

UDC 547.233.4:54-145:547.867:54.057:544.537

*O.S. Sverdlikovska, O.V. Chervakov, D.O. Chervakov, B.V. Burkevich, Ye.P. Levchenko***POLYMERIC IONIC LIQUIDS AND IONIC LIQUIDS OF IONEN TYPE****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

A set of new experimental data was obtained regarding the influence of the structure of dimer ionene ionic liquids on their physical and chemical properties, which is the basis of the methodology for the synthesis of polymer ionene ionic liquids. It was established that the introduction of allyl and  $\beta$ -hydroxyethyl groups into the quaternary nitrogen atom, the presence of a dibenzyl fragment at the cationic center and alkylaromatic radicals permit obtaining polymeric ionic liquids of the ionene type with a high level of ionic conductivity at a low glass transition temperature. Newly synthesized polymeric ionic liquids and ionene ionic liquids based on 1,2-epoxy-4,7-dioxononen-8 and tetrahydro-1,4-oxazine derivatives with an ionic conductivity of  $\sim 10^{-1}$ – $10^{-4}$  S cm<sup>-1</sup> with glass transition temperature range of  $-140^{\circ}\text{C}$  to  $-16^{\circ}\text{C}$  exhibited five to six orders of magnitude higher ionic conductivity as compared with known analogues. Recommendations for solving the problem of developing polymeric ionic liquids and ionene ionic liquids exhibiting high ionic conductivity while maintaining their liquid state in a wide temperature range have been developed.

**Keywords:** polymeric ionic liquids, ionic liquids, ionic conductivity, glass transition temperature, physical and chemical properties.

**DOI:** 10.32434/0321-4095-2022-145-6-68-79

**Introduction**

Currently, one of the important areas of polymer chemistry is a development of new polymeric ionic liquids (ILs) with specific structural and chemical characteristics of carriers, which ensure the high efficiency of polymeric ILs as solvents and catalytic media in organic synthesis and synthesis of polymers, functional additives for paints and decorative coatings, components of alternative solvents of biodegradable materials, etc. [1–7]. Summarizing the results of research in recent years in the field of polymeric and ionene ILs [8–11] allows us to predict a high level of ionic conductivity and wide temperature range of liquid state in polymeric and ionene ILs based on derivatives of tetrahydro-1,4-oxazine and 1, 2-epoxy-4,7-dioxononen-8 (PIL and IIL).

The suitability of tetrahydro-1,4-oxazine and 1,2-epoxy-4,7-dioxononen-8 as monomers for the synthesis of a new series of polymeric ionene ionic liquids is confirmed by the high ionic conductivity of previously synthesized polymeric ionic liquids based on epoxide derivatives of 1,2-epoxy-4,7-

dioxononen-8 [11], morpholine-based polymeric ionic liquids and ionene ionic liquids [8–10] at very low temperatures, as well as significant technical and economic advantages of using these compounds, which led to the use of the developed polymeric ionic liquids and ionic liquids in general in various fields to solve pressing problems of chemistry and chemical technology.

Based on the above, it is important to address the following issues:

- to supplement a number of polymeric ionic liquids and ionene ionic liquids with new low-cost compounds from readily available raw materials;
- to improve the scientific and methodical approach to the synthesis of PIL and IIL with given properties;
- to establish the dependence of their physical and chemical properties on the structure and external factors to solve urgent problems of chemical and food technologies;
- to solve the scientific and applied problem of developing ionic liquids with high ionic conductivity with a wide temperature range of liquid state;

© O.S. Sverdlikovska, O.V. Chervakov, D.O. Chervakov, B.V. Burkevich, Ye.P. Levchenko, 2022



This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

*O.S. Sverdlikovska, O.V. Chervakov, D.O. Chervakov, B.V. Burkevich, Ye.P. Levchenko*



TDA based on tetrahydro-1,4-oxazine and epoxidized derivatives of 1,2-epoxy-4,7-dioxononen-8 EPS-602 (TDA-1), EPS-254 (TDA-2), EPS-258 (TDA-3), EP-6 (TDA-4) were selected as starting monomers for the synthesis of PIL and IIL with high yields.

Synthesis of dimeric ionene ILs based on diquaternary ammonium salts with chlorine or bromine anion was carried out (Fig. 3) by the reaction of previously synthesized TDA with the corresponding halogen derivatives. Allyl bromide (HD-21), benzyl chloride (HD-22), butyl bromide (HD-23), ethylene chlorohydrin (HD-24) were used as halogen derivatives (HD) for IL synthesis. The

reaction was carried out at a temperature of 50–60°C for 12 hours. It has been established that IILs are formed with high yields of ~78–98%.

PILs were synthesized by the Menshutkin reaction of equimolar amounts of tetrahydro-1,4-oxazine derivatives and 1,2-epoxy-4,7-dioxononen-8 TDA with alkylaromatic and aliphatic dihalogen derivatives of diepoxide compounds. The syntheses were carried out according to the general scheme (Fig. 4). According to ref. [14], the reaction of TDA with DH occurs by the mechanism ( $S_N2$ ) of bimolecular nucleophilic substitution in various solvents. The possibility of obtaining the largest molecular mass of new ionene ionic liquids at the

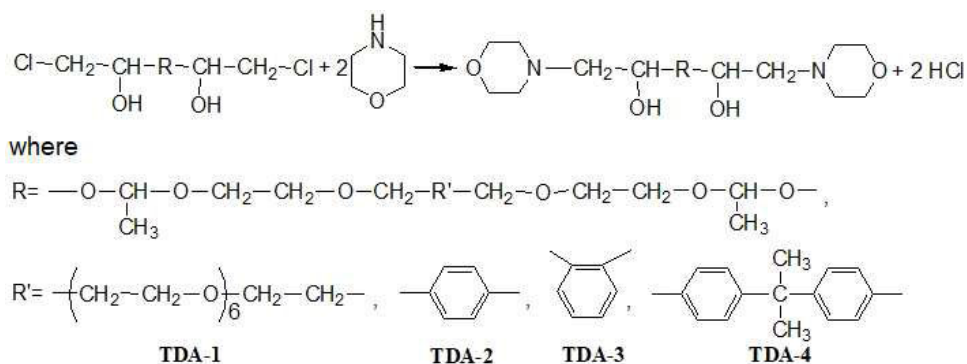


Fig. 2. Synthesis of tetrahydro-1,4-oxazine and 1,2-epoxy-4,7-dioxononen-8 derivatives based TDA

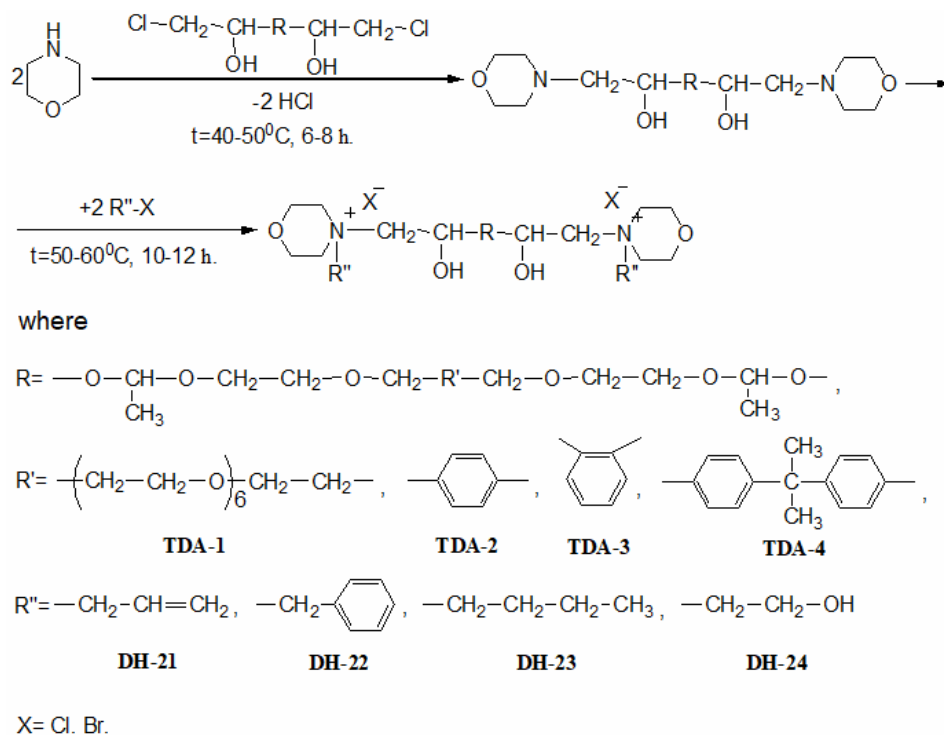


Fig. 3. Synthesis of the ionene ionic liquids with chlorine and bromine anions. The code of synthesized IILs consists of the letter «C» and two numbers: the first number is the TDA number, and the second number is the DH number



must be established for each individual ionic liquid. The studies conducted earlier [8–10] revealed that the ionic conductivity of morpholine-based ionene ionic liquids decreases with increasing melting point and decreasing temperature, but the ionic conductivity of morpholine-based polymeric ionene ionic liquids increases with rising temperature. The latter dependence correlates well with the viscosity of morpholine-based polymeric ionene ionic liquids: with decreasing viscosity, the level of ionic conductivity increases.

Due to the established analytical dependences, it becomes possible to vary the cation-anion pair to ensure the necessary properties of polymeric and ionene ionic liquids. Despite the practical significance of those results [8–11], it should be noted that for each series of ionic liquids, it is necessary to study the general correlations between individual parameters and their ionic conductivity separately, and the established regularities will be inherent only to ionic liquids of a certain structure.

Considering all of the above, research aimed at supplementing or confirming the previously established dependences of the ionic conductivity of polymeric ionic liquids and ionene ionic liquids on their structure and temperature should be considered relevant in order to make a reasonable choice of the structural and chemical characteristics of the carriers of ionic liquids, which ensure their high efficiency in various fields of practical applications.

In order to further develop the foundations for the synthesis of new polymeric ionic liquids and ionene ionic liquids with specified properties, the correlation dependences between temperature, chemical structure of PIL, IIL and their ionic conductivity were established. A comparative analysis of the influence of the chemical structure of PIL and IIL on their ionic conductivity was carried out based on the results of research in a wide temperature range (15–50°C) of the ionic conductivity of PIL and IIL with different groups at the quaternary nitrogen atom. Based on the previous recommendations [8], IIL samples with the smallest intrinsic radii, IIL with chloride and bromide anions, were chosen as the objects of this study.

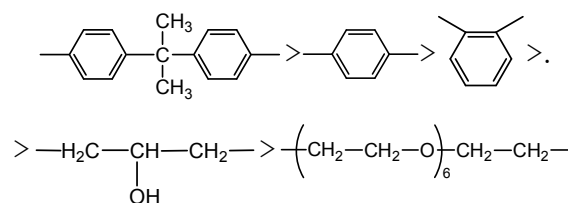
A comparison of IILs with the same radical at the cationic center, which is a residue of the original TDA (both for the synthesis of PIL and IIL), clearly shows (Table 1) that there is a decrease in the ionic conductivity of butyl- and benzyl-containing IIL due to an increase in steric hindrance. The series of dependences of the ionic conductivity on the nature of the substituents at the quaternary nitrogen atom of IIL have been established:



In general, a similar dependence was proposed in ref. [8] for monomeric and dimeric morpholine-based ionene ionic liquids containing a halide anion.

Therefore, the data indirectly indicate the weakening of interionic interactions, differences between the diffusion coefficients of ionic liquids.

In order to predict the influence of the structural and chemical characteristics of the carriers on the ionic conductivity of PILs, a detailed analysis of the dependence of the ionic conductivity of IILs on their radical at the cationic center, which is the residue of the original TDA (both for the synthesis of PIL and IIL), was carried out. It was established that the ionic conductivity of IIL decreases in the following series:



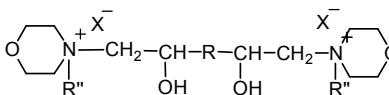
Transition from IIL with an aliphatic radical at the cationic center to IIL with an alkylaromatic radical leads to an increase in the ionic conductivity of IIL, which is probably due to a decrease in the interaction with protons of hydroxyl or oxyethyl groups of substituents at the nitrogen atom and the corresponding anions.


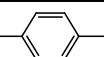

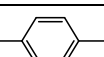
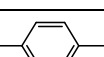
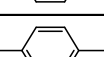




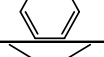
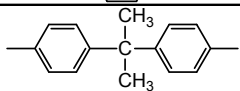

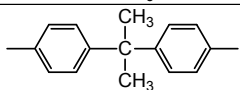
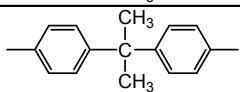
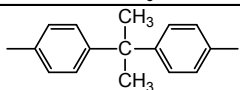

Note that the replacement of the  $\text{---CH}_2\text{CH}_2\text{O---}$  group by  $\text{---CH}_2\text{CH}(\text{OH})\text{CH}_2\text{---}$  leads to an increase in ionic conductivity, probably due to an increase in the conformational lability of the  $\text{---CH}_2\text{CH}(\text{OH})\text{CH}_2\text{---}$  group compared to that of oxyethylene. This dependence corresponds to the previously found dependence [8] for monomeric morpholine-based ionene ionic liquids: «... the specific conductivity of ionic liquids increases when  $\beta$ -hydroxyethyl groups are introduced into the molecule ...».

It is practically important to establish correlations between the melting point and the ionic conductivity of ionic liquids. Thus, previous studies [8–11] established that the ionic conductivity of polymeric ionic liquids and morpholine-based ionene ionic liquids increases in direct proportion with a decrease in the melting point (glass transition temperature), which is confirmed by correlations between these parameters for each ionic liquid. Thanks to the established correlation dependences, it becomes possible to more effectively adjust the cation-anion pair of the ionic liquid to ensure their

Table 1

## Melting point, ionic conductivity of tetrahydro-1,4-oxazene derivatives and 1,2-epoxy-4,7-dioxononen-8

based ionene ionic liquids of the general formula 

Designation	R	R'=R''	X	T <sub>m</sub> , °C	σ, S cm <sup>-1</sup>
C-1-22	$\text{-(CH}_2\text{-CH}_2\text{-O)}_6\text{-CH}_2\text{-CH}_2\text{-}$	$\text{-CH}_2\text{-}$ 	Cl	-95	$0.35 \cdot 10^{-3}$
C-1-23	$\text{-(CH}_2\text{-CH}_2\text{-O)}_6\text{-CH}_2\text{-CH}_2\text{-}$	$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	Br	-117	$0.16 \cdot 10^{-2}$
C-1-24	$\text{-(CH}_2\text{-CH}_2\text{-O)}_6\text{-CH}_2\text{-CH}_2\text{-}$	$\text{-CH}_2\text{-CH}_2\text{-OH}$	Cl	-126	$0.28 \cdot 10^{-2}$
C-1-21	$\text{-(CH}_2\text{-CH}_2\text{-O)}_6\text{-CH}_2\text{-CH}_2\text{-}$	$\text{-CH}_2\text{-CH=CH}_2$	Br	-132	$0.24 \cdot 10^{-1}$
C-2-22		$\text{-CH}_2\text{-}$ 	Cl	-109	$0.73 \cdot 10^{-2}$
C-2-23		$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	Br	-123	$0.44 \cdot 10^{-1}$
C-2-24		$\text{-CH}_2\text{-CH}_2\text{-OH}$	Cl	-129	$0.49 \cdot 10^{-1}$
C-2-21		$\text{-CH}_2\text{-CH=CH}_2$	Br	-138	$0.78 \cdot 10^{-1}$
C-3-22		$\text{-CH}_2\text{-}$ 	Cl	-107	$0.69 \cdot 10^{-2}$
C-3-23		$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	Br	-122	$0.29 \cdot 10^{-1}$
C-3-24		$\text{-CH}_2\text{-CH}_2\text{-OH}$	Cl	-129	$0.32 \cdot 10^{-1}$
C-3-21		$\text{-CH}_2\text{-CH=CH}_2$	Br	-137	$0.66 \cdot 10^{-1}$
C-4-22		$\text{-CH}_2\text{-}$ 	Cl	-113	$0.84 \cdot 10^{-2}$
C-4-23		$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	Br	-125	$0.56 \cdot 10^{-1}$
C-4-24		$\text{-CH}_2\text{-CH}_2\text{-OH}$	Cl	-130	$0.63 \cdot 10^{-1}$
C-4-21		$\text{-CH}_2\text{-CH=CH}_2$	Br	-140	$0.91 \cdot 10^{-1}$
C-20-1*	$\text{-H}_2\text{C-CH(OH)-CH}_2\text{-}$	$\text{-CH}_2\text{-}$ 	Cl	-102	$0.59 \cdot 10^{-2}$
C-20-3*	$\text{-H}_2\text{C-CH(OH)-CH}_2\text{-}$	$\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	Br	-120	$0.12 \cdot 10^{-1}$
C-20-2*	$\text{-H}_2\text{C-CH(OH)-CH}_2\text{-}$	$\text{-CH}_2\text{-CH}_2\text{-OH}$	Cl	-128	$0.13 \cdot 10^{-1}$
C-20-4*	$\text{-H}_2\text{C-CH(OH)-CH}_2\text{-}$	$\text{-CH}_2\text{-CH=CH}_2$	Br	-135	$0.52 \cdot 10^{-1}$

high level of ionic conductivity while maintaining properties at very low temperatures.

Summarizing the results of the study of the melting temperature and ionic conductivity of IILs (Table 1) allows us to state the presence of an interesting regularity in the series of IILs with the same radical at the cationic center, which is the residue of the original TDA (both for the synthesis of PIL and IIL), which is associated with the growth of the ionic conductivity of ionic liquids with a decrease in their melting point. A decrease in the melting point of IIL C-1-21÷C-1-24 from  $-95^{\circ}\text{C}$  to  $-132^{\circ}\text{C}$  leads to an increase in specific conductivity from  $0.35 \cdot 10^{-3} \text{ S cm}^{-1}$  to  $0.24 \cdot 10^{-1} \text{ S cm}^{-1}$  IIR (Table 1). Taking into account the fact that the system is multicomponent, the establishment of correlation dependences between the properties of IIL was carried out while excluding from consideration the effect of the covalent radius of the anion. For the first time, the correlation dependences between the melting temperature and the ionic conductivity of IIL were established:

IIL C-1-21÷C-1-24 ( $\sigma = -0.046 \cdot 10^{-2} T_m - 4.7$ ,  $r = -0.663$ );  
 IIL C-2-21÷C-2-24 ( $\sigma = -0.024 \cdot 10^{-1} T_m - 2.5$ ,  $r = -0.990$ );  
 IIL C-3-21÷C-3-24 ( $\sigma = -0.018 \cdot 10^{-1} T_m - 1.9$ ,  $r = -0.940$ );  
 IIL C-4-21÷C-4-24 ( $\sigma = -0.030 \cdot 10^{-1} T_m - 3.3$ ,  $r = -0.989$ );  
 IIL C-20-1÷C-20-4 ( $\sigma = -0.011 \cdot 10^{-1} T_m - 1.1$ ,  $r = -0.749$ ).

Based on previous studies, correlation equations prove the dependence of the ionic conductivity of IILs on their radical at the cationic center, which is the residue of the original TDA (both for the synthesis of PIL and IIL). Thus, the corresponding correlation equations are as follows:

IIL C-1-22÷C-4-22, C-20-1\* ( $\sigma = -0.048 \cdot 10^{-2} T_m - 4.5$ ,  $r = -0.974$ );  
 IIL C-1-23÷C-4-23, C-20-3\* ( $\sigma = -0.066 \cdot 10^{-1} T_m - 7.7$ ,  $r = -0.984$ );  
 IIL C-1-24÷C-4-24, C-20-2\* ( $\sigma = -0.135 \cdot 10^{-1} T_m - 16.9$ ,  $r = -0.943$ );  
 IIL C-1-21÷C-4-21, C-20-4\* ( $\sigma = -0.087 \cdot 10^{-1} T_m - 11.2$ ,  $r = -0.999$ ).

These newly found dependences and their confirmation by correlation equations are extremely important for the further synthesis of polymeric ionic liquids and ionene ionic liquids, due to them being tied to the defining parameters of ionic liquids: melting temperature and ionic conductivity.

Taking into account all of the aforementioned data, we can state that the introduction of allyl and  $\beta$ -hydroxyethyl groups into the quaternary nitrogen

atom, the presence of dibenzyl fragment at the cationic center and alkylaromatic radicals will allow obtaining PILs with high ionic conductivity at low glass transition temperatures.

Experimental studies have established that the ionic conductivity of IIL increases with an increase in the temperature (Fig. 5) due to a decrease in the viscosity of ionic liquids and a decrease in the solvation of ions and, consequently, due to increased speed of movement of the ions. However, this paper does not provide physical and chemical calculations to confirm this hypothesis, which can be the basis of further research.

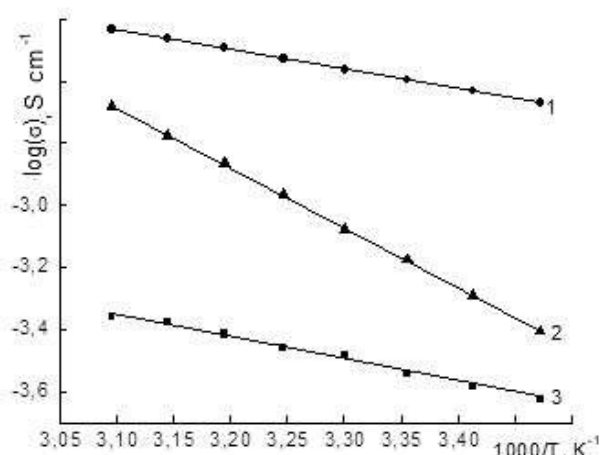


Fig. 5. Dependences of ionic conductivity (logs) of IILs on reciprocal temperature ( $1000/T$ ):  
 1 – C-4-22; 2 – C-3-22; and 3 – C-1-22

Thus, the generalization of the established results of previous work [8–11] and newly obtained data can be formulated in the form of the following thesis: «The ionic conductivity of ionene ionic liquids increases with a decrease in the melting point and an increase in temperature.»

Further research was aimed at determining the peculiarities of the influence of the polymeric nature of the synthesized PILs on their ionic conductivity. To do so, it was necessary to establish the dependences between the substituents at the quaternary nitrogen atom, the distance between the quaternary nitrogen atoms in the macromolecule, the chain length of the PIL macromolecule, temperature and their ionic conductivity; and to confirm the found dependences with correlation equations and explain their chemical nature.

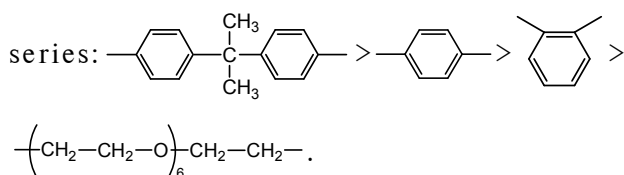
In order to prove the correspondence of the found dependence of the ionic conductivity of IILs

on their radical at the cationic center, it is sufficient to carefully study the ionic conductivity of a series of PILs with a radical that has a dibenzyl fragment in its structure (Table 2), in which the ionic conductivity decreases. This correlates well with the results of the study of their dimeric analogues.

Comparison of the ionic conductivity of PIL with an alkylaromatic substituent at the nitrogen atom and PIL with an aliphatic substituent indicates a higher ionic conductivity in the first case, which is due to the «loosening» of the packing of the polymer chain. This does not differ from the practical data of the predicted results of the dimeric model systems of PIL and work [8–10], where, from a theoretical point of view, this fact is related to the greater rigidity of the macromolecule of a polymer with an alkylaromatic substituent, which is more expanded compared to a polymer containing aliphatic substituents.

The distance between quaternary nitrogen atoms in the polymer macromolecule is also a determining factor affecting the ionic conductivity of a polymer macromolecule: as the distance between the atoms of quaternized nitrogen in the polymer macromolecule increases, the ionic conductivity decreases in the following series of PIL C-4-6>C-4-7>C-4-1 (Table 2), which is caused by a decrease in the number of charges in the polymer macromolecule. However, in contrast to the conclusions drawn from the research results given in studies [8–10], the data obtained allows us to state that the main factor impacting the ionic conductivity of the studied polymer ionene ionic liquids is not only the size of the polymer macromolecule, but also the distance between quaternary nitrogen atoms in this macromolecule.

So, for PILs it is possible to construct following



Comparative analysis of data on PILs with the same structure, but with different degrees of polymerization, (Table 2) showed that an increase in molecular weight leads to a decrease in the ionic conductivity of PILs. Despite the practical value of such results, this line of research has not been sufficiently pursued in this work.

Obviously, this is related to the completeness of the theoretical and practical results of systematic research on this issue in the previous works [8–10], which substantiates the following: an increase in the

chain length of a polymer macromolecule leads to a decrease in the linearity of the polymer macromolecule, an increase in the number of steric hindrances and charges in the chain, and therefore a decrease in the mobility of charge carriers.

The nature of the temperature dependence of the ionic conductivity of the synthesized PILs is the same (Fig. 6). It should be noted that as the temperature decreases, the ionic conductivity of the PIL decreases. At the same time, the viscosity of the solutions of the corresponding PIL increases. This dependence is explained by a complex of intra- and intermolecular interactions of polymer macromolecules.

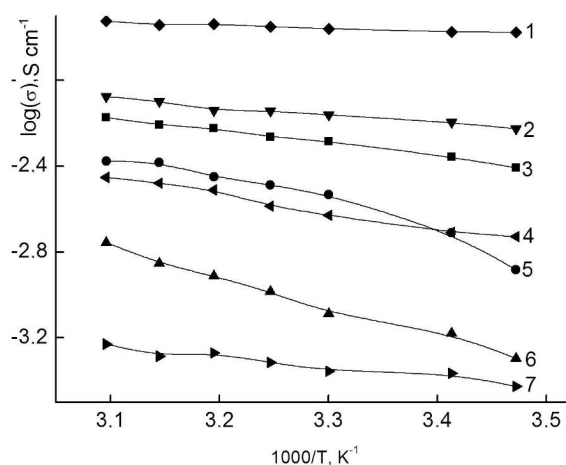


Fig. 6. Dependences of ionic conductivity ( $\log\sigma$ ) of polyionenes on reciprocal temperature ( $1000/T$ ): 1 – C-1-1; 2 – C-1-2; 3 – C-1-3; 4 – C-1-4; 5 – C-2-2; 6 – C-3-3; and 7 – C-4-4

When establishing the dependences between the ionic conductivity of PILs and their glass transition temperature, which follow from the obtained results, simultaneous decrease in the glass transition temperature corresponds to an increase in the ionic conductivity of PIL. This is probably due to an increase in the entropy factor, which reduces the order and increases the mobility of the chain segments of the polymer macromolecule with ionic groups. In particular, the correlation equations confirming these dependencies are as follows:

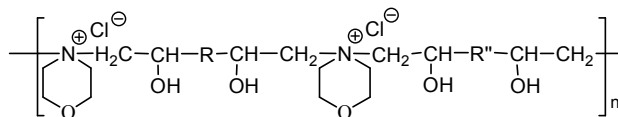
$$\begin{aligned} \text{IIL C-1-1} \div \text{C-1-7} & (\sigma = -0.018 \cdot 10^{-2} T_m - 0.5, r = -0.786); \\ \text{IIL C-2-2} \div \text{C-2-7} & (\sigma = -0.033 \cdot 10^{-2} T_m - 1.5, r = -0.915); \\ \text{IIL C-3-3} \div \text{C-3-7} & (\sigma = -0.060 \cdot 10^{-2} T_m - 4.6, r = -0.972); \\ \text{IIL C-4-3} \div \text{C-4-7} & (\sigma = -0.009 \cdot 10^{-1} T_m - 0.8, r = -0.943). \end{aligned}$$

Similar dependences of ionic conductivity and



Table 2

## Melting point, ionic conductivity of polymeric ionic liquids of the general formula



Designation	R'	R''	n	$\bar{M}_n$	$\eta_{sp}/C$ , dl/g	$\sigma$ , S cm <sup>-1</sup>
C-1-4	$\left(\text{CH}_2-\text{CH}_2-\text{O}\right)_6\text{CH}_2-\text{CH}_2-$		7	9639	5.93	$0.636 \cdot 10^{-2}$
C-2-4			9	10449	4.24	$0.167 \cdot 10^{-1}$
C-3-4			9	10449	4.47	$0.276 \cdot 10^{-1}$
C-4-4			8	10232	3.84	$1.732 \cdot 10^{-1}$
C-4-1		$\left(\text{CH}_2-\text{CH}_2-\text{O}\right)_6\text{CH}_2-\text{CH}_2-$	5	6885	4.72	$0.967 \cdot 10^{-2}$
C-4-7		$-\text{CH}_2\left(\text{O}-\text{CH}_2-\text{CH}_2\right)_3\text{O}-\text{CH}_2-$	6	6150	4.81	$0.143 \cdot 10^{-1}$
C-4-6		$-\text{CH}_2\left(\text{O}-\text{CH}_2-\text{CH}_2\right)_2\text{O}-\text{CH}_2-$	7	6867	4.43	$0.186 \cdot 10^{-1}$

glass transition (melting) temperature were observed both for IILs and for morpholine-based polymeric ionic liquids in refs. [8–10].

The conducted studies established the effect of temperature and chemical structure of synthesized PILs on their ionic conductivity: the ionic conductivity of PILs increases with an increase in the melting point and a decrease in temperature, with the introduction of alkylaromatic substituents at the quaternary nitrogen atom, with a decrease in the distance between the quaternized nitrogen atoms and chain length of the polymer macromolecule.

The expediency of using low-molecular analogs of polymeric ionic liquids as model systems for predicting the behavior of polymeric ionic liquids is confirmed by the established similar dependences between temperature, substituents at the quaternary nitrogen atom, and ionic conductivity of PIL and their dimeric analogs.

It was shown that synthesized polymeric ionic liquids and ionene ionic liquids based on tetrahydro-1,4-oxazine and 1,2-epoxy-4,7-dioxonon-8 derivatives with an ionic conductivity of  $\sim 10^{-1}$ –

$\div 10^{-4}$  S cm<sup>-1</sup> in the glass transition temperature range of  $-140^\circ\text{C}$ – $-16^\circ\text{C}$  exhibited five to six orders of magnitude higher ionic conductivity than the world-known polymeric ionic liquids-based analogues ( $s=10^{-6}$ – $10^{-10}$  S cm<sup>-1</sup>;  $T_m=-8$ – $80^\circ\text{C}$ ) [15], which makes it possible to supplement a number of existing effective polymeric ionic liquids and their low-molecular ionene analogs with compounds with a higher level of ionic conductivity in the range of  $-140^\circ\text{C}$  to  $+330^\circ\text{C}$ .

Thus, scientific ideas regarding polymeric ionic liquids and ionene ionic liquids were further developed as a result of the establishing dependences of the ionic conductivity of these compounds on temperature, the nature of the substituents at the quaternary nitrogen atom, the number of quaternary ammonium groups in the cation radical, and the length of the macromolecule chain, which were confirmed by correlation equations.

Based on the results obtained in previous studies and this work, it is possible to generalize the theories of existing knowledge of the justified choice of structural and chemical characteristics of media,

which will contribute to solving the scientific and applied problem of the development of polymeric ionic liquids and ionene ionic liquids with high ionic conductivity while preserving their liquid state in a wide temperature range:

1. Ionic conductivity of polymeric and ionene ionic liquids increases with an increase in temperature and a decrease in viscosity and glass transition temperature (melting point).

2. Introduction of allyl and  $\beta$ -hydroxyl groups into the quaternary nitrogen atom and the presence of dibenzyl fragment near the cation center lead to increased ionic conductivity in polymeric and ionene ionic liquids at low glass transition temperature.

3. Introduction of different radicals into the quaternary nitrogen atom increases specific conductivity compared to ionene ionic liquids with the same radicals.

4. Introduction of an alkylaromatic radical into the main chain of a macromolecule of polymeric ionene ionic liquids increases their ionic conductivity compared to a polymer of an aliphatic structure.

5. Substituting ethylene bridge for the  $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$  group into the cation part radical of the polymeric and ionene ionic liquids leads to increased ionic conductivity.

6. Decreasing the length of the polymer macromolecule leads to increased ionic conductivity in polymeric ionene ionic liquids.

7. Decrease in radius of an anion leads to an increase in the conductivity of the polymeric and ionene ionic liquids: high ionic conductivity is exhibited by ILs containing chlorine anion.

### Conclusions

New experimental data regarding the influence of the structure of dimer ionene ionic liquids on their physical and chemical properties has been obtained and used as the basis of the methodology for the synthesis of polymeric ionene ionic liquids. It has been established that the introduction of allyl and  $\beta$ -hydroxyethyl groups into the quaternary nitrogen atom, the presence of a dibenzyl fragment at the cationic center and alkylaromatic radicals will allow obtaining polymeric ionene ionic liquids with a high ionic conductivity at a low glass transition temperature.

It has been shown for the first time that the synthesized polymeric ionic liquids and ionene ionic liquids based on 1,2-epoxy-4,7-dioxononen-8 and tetrahydro-1,4-oxazine derivatives with an ionic conductivity of  $\sim 10^{-1} \div 10^{-4} \text{ S cm}^{-1}$  in the glass transition temperature range of  $-140^\circ\text{C} \div -16^\circ\text{C}$  exhibit five to six orders of magnitude higher ionic conductivity than the known analogues based on

polymeric ionic liquids. This allows supplementing the range of existing effective polymeric ionic liquids and their low-molecular weight ionene analogs with compounds with a higher ionic conductivity in the range of  $-140^\circ\text{C}$  to  $+330^\circ\text{C}$ .

For the first time, the physicochemical properties of the synthesized polymeric ionic liquids and ionene ionic liquids based on 1,2-epoxy-4,7-dioxononen-8 and tetrahydro-1,4-oxazine derivatives have been determined; correlations between the chemical structure of these compounds and their properties have been established. Said correlations can be used as the basis for the synthesis of new compounds. Scientific ideas about polymeric ionic liquids and ionene ionic liquids have been further developed by establishing dependences of the ionic conductivity of these compounds on temperature, symmetry of the cationic part, the nature of the substituents at the quaternary nitrogen atom, the number of quaternary ammonium groups in the cation radical, and the length of the macromolecule chain, the type of the anionic part. Parameters discovered are proposed to be used as correlation parameters for predicting the efficiency of polymeric and ionene ionic liquids.

Recommendations for solving the scientific and applied problem of developing polymeric ionic liquids and ionene ionic liquids with high ionic conductivity while maintaining their liquid state in a wide temperature range have been developed.

### REFERENCES

1. *Mecerreyes D.* Polymeric ionic liquids: broadening the properties and applications of polyelectrolytes // *Prog. Polym. Sci.* – 2011. – Vol.36. – P.1629-1648.
2. *Synthesis and properties of polymeric analogs of ionic liquids / Shaplov A.S., Ponkratov D.O., Vlasov P.S., Lozinskaya E.I., Komarova L.I., Malyshkina I.A., Vidal F., Nguyen G.T.M., Armand M., Wandrey C., Vygodskii Ya.S.* // *Polym. Sci. Ser. B.* – 2013. – Vol.55. – No. 3-4. – P.122-138.
3. *Shaplov A.S., Marcilla R., Mecerreyes D.* Recent advances in innovative polymer electrolytes based on poly(ionic liquid)s / *Electrochim. Acta.* – 2015. – Vol.175. – P.18-34.
4. *Architecture, assembly, and emerging applications of branched functional polyelectrolytes and poly(ionic liquid)s / Xu W., Ledin P.A., Shevchenko V.V., Tsukruk V.V.* // *ACS Appl. Mater. Interfaces.* – 2015. – Vol.7. – P.12570-12596.
5. *Reactive oligomeric protic cationic linear ionic liquids with different types of nitrogen centers / Shevchenko V.V., Gumennaya M.A., Stryutsky A.V., Klimenko N.S., Trachevskii V.V., Klepko V.V., Davidenko V.V.* // *Polym. Sci. Ser. B.* – 2018. – Vol.60. – No. 5. – P.598-611.

6. *Кислова О.В.* Перспективи застосування іонних рідин в електрохімії // Вісн. Київського нац. ун-ту технол. та ди-зайну. Сер. техн. науки. – 2018. – № 3 (122). – С.38-44.

7. *Tuzimski T., Petruczyk A.* Ionic liquids applied to extraction of xenobiotics from food, environmental, and biological samples and for analysis by liquid chromatography // *J. AOAC Int.* – 2019. – Vol.102. – No. 1. – P.3-22.

8. *Свердліковська О.С.* Полімерні четвертинні амонієві солі та їх аналоги – перспективні іонні рідини. – Дніпропетровськ, 2014. – 264 с.

9. *Sverdlikovska O., Burmistr M., Chervakov O.* Perspective of ionic liquids based on polymeric quaternary salts of ammonium (derivates morpholine) // *Eur. Appl. Sci.* – 2014. – No. 10. – P.109-112.

10. *Свердліковська О.С., Бурмістр М.В., Феденко О.А.* Апротонні полімерні іонні рідини іоненового типу // *Наука, технології, інновації.* – 2018. – № 2(6). – С.61-70.

11. *Іонні рідини на основі четвертинних амонієвих солей – похідних оксиранових сполук в якості компонентів рідких і полімерних електролітів для електрохімічних пристроїв / Бурмістр О.М., Свердліковська О.С., Бурмістр М.В., Шапка В.Х. // Вопр. хімії и хим. технологии.* – 2010. – № 5. – С.26-31.

12. *Пакен А.М.* Эпоксидные соединения и эпоксидные смолы – Л.: Гостхимиздат, 1962. – 964 с.

13. *Производные морфолина. IV. Взаимодействие йодистого метила и галогенводородных кислот с производными оксациклубутана, содержащими морфолинометильные заместители / Каплан С.З., Захарова Н.А., Звонцова А.С., Хромов-Борисов Н.В., Кожевников С.П., Павлюченкова Л.В. // Химия гетероцикл. соед.* – 1974. – № 10. – С.1320-1324.

14. *Бурмістр М.В., Бурмістр Е.М.* Алкилароматические полиионены. – Днепропетровск: УГХТУ, 2005. – 131 с.

15. *Yoshizawa M., Narita A., Ohno H.* Design of ionic liquids for electrochemical applications // *Aust. J. Chem.* – 2004. – Vol.57. – No. 2. – P.139-144.

Received 26.07.2022

## ПОЛІМЕРНІ ІОННІ РІДИНИ ТА ІОННІ РІДИНИ ІОНЕНОВОГО ТИПУ

*Свердліковська, О.В. Черваков, Д.О. Черваков, Б.В. Буркевич, Є.П. Левченко*

Отримано комплекс нових експериментальних даних щодо впливу будови димерних іонних рідин іоненового типу на їх фізико-хімічні властивості, що є основою методології синтезу полімерних іонних рідин іоненового типу. Встановлено, що введення алільних і  $\beta$ -гідроксиетильних груп до четвертинного атома азоту, наявність дибензиллового фрагмента при катіонному центрі та радикалів алкілароматичної будови дозволять одержати полімерні іонні рідини іоненового типу з високим рівнем іонної провідності при низькій температурі склування. Синтезовані полімерні іонні рідини та іонні рідини іоненового типу на основі похідних 1,2-епоксі-4,7-діоксононен-8 та тетрагідро-1,4-оксазину з іонною провідністю  $\sim 10^{-1}$ – $10^{-4}$  См·см<sup>-1</sup> у діапазоні температур склування  $-140^{\circ}\text{C}$ ... $-16^{\circ}\text{C}$  на п'ять–шість порядків мають більшу іонну провідність у порівнянні з відомими світовими аналогами. Розроблені рекомендації щодо вирішення науково-прикладної проблеми розробки полімерних іонних рідин та іонних рідин іоненового типу з високою іонною провідністю зі збереженням їх рідкого стану у широкому діапазоні температур.

**Ключові слова:** полімерні іонні рідини, іонні рідини, іонна провідність, температура склування, температура плавлення, фізичні і хімічні властивості.

## POLYMERIC IONIC LIQUIDS AND IONIC LIQUIDS OF IONEN TYPE

*O.S. Sverdlikovska\*, O.V. Chervakov, D.O. Chervakov, B.V. Burkevich, Ye.P. Levchenko*

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

\* e-mail: o.sverdlikovska@gmail.com

A set of new experimental data was obtained regarding the influence of the structure of dimer ionene ionic liquids on their physical and chemical properties, which is the basis of the methodology for the synthesis of polymer ionene ionic liquids. It was established that the introduction of allyl and  $\beta$ -hydroxyethyl groups into the quaternary nitrogen atom, the presence of a dibenzyl fragment at the cationic center and alkylaromatic radicals permit obtaining polymeric ionic liquids of the ionene type with a high level of ionic conductivity at a low glass transition temperature. Newly synthesized polymeric ionic liquids and ionene ionic liquids based on 1,2-epoxy-4,7-dioxononen-8 and tetrahydro-1,4-oxazine derivatives with an ionic conductivity of  $\sim 10^{-1}$ – $10^{-4}$  S cm<sup>-1</sup> with glass transition temperature range of  $-140^{\circ}\text{C}$  to  $-16^{\circ}\text{C}$  exhibited five to six orders of magnitude higher ionic conductivity as compared with known analogues. Recommendations for solving the problem of developing polymeric ionic liquids and ionene ionic liquids exhibiting high ionic conductivity while maintaining their liquid state in a wide temperature range have been developed.

**Keywords:** polymeric ionic liquids; ionic liquids; ionic conductivity; glass transition temperature; physical and chemical properties.

## REFERENCES

1. Mecerreyes D. Polymeric ionic liquids: broadening the properties and applications of polyelectrolytes. *Prog Polym Sci.* 2011; 36: 1629-1648. doi: 10.1016/j.progpolymsci.2011.05.007.
2. Shaplov AS, Ponkratov DO, Vlasov PS, Lozinskaya EI, Komarova LI, Malyshkina IA, et al. Synthesis and properties of polymeric analogs of ionic liquids. *Polym Sci Ser B.* 2013; 55: 122-138. doi: 10.1134/S1560090413030044.
3. Shaplov AS, Marcilla R, Mecerreyes D. Recent advances in innovative polymer electrolytes based on poly(ionic liquid)s. *Electrochim Acta.* 2015; 175: 18-34. doi: 10.1016/j.electacta.2015.03.038.
4. Xu W, Ledin PA, Shevchenko VV, Tsukruk VV. Architecture, assembly, and emerging applications of branched functional polyelectrolytes and poly(ionic liquid)s. *ACS Appl Mater Interfaces.* 2015; 7: 12570-12596. doi: 10.1021/acsami.5b01833.
5. Shevchenko VV, Gumennaya MA, Stryutsky AV, Klimenko NS, Trachevskii VV, Klepko VV, et al. Reactive oligomeric protic cationic linear ionic liquids with different types of nitrogen centers. *Polym Sci Ser B.* 2018; 60: 598-611. doi: 10.1134/S1560090418050160.
6. Kislova OV. Perspektyvy zastosuvannya ionnykh ridyn v elektrokhimiyi [Prospects for the use of ionic liquids in electrochemistry]. *Bull Kyiv Nat Univer Technol Des Ser Techn Sci.* 2018; 3(122): 38-44. (in Ukrainian).
7. Tuzimski T, Petruczynik A. Ionic liquids applied to extraction of xenobiotics from food, environmental, and biological samples and for analysis by liquid chromatography. *J AOAC Int.* 2019; 102(1): 3-22. doi: 10.5740/jaoacint.18-0293.
8. Sverdlikovska OS. Polimerni chetvertynni amoniyevi soli ta yikh analohy – perspektyvni ionni ridyny [Polymeric quaternary ammonium salts and their analogs are promising ionic liquids]. Dnipropetrovsk; 2014. 264 p. (in Ukrainian).
9. Sverdlikovska O, Burmistr M, Chervakov O. Perspective of ionic liquids based on polymeric quaternary salts of ammonium (derivates morpholine). *Eur Appl Sci.* 2014; (10): 109-112.
10. Sverdlikovska OS, Burmistr MV, Fedenko OA. Aprotic polimerni ionni ridyny ionenovooho typu [Aprotic polymer ionic liquids of the ionene type]. *Sci Innov Technol.* 2018; 2(6): 61-70. (in Ukrainian).
11. Burmistr OM, Sverdlikovska OS, Burmistr MV, Shapka VKh. Ionni ridyny na osnovi chetvertynnykh amoniyevykh soley – pokhidnykh oksyranovykh spoluk v yakosti komponentiv ridkykh i polimernykh elektrolitiv dlya elektrokhimichnykh prystroyiv [Ionic liquids based on quaternary ammonium salts, derivatives of oxirane compounds, as components of liquid and polymer electrolytes for electrochemical devices]. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2010; (5): 26-31. (in Ukrainian).
12. Paken AM. Epoksidnyye soyedineniya i epoksidnyye smoly [Epoxy compounds and epoxy resins]. Leningrad: Gosthimizdat; 1962. 964 p. (in Russian).
13. Kaplan SZ, Zakharova NA, Zvontsova AS, Khromov-Borisov NV, Kozhevnikov SP, Pavlyuchenkova LV. Proizvodnyye morfolina. IV. Vzaimodeystviye yodistogo metila i galogenvodorodnykh kislot s proizvodnymi oksatsiklobutana, soderzhashchimi morfolinometilnennyye zamestiteli [Morpholine derivatives. IV. Interaction of methyl iodide and hydrohalic acids with oxacyclobutane derivatives containing morpholinomethyl substituents]. *Chem Heterocycl Compd.* 1974; (10): 1320-1324. (in Russian).
14. Burmistr MV, Burmistr EM. Alkylaromaticheskiye poliioneny [Alkylaromatic polyionenes]. Dnipropetrovsk: UDChTU; 2005. 131 p. (in Russian).
15. Yoshizawa M, Narita A, Ohno H. Design of ionic liquids for electrochemical applications. *Aust J Chem.* 2004; 57(2): 139-144. doi: 10.1071/CH03240.