes D., Gerbaldi C.* Single-ion block copoly(ionic liquid)s as electrolytes for all-solid state lithium batteries. *ACS Applied Materials & Interfaces*, 2016, **8**, 16: 10350-10359. <https://doi.org/10.1021/acsami.6b01973>.
9. *Porcarelli L., Vlasov P.S., Ponkratov D.O., Lozinskaya E.I., Antonov D.Y., Nair J.R., Gerbaldi C., Mecerreyes D., Shaplov A.S.* Design of ionic liquid like monomers towards easy-accessible single-ion conducting polymer electrolytes. *European Polymer Journal*, 2018, **107**: 218-228. <https://doi.org/10.1016/j.eurpolymj.2018.08.014>.
10. *Gumenna M.A., Klimenko N.S., Stryutsky O.V., Kovalenko L.L., Kravchenko V.V., Shevchuk O.V., Shevchenko V.V.* Polymeric proton exchange media with ionic bonds in the main chain of the polymer. *Reports of the National Academy of Sciences of Ukraine*, 2020, **12**: 60-66. <https://doi.org/10.15407/dopovidi2020.12.060>.
11. *Gumenna M.A., Stryutsky A.V., Sobko O.O., Kozachuk D.V., Kravchenko V.V., Kovalenko L.L., Trachevsky V.V., Shevchenko V.V.* Protic ion-crosslinked polymer ionic liquid (PIL) based on linear oligomers. *Polimernyi Zhurnal*, 2023, **45**, 1: 27-36. <https://doi.org/10.15407/polymerj.45.01.027>.
12. *Hazra A., Samanta S.K.* Main-Chain Cationic Polyelectrolytes: Design, Synthesis, and Applications. *Langmuir*, 2024, **40**, 5: 2417-2438. <https://doi.org/10.1021/acs.langmuir.3c02670>.
13. *Venkataraman Sh., Tan J.P.K., Chong Sh. T., Chu C.Y.H., Wilianto E.A., Cheng C.X., Yang Y.Y.* Identification of structural attributes contributing towards potency and selectivity of antimicrobial polyionenes: Amides are better than esters. *Biomacromolecules*, 2019, **20**, 7: 2737-2742. <https://doi.org/10.1021/acs.biomac.9b00489>.
14. *Shevchenko V.V., Gumennaya M.A., Stryutsky A.V., Klimenko N.S., Trachevskii V.V., Klepko V.V., Davydenko V.V.* Reactive oligomeric protic cationic linear ionic liquids with different types of nitrogen centers. *Polymer Science, Series B*, 2018, **60**, 5: 598-611. <https://doi.org/10.1134/S1560090418050160>.
15. *Shevchenko V.V., Stryutsky A.V., Klymenko N.S., Gumenna M.A., Fomenko A.A., Bliznyuk V.N., Trachevsky V.V., Davydenko V.V., Tsukruk V.V.* Protic and aprotic anionic oligomeric ionic liquids. *Polymer*, 2014, **55**, 16: 3349-3359. <https://doi.org/10.1016/j.polymer.2014.04.020>.
16. *Shevchenko V.V., Gumenna M.A., Korolovych V.F., Stryutsky A.V., Trachevsky V.V., Hrebunov O., Klepko V.V., Klymenko N.S., Shumsky V.F., Davydenko V.V., Ledin P.A.* Synthesis and properties of protic hydroxylic ionic liquids with two types of basic centers in their composition. *Journal of Molecular Liquids*, 2017, **235**: 68-76. <https://doi.org/10.1016/j.molliq.2017.01.020>.
17. *Shevchenko V.V., Gumenna M.A., Klimenko N.S., Stryutsky O.V., Trachevsky V.V., Kovalenko L.L., Kravchenko V.V.* Protic oligosilsesquioxane dicationic ionic liquids with two types of ionic sites in organic frame. *Theoretical and Experimental Chemistry*, 2022, **58**, 2: 143-149. <https://doi.org/10.1007/s11237-022-09732-7>.
18. *Toroptseva A.M., Belogorodskaya K.V., Bondarenko V.M.* Laboratory workshop on chemistry and technology of high-molecular compounds. L.: Chemistry, 1972: 416.
19. *Kadar E.P., Wujcik C.E., Wolford D.P., Kavetskaia O.* Rapid determination of the applicability of hydrophilic interaction chromatography utilizing ACD Labs Log D Suite: A bioanalytical application. *Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences*, 2008, **863**, no.1: 1-8. <https://doi.org/10.1016/j.jchromb.2007.11.036>.
20. *Greaves T.L., Drummond C.J.* Protic ionic liquids: properties and applications. *Chemical Reviews*, 2008, **108**, 1: 206-237. <https://doi.org/10.1021/cr068040u>.



21. *Pretsch E., Bühlmann Ph., Badertscher M.* Structure determination of organic compounds. Tables of spectral data. 4th Edition. Springer-Verlag, Berlin / Heidelberg, 2009: 443. ISBN 978-3-540-93809-5.
22. *Kyritsis A., Pissis P., Grammatikakis J.* Dielectric relaxation spectroscopy in poly(hydroxyethyl acrylates)/water hydrogels. *Journal of Polymer Science Part B: Polymer Physics*, 1995, **33**, 12: 1737-1750. <https://doi.org/10.1002/polb.1995.090331205>.

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