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*O.S. Sverdlikovska, B.V. Burkevich, O.V. Chervakov, K.Ye. Varlan, D.O. Chervakov***SYNTHESIS OF POLYMER IONIC LIQUIDS OF THE IONENE TYPE****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

New regularities have been discovered in the synthesis of polymer ionic liquids and ionene-type ionic liquids based on polyionenes derived from tetrahydro-1,4-oxazine. The methods for regulating the molecular weight of the synthesized polymers have been improved by varying the nature and composition of the solvent, as well as the concentration of the starting monomers. These improvements have resulted in the creation of new and promising materials. For the first time, we investigated the effects of temperature, solvent type and composition, chemical structure, and concentration of polyionenes derived from tetrahydro-1,4-oxazine on their behavior in water and water-ethanol solutions, as well as the shape of macromolecules in different solvents. Newly synthesized polymeric ionic liquids and ionene ionic liquids with an ionic conductivity of $\approx 10^{-2}$ – 10^{-5} S·cm⁻¹ and a glass transition temperature range of -150°C – -15°C exhibit five to six orders of magnitude higher ionic conductivity compared to known analogues.

Keywords: polymeric ionic liquids, ionic liquids, ionic conductivity, glass transition temperature, synthesis.

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Introduction

At this stage of industrial development, it is urgent to solve problems related to ecology, energy, conservation of natural resources, and the use of safe technologies. One promising direction for the development of high molecular compound chemistry is the synthesis of new polymers with high ionic conductivity, which are promising multipurpose materials. Currently, the development of polymer ionic liquids with a liquid state in a wide temperature range is a priority area of polymer chemistry. Polymer ionic liquids of the ionene type with specific structural and chemical characteristics of the carriers are of particular interest. They can be used as modifiers of paint and varnish materials, catalysts during chemical reactions, and solvents of natural polymers.

The effective combination of the high level properties of polymeric ionic liquids of ionene type, along with their ability to remain in a liquid state over a wide temperature range, has resulted in significant technical and economic advantages in various fields of chemistry and chemical technology. These

compounds are being used to solve urgent problems [1–7].

Considering the high ionic conductivity of ionene-type polymeric ionic liquids based on tetrahydro-1,4-oxazine derivatives [8–10] at low temperatures, it is relevant to explore methods for improving and developing new, cost-effective polymeric ionic liquids from readily available raw materials. The aim of this work is to determine the dependences of physical and chemical properties on the structure and external factors of polymeric ionic liquids of ionene type. This will involve formulating hypotheses, theories, and practical information that can be used to recommend these liquids for solving urgent scientific and technical problems in chemical technology.

Experimental

An assessment was conducted to predict the influence of the nature of radicals near the nitrogen atom of macromolecules of polymer ionic liquids of the ionene type. This was based on the results of studying the properties of synthesized ionic monomers

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with various organic cationic parts. The influence of a certain cationic part near the nitrogen atom on the properties of ionic liquids was determined on samples with a known molecular weight.

The selection of starting monomers for the synthesis of polymers and low-molecular ionic liquids in a liquid state over a wide temperature range depends on the availability of raw materials and the ability to vary the structure and molecular weight of the polymers. It was previously established [8–11] that introducing allylic and β -hydroxyethyl groups to the quaternary nitrogen atom, along with dibenzyl fragments at the cationic center and alkyl aromatic radicals, can result in the formation of ionene-type polymer ionic liquids with a low glass transition temperature and high ionic conductivity.

In the work, a new type of monomeric and dimeric ionic liquids of the ionene type based on tetrahydro-1,4-oxazine derivatives was prepared.

Halogen derivatives based on monofunctional epoxidized compounds of the brands EX-192 (HD-1, HD-2), EX-171 (HD-3), EX-141 (HD-4), and EX-145 (HD-5) were used as starting monomers for the synthesis of tertiary amines and as monomers for the synthesis of dimeric ionic liquids of the ionene type.

Dihalogen derivatives based on difunctional epoxidized compounds of the brands EX-201 (DH-1), EX-811 (DH-2), EX-214 (DH-3), EX-212 (DH-4) were used as starting monomers for the synthesis of tertiary diamines and as monomers for the synthesis of polymer ionic liquids of the ionene type.

Halogen derivatives based on monofunctional epoxidized compounds of the brand EX-192 (HD-1,

HD-2), EX-171 (HD-3), EX-141 (HD-4), and EX-145 (HD-5) and dihalogen derivatives based on difunctional epoxidized compounds of the brands EX-201 (DH-1), EX-811 (DH-2), EX-214 (DH-3), and EX-212 (DH-4) were obtained as a result of the reaction of the interaction of epoxy compounds with hydrogen chloride according to the known by the method given in ref. [13]. The reaction of the interaction of the epoxy group with hydrogen chloride is well studied and occurs unambiguously, which is confirmed by the PMR spectra of epoxy resin and the products of its interaction with hydrogen chloride at different ratios of reagents [13].

Halogen derivatives were obtained (Fig. 1) by the interaction of monofunctional epoxidized compounds with concentrated hydrochloric acid [13]. The reaction was carried out in isopropanol at room temperature for 2 hours.

Dihalogen derivatives were obtained (Fig. 2) by the interaction of difunctional epoxidized compounds with concentrated hydrochloric acid [12]. The reaction was carried out in isopropanol at room temperature for 2 hours.

The initial tertiary diamines were obtained (Fig. 3) by the interaction of tetrahydro-1,4-oxazine with dihalogen derivatives based on difunctional epoxidized compounds. The reaction (with a two-fold excess of tetrahydro-1,4-oxazine) was carried out at a temperature of 50–60°C for 8 hours. Interaction reactions of dihalogen derivatives based on difunctional epoxidized compounds with tetrahydro-1,4-oxazine occur by the mechanism of nucleophilic substitution of chlorine atoms for nitro groups [14]. The reactivity of dihalogen derivatives based on difunctional epoxidized compounds is determined by the large

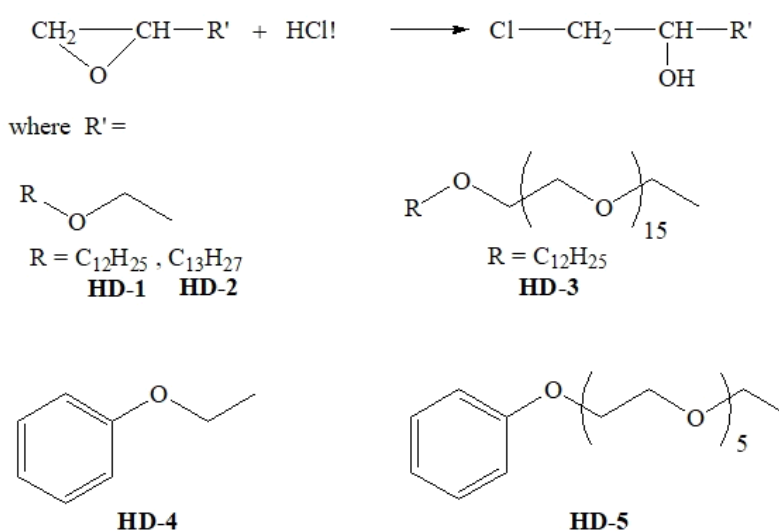


Fig. 1. Synthesis scheme of halogen derivatives based on monofunctional epoxidized compounds

negative charge of chlorine in the carbon–chlorine group. At the same time, there is a partial negative charge on the chlorine atom, and a positive charge on the carbon atom, which causes bond polarization.

Tertiary diamines based on tetrahydro-1,4-oxazine and difunctional epoxy compounds of EX-201 (DH-1), EX-811 (DH-2), EX-214 (DH-3), EX-212 (DH-4) grades were selected as initial monomers for the synthesis of polymeric ionic liquids and for the synthesis of dimeric ionic liquids with high initial

substances.

The synthesis of ionene-type ionic liquids was carried out by the interaction of tertiary amines based on tetrahydro-1,4-oxazine with halogen derivatives. General synthesis schemes are shown in Fig. 4.

The synthesis of ionene-type ionic liquids was carried out in two stages. The first stage consisted in obtaining tertiary amines as a result of the interaction of morpholine with an equimolecular amount of a halogen derivative. The synthesis was carried out at a

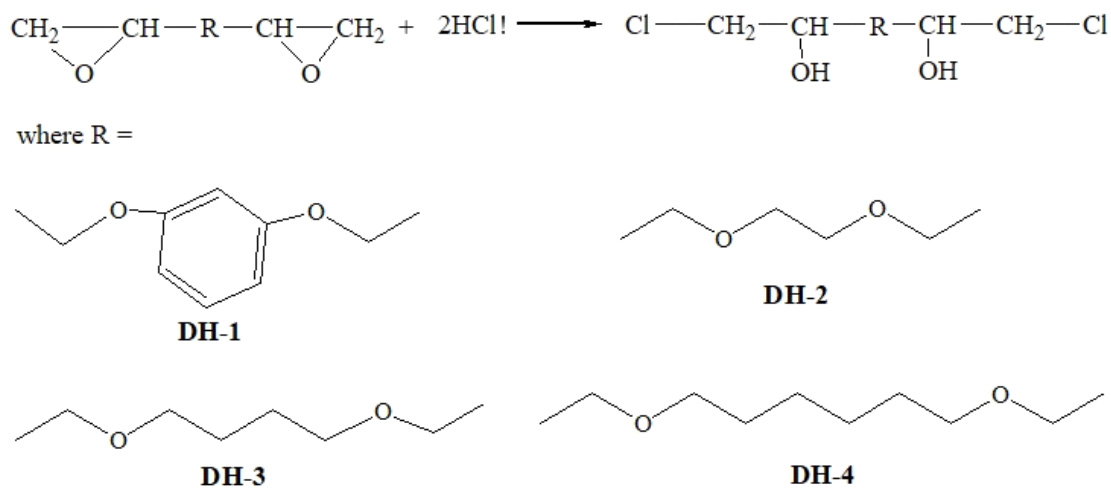


Fig. 2. Scheme of the synthesis of dihalogen derivatives based on difunctional epoxidized compounds

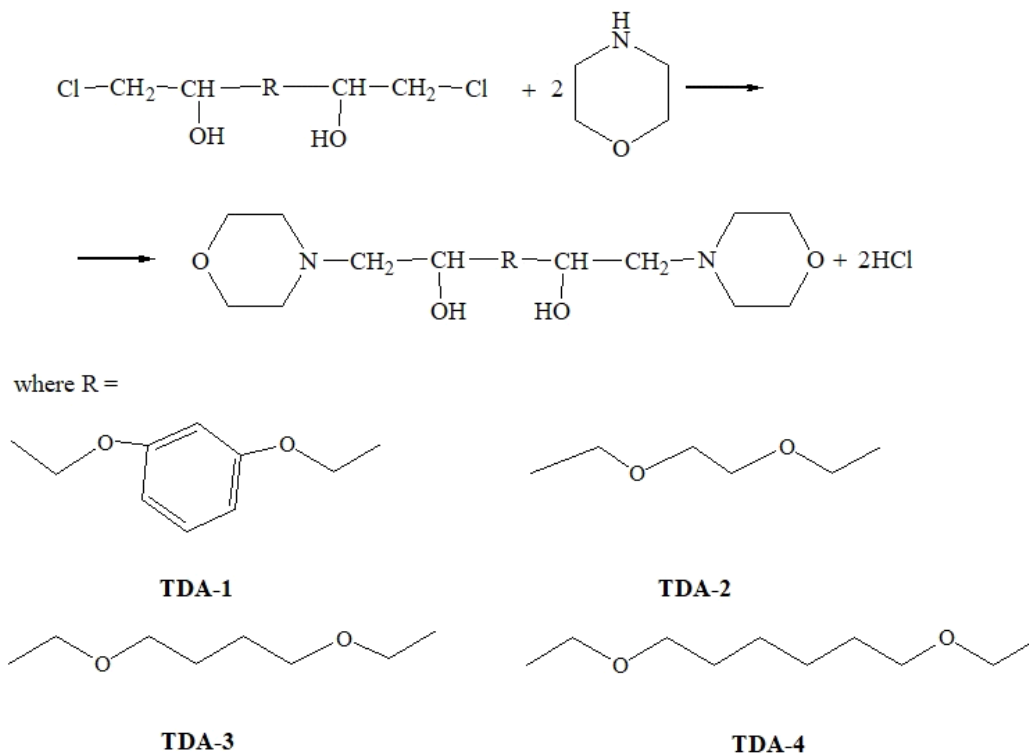


Fig. 3. Scheme of the synthesis of tertiary diamines based on tetrahydro-1,4-oxazine and epoxidized compounds

temperature of 50–60°C for 6–8 hours. At the second stage, quaternization of tertiary amine with halogen derivatives was carried out. The reaction occurs with the formation of target ionic liquids of the ionene type. The synthesis was carried out at a temperature of 50–60°C for 10–12 hours. It was established that monomeric ionic liquids of the ionene type are formed with high yields of approximately 80–95%.

The synthesis of dimeric ionic liquids of the ionene type was carried out (Fig. 5) according to the Menshutkin reaction at a temperature of 50–60°C for 10 hours according to the general scheme.

It was established that dimeric ionic liquids of the ionene type are formed with high yields of approximately 80–95%.

The ionene-type polymer ionic liquids were synthesized by reacting equimolar amounts of tertiary diamines based on tetrahydro-1,4-oxazine derivatives with dihalogen derivatives based on difunctional epoxidized compounds, following the general scheme shown in Fig. 6. As reported in ref. [15], the Menshutkin reaction takes place via the bimolecular nucleophilic substitution (SN2) mechanism in different solvents.

The results of elemental analysis and IR spectroscopy confirmed the structure of the synthesized polymer ionic liquids of the ionene type. Based on the results of IR spectroscopy of polymer ionic liquids of the ionene type, the characteristic absorption bands corresponding to the original monomer molecules

were determined. The spectra characteristic of functional groups of monomers disappear, namely: in the frequency range of 2780–2840 cm^{-1} , which correspond to the valence vibrations of the N–CH₃ group, and in the frequency range of 660 cm^{-1} , which correspond to the valence vibrations of the C–Cl group. There are characteristic bands of vibrations of the benzene fragment in the region of 1620–1520 cm^{-1} (for alkylaromatic polymer ionic liquids of the ionene type). When studying the spectrum, special emphasis should be placed on the appearance of a strong broad band at 3600–3100 cm^{-1} , which corresponds to the fluctuations of chemically bound moisture (water of crystallization) and indicates the hydrophilicity of the synthesized polymers: a property characteristic of high-molecular quaternary ammonium compounds.

Results and discussions

Study [15] has demonstrated that the synthesis of polyionenes through the Menshutkin reaction can be conducted in various solvents, including organic solvents, mixtures of organic solvents and water, and mixtures of organic solvents and ethanol. The effect of the solvent on the reaction rate of polymer formation has been studied extensively. It is important to note that synthesizing polyionenes in acetone-methanol or acetone-ethanol mixtures results in the formation of a low molecular weight polymer. Both the starting monomers and the resulting polymer are highly soluble in these solvents. This is because the reaction rate of

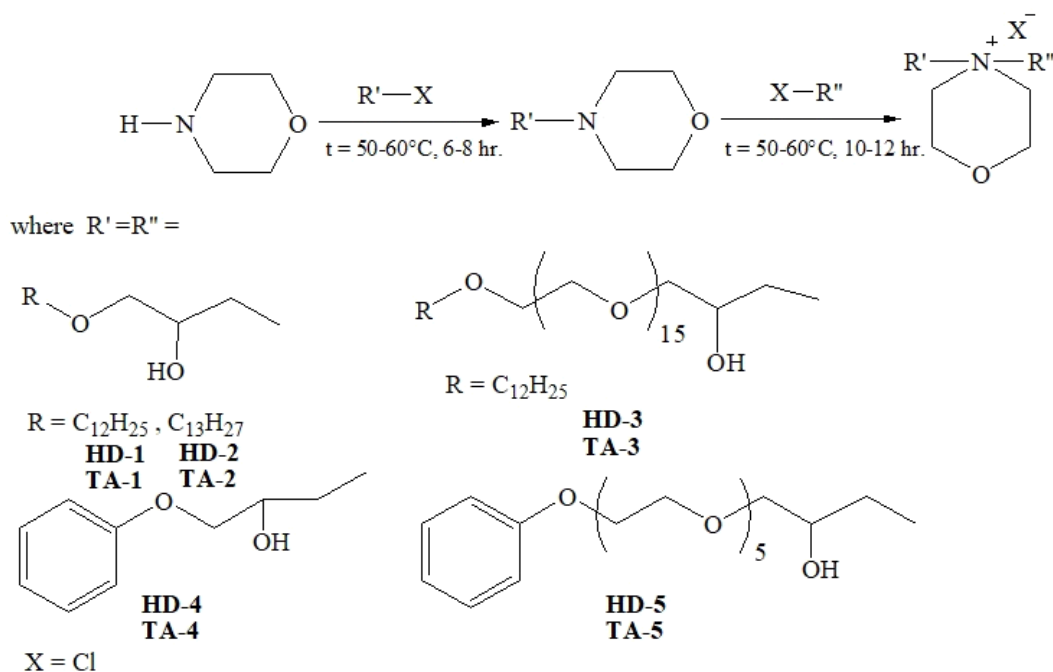


Fig. 4. Synthesis scheme of ionene-type ionic liquids. The cipher of the synthesized ionic liquids of the ionene type consists of the letter «C» and two numbers: the first number is the TA number, and the second number is the HD number

polyionene formation is mainly dependent on the solvent's dielectric constant. In their well-known work [15], the authors demonstrated that obtaining polyionene with a sufficiently large molecular weight in an acetone-water mixture is impossible. This is due to the fact that the addition of large amounts of water to the reaction mixture leads to a deterioration in the solubility of monomers and polymer chain growth products, as well as the hydrolysis of the latter and the dihalogenide. This finding is supported by the work [8] on the synthesis of polymeric ionic liquids in an acetone-water mixture. However, it is worth noting that the dielectric constant in the ethanol-water mixture is higher than in the ethanol-

methanol and acetone-ethanol mixtures. Therefore, the rate of polymer formation in the ethanol-water mixture is higher.

Research into the synthesis of polyionenes in solvents of varying composition [15] has shown this to be the most promising method of polymer production. Practically, the method involves using solvents of different natures for synthesizing a polymer product. This is because the starting monomers are soluble in organic solvents, while polyionenes are soluble in water and partially in aprotic solvents.

According to the authors of study [15], the reaction rate of polymer formation depends on both the dielectric constant of the solvent and the

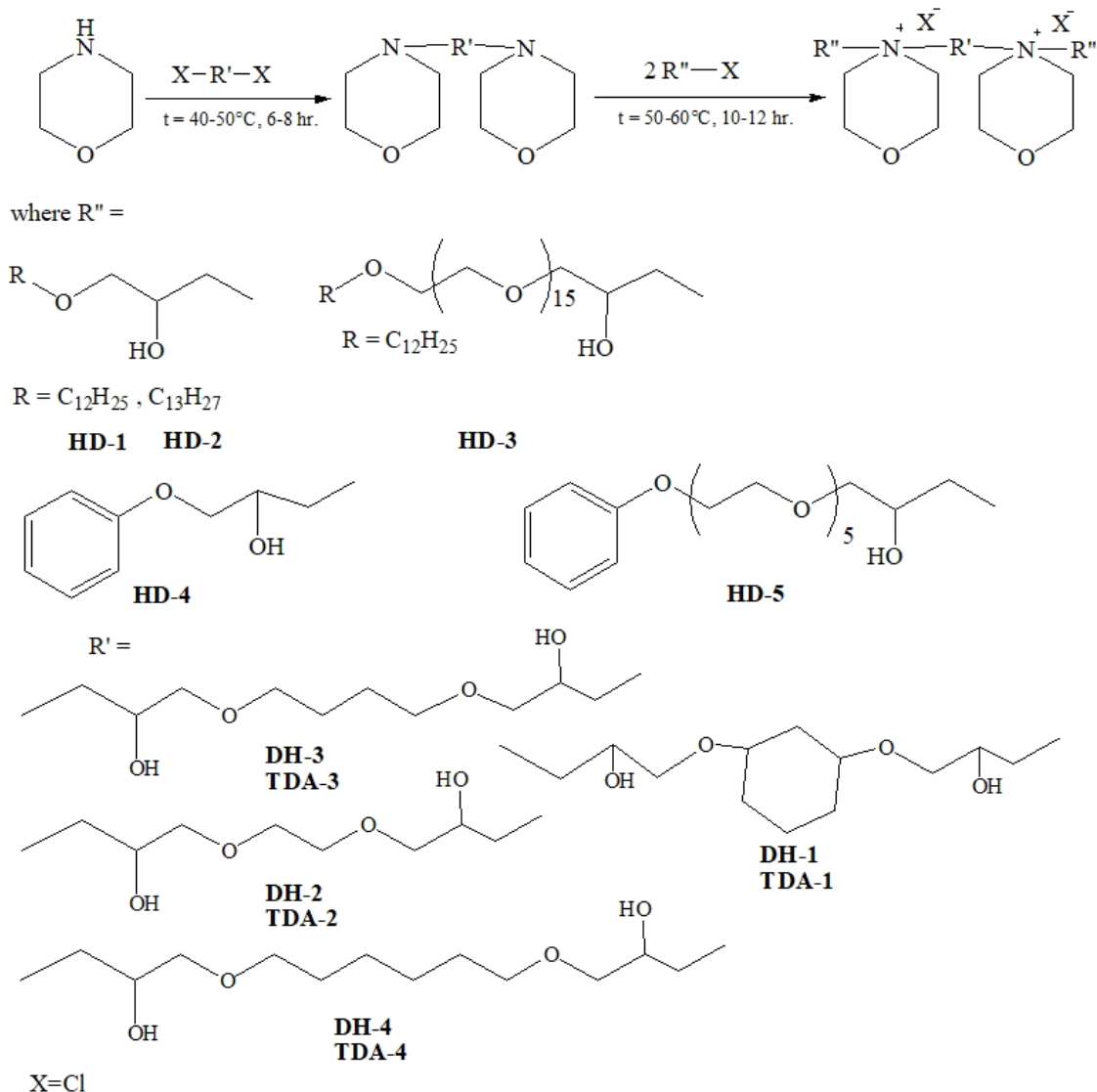


Fig. 5. Synthesis scheme of ionene-type dimeric ionic liquids. The cipher of the synthesized dimer ionic liquids of the ionene type consists of the letter «C» and two numbers: the first number is the TDA number, and the second number is the HD number

conformational state of the macromolecule of the growing polymer chain. This information does not contradict the practical data. It is important to note that if a polymer precipitates in the reaction mixture, its macromolecule is in a tangle state. When solvents that dissolve the polymer are used, the macromolecule is in an unfolded state, and active terminal functional groups are available for the reaction of polymer chain growth.

Despite the practical significance of these results, it is necessary to determine the effect of the solvent on the reaction rate of polymer formation in each case, considering the solubility of the starting monomers and polymers, as well as the conformational factor of the growing chain of the polymer macromolecule in the reaction medium.

The practicality of predicting the behavior of macromolecules in polymeric ionic liquids of the ionene type within a reaction mixture is evident. This

approach can be used to improve the methodology of synthesizing polymeric ionic liquids of the ionene type.

We investigated the dependence of the reduced viscosity of polymers of different structures on the composition of the ethanol-water mixture (Fig. 7). With an increase in the ethanol content in the ethanol-water mixture, the reduced viscosity for PIR C-4-1 and C-4-4 (Fig. 7, curves 3 and 4) increases up to an ethanol content of 30–50 vol.%. These dependences are characterized by one maximum. The dependence of the reduced viscosity of PIR C-1-1 (Fig. 7, curve 1) exhibits a maximum and a minimum: with ethanol content up to 30 vol.% and 50 vol.%, an increase in the reduced viscosity is observed, then a slight decrease viscosity, and with a further increase in the concentration of ethanol above 70 vol.%, the value of the reduced viscosity increases sharply again.

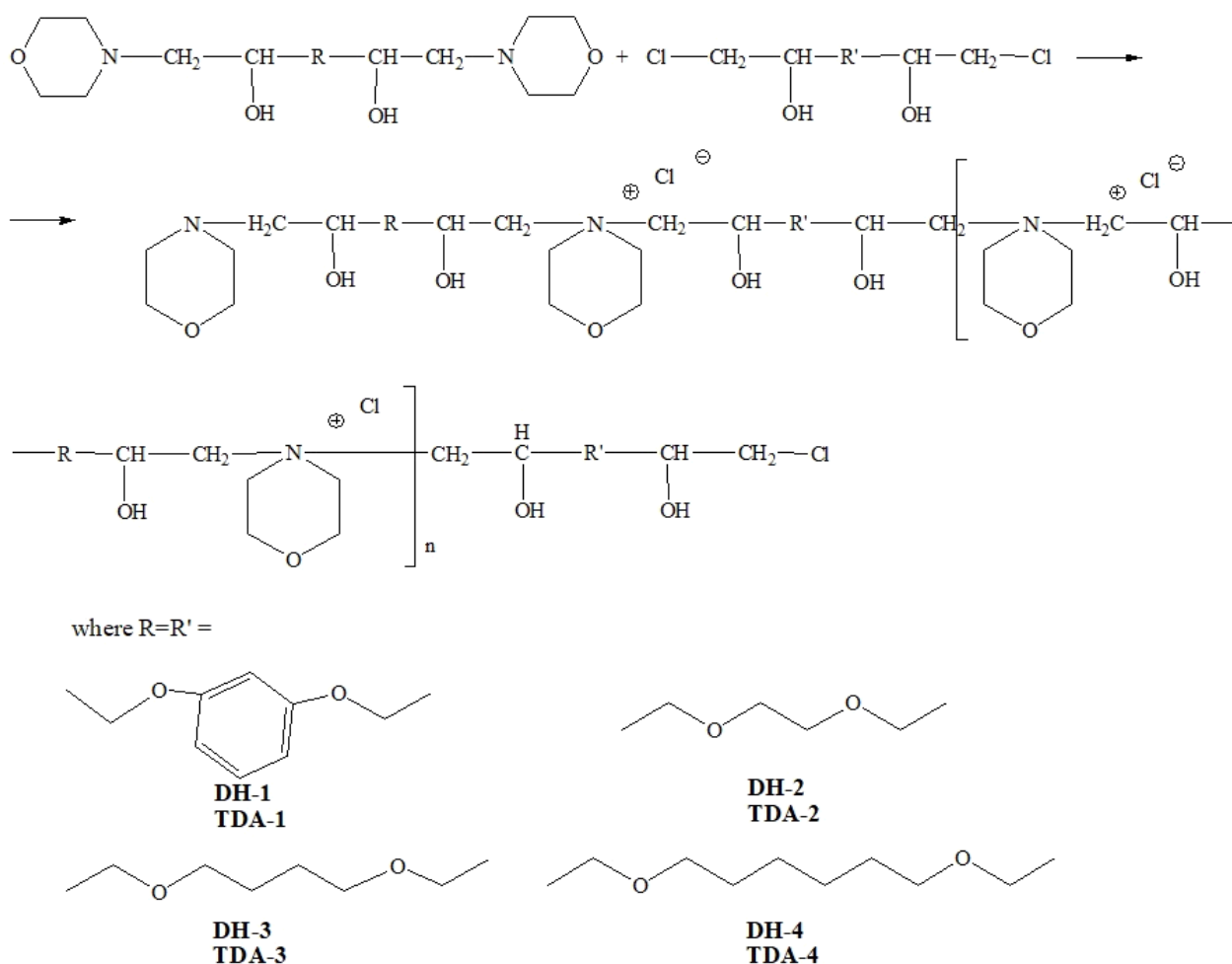


Fig. 6. Scheme of the synthesis of polymer ionic liquids of the ionene type. The code of the synthesized polymer ionic liquids consists of the letter «C» and two numbers: the first number is the TDA number, and the second number is the DH number

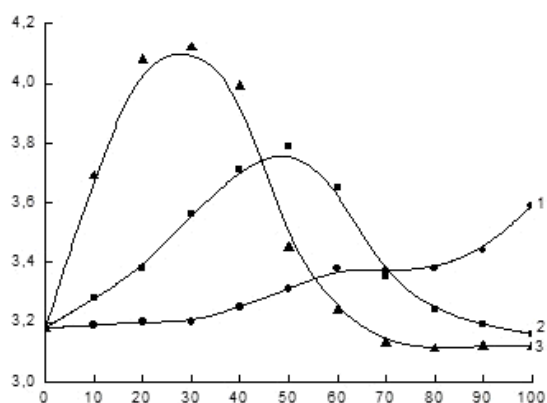


Fig. 7. Dependence of the reduced viscosity of the solution of polymer ionic liquids of the ionene type on the composition of the ethanol-water solvent at a polymer concentration of 0.1 g/dl: 1 – C-1-1; 2 – C-4-1; and 3 – C-4-4

It should be noted that, according to ref. [15], the nature of the dependence of the reduced viscosity of polymeric ionic liquids of the ionene type on the composition of the ethanol-water mixture is indicated by a decrease in the polymer viscosity is due to the suppression of the degree of dissociation of its ionogenic groups (the macromolecule acquires a more coiled conformation); an increase in the polymer viscosity in a medium with a lower dielectric constant is due to better solubility of organic polyelectrolyte molecules (unfolding of the polymer macromolecule). Changing the amount of organic solvent in the organic solvent-water mixture of a polymeric ionic liquid solution of the ionene type leads to inhibition of the degree of dissociation of the ionogenic groups of the polymer, which is determined by its hydrophobicity. This is manifested, first of all, by the fact that a small amount of organic solvent is required to inhibit the dissociation of a more coiled polymer macromolecule with a higher hydrophobicity, and a larger amount of organic solvent is required to inhibit the dissociation of a less coiled polymer macromolecule with a higher hydrophobicity.

Based on these results, it can be stated that the newly synthesized polymeric ionic liquids of the ionene type are characterized by the classical behavior of polyelectrolyte macromolecules in aqueous-organic solutions, which is a distinctive feature of the quaternary ammonium group.

The results suggest that changes in the conformation of polymer chain growth products must be considered in the synthesis of ionene-type polymeric ionic liquids in aqueous-organic solvents. This affects the activity of terminal functional groups. However, the data obtained suggest that the quality of

the solvent for polymeric ionic liquids of ionene type improves only with an increase in the ethanol content of more than 50–70 vol.% in the ethanol-water mixture, in contrast to the results of studies published in ref. [15].

It should be noted that in the synthesis of polyionenes in different solvents, the following factors are decisive for the molecular weight of the synthesized polymers: temperature, duration, reactivity and concentration of the starting monomers, etc.

Figure 8 displays the results of a study on the effect of synthesis temperature on the reduced viscosity of polymeric ionic liquids of ionene type. The data shows that the maximum molecular weight of the polymers is achieved at 50°C. The temperature dependence curves of the reduced viscosity of ionene-type polymeric ionic liquids exhibit distinct changes that can be explained as follows: Initially, there is a sharp increase in temperature due to the accelerated growth rate of the polymer chain during the synthesis process. Subsequently, the curves reach a maximum at the optimum temperature for the reaction of tertiary diamines with dihalides. Finally, a decrease in temperature above the optimum temperature is attributed to side reactions of the halogen methyl groups of dihalides. It is important to note that these observations are objective and based on empirical evidence.

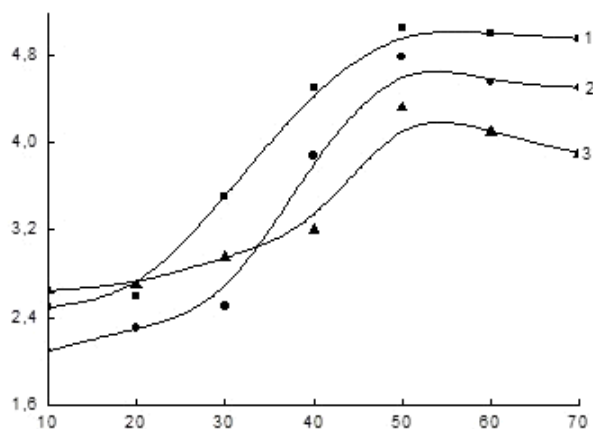


Fig. 8. Temperature dependence of the reduced viscosity of solutions of polymer ionic liquids of the ionene type at a monomer concentration of 0.5 mol/l for 8 hours:

1 – C-1-1; 2 – C-4-4; and 3 – C-1-4

It was established (Fig. 9) that the optimal time for the synthesis of polymer ionic liquids of ionene type with maximum viscosity is within 14–16 hours.

Figure 10 illustrates the relationship between the concentration of starting monomers and the reduced

viscosity of the synthesized polymeric ionic liquids of the ionene type. The viscosity reduction of synthesized polymeric ionic liquids of the ionene type occurs when the concentration of starting monomers is above 0.4 mol/L for polymeric ionic liquids of the ionene type containing radicals of aliphatic structure, and 0.5 mol/L for those containing radicals of alkylaromatic structure. The increase in the number and intensification of intra- and intermolecular interactions between the products of polymer chain growth in the reaction mixture determines the coagulation of the polymer macromolecule. Research has demonstrated that the concentration of starting monomers required to produce polymeric ionic liquids of the ionene type with maximum viscosity corresponds to the peak on this dependence, which is determined by the polymer structure. The influence of the polymer's orderly structure on the conformation of its macromolecule's growing chain and the activity of the terminal functional groups causes this phenomenon. This study is distinctive for determining the effect of electron-donating groups' presence and number in the polymer macromolecule's chain.

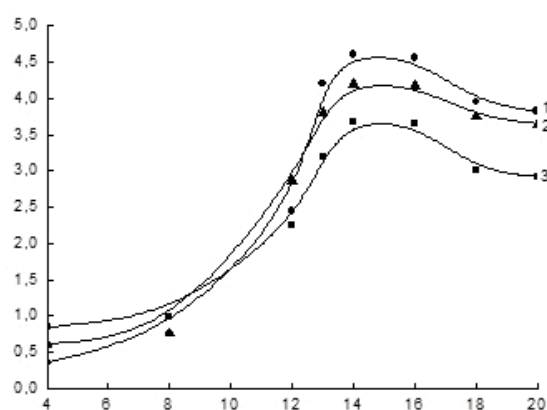


Fig. 9. Dependence of the reduced viscosity of polymer ionic liquids of ionene type on the reaction time at a monomer concentration of 0.4 mol/l and a temperature of 50°C:

1 – C-1-1; 2 – C-1-4; and 3 – C-1-2

When studying the influence of the nature of the solvent on the molecular weight of the synthesized polymers (Table), it is natural to establish the dependence of the viscosity of the obtained polymer ionic liquids of the ionene type on the composition of the solvent in which their synthesis was carried out.

It is important to note that the synthesis of polyonenes with minimal viscosity and low yield occurs in the acetone-organic solvent mixture. However, the addition of water to the solvent mixture

in different ratios of ethanol-water components results in the production of polymers with higher viscosity and lower yield. It has been established that the optimal solvent composition for synthesizing the polymeric ionic liquids of the ionene type with higher viscosity and polycondensation product yield is as follows: for polymeric ionic liquids containing alkylaromatic radicals, a solvent of variable composition consisting of 60% ethanol and 40% water should be used; for polymeric ionic liquids containing aliphatic radicals, a solvent of variable composition consisting of 50% ethanol and 50% water should be used.

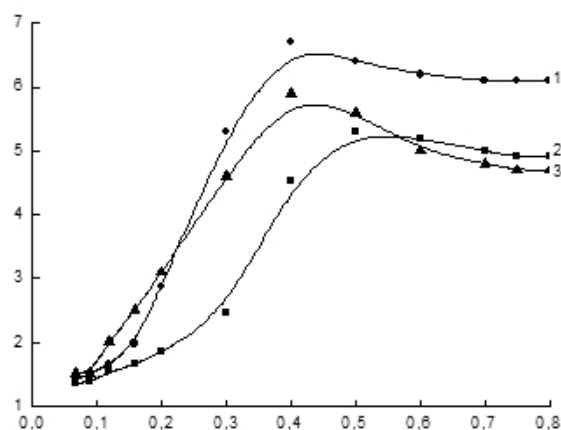


Fig. 10. Dependence of the reduced viscosity of solutions of polymer ionic liquids of the ionene type on the concentration of the initial monomers at a temperature of 50°C for 10 hours:

1 – C-1-1; 2 – C-4-4; and 3 – C-2-2

The synthesis of polymeric ionic liquids of the ionene type in a mixture of organic solvent-water of variable composition involves dissolving the starting monomers in ethanol. During the synthesis, water is gradually added to the reaction mixture to dissolve the products of the growth of the polymer macromolecule chain. This process allows for the production of a polymer with a higher viscosity and polycondensation product yield.

The studies have revealed the influence of the concentration of starting monomers, temperature, and reaction time on the synthesis of polymeric ionic liquids of the ionene type. These findings can improve the methodological approach to synthesizing polymeric ionic liquids with high ionic conductivity while maintaining their liquid state in a wide temperature range. The synthesis is achieved through the reaction of tertiary diamines and digalogenides (Fig. 8). The starting monomers were dissolved in acetone and then added to a solvent of variable composition of ethanol

Viscosity and solubility of polymer ionic liquids of the ionene type *

Tertiary diamine cipher	Dihalide cipher	Solvent (ratio)	Polymer solubility	η/C , dl/g	Yield, %
TDA-2	DH-1	ethanol-water (70:30)	well soluble	0.98	93.65
		ethanol-water (60:40)	well soluble	1.17	92.11
		ethanol-water (50:50)	well soluble	0.84	91.61
		ethanol-water (60:40 variable composition) **	well soluble	1.72	94.53
		acetone-C ₂ H ₅ OH (30:70)	insoluble or partially soluble	0.62	85.11
		acetone-C ₂ H ₅ OH (50:50)	insoluble or partially soluble	0.78	81.44
		acetone-CH ₃ OH (60:40)	insoluble or partially soluble	0.65	78.21
TDA-2	DH-3	ethanol-water (70:30)	well soluble	1.04	92.64
		ethanol-water (60:40)	well soluble	1.13	94.41
		ethanol-water (50:50)	well soluble	1.19	95.67
		ethanol-water (50:50 variable composition) **	well soluble	2.09	97.58
		acetone-C ₂ H ₅ OH (30:70)	insoluble or partially soluble	0.93	86.57
		acetone-C ₂ H ₅ OH (50:50)	insoluble or partially soluble	0.98	82.64
		acetone-CH ₃ OH (60:40)	insoluble or partially soluble	0.86	88.57
TDA-2	DH-4	ethanol-water (70:30)	well soluble	0.96	96.75
		ethanol-water (60:40)	well soluble	1.04	96.81
		ethanol-water (50:50)	well soluble	1.13	95.80
		ethanol-water (50:50 variable composition) **	well soluble	1.75	95.72
		acetone-C ₂ H ₅ OH (30:70)	insoluble or partially soluble	0.86	87.56
		acetone-C ₂ H ₅ OH (50:50)	insoluble or partially soluble	0.96	92.42
		acetone-CH ₃ OH (60:40)	insoluble or partially soluble	0.93	92.43
TDA-3	DH-2	ethanol-water (70:30)	well soluble	1.68	79.45
		ethanol-water (60:40)	well soluble	1.41	83.15
		ethanol-water (50:50)	well soluble	1.37	79.51
		ethanol-water (50:50 variable composition) **	well soluble	2.57	94.55
		acetone-C ₂ H ₅ OH (50:50)	insoluble or partially soluble	1.69	81.64
		acetone-CH ₃ OH (60:40)	insoluble or partially soluble	1.84	82.67
		C ₂ H ₅ OH	insoluble or partially soluble	1.76	85.55
CH ₃ OH	insoluble or partially soluble	1.63	81.52		

Notes: * – the synthesis of polymer ionic liquids of the ionene type was carried out at a temperature of 50°C for 8 hours. The concentration of initial monomers was 0.3 mol/l. ** – the initial ratio of ethanol-water in a mixture of variable composition was 70:30.

and water at an initial ratio of 70:30. The synthesis was carried out at 50°C for 14–16 hours until the reaction products began to precipitate. An ethanol-water mixture is then added to ionene-type polymeric ionic liquids. For those with a lower charge density in the polymer chain, the ethanol content should be 50 vol.%. For those with a higher charge density, the ethanol content should be 60%. The stages should be repeated until polymer precipitation ceases. This allows the reaction to be carried out in a homogeneous medium. As the degree of conversion of the reaction increases, the solubility of the polymer chain growth product decreases, reducing their reactivity due to coagulation. Adding an ethanol-water mixture increases the dielectric constant of the reaction medium, improving the solubility of the growing chain of polymeric ionic liquids of the ionene type due to a

change in the conformation of its macromolecule. To obtain polymeric ionic liquids of the ionene type with the highest molecular weight containing radicals of aliphatic structure, the initial concentration of the starting monomers should be 0.4 mol/l. For polymeric ionic liquids of the ionene type with the highest molecular weight containing radicals of alkyaromatic structure, the initial concentration of the starting monomers should be 0.5 mol/l.

Conclusions

1. The foundations of the methodology for obtaining monomeric and dimeric ionic liquids of the ionene type have been created for the predicted assessment of the influence of the nature of radicals near the nitrogen atom of macromolecules of polymer ionic liquids of the ionene type.

2. Methods for the synthesis of initial monomers

based on the interaction of aliphatic and alkylaromatic dihalides based on derivatives of epoxidized compounds with tetrahydro-1,4-oxazine to obtain new polymer ionic liquids of the ionene type have been developed.

3. New approaches to the synthesis of polymer ionic liquids of the ionene type have been found, which consist in the purposeful use of the features of the structure of tertiary derivatives of tetrahydro-1,4-oxazine, dihalides, and the nature and composition of the solvent. It was established that when the reaction is carried out in ethanol-water solutions of variable composition with a gradual increase in the content of the latter during the reaction. Polymer ionic liquids of the ionene type with the highest molecular weight are formed with an initial concentration of the initial monomers of 0.4–0.5 mol/l and the use of an ethanol-water solvent of variable composition at a temperature of 50°C for 14–16 hours.

4. The synthesized mono-, dimeric and polymer ionic liquids of the ionene type can be used as modifying additives of compositions based on natural polymer materials, components of liquid electrolytes for various electrochemical devices, coagulants, etc.

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СИНТЕЗ ПОЛІМЕРНИХ ІОННИХ РІДИН ІОНЕНОВОГО ТИПУ

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Виявлено нові закономірності при синтезі полімерних іонних рідин та іонних рідин іоненового типу на основі полііоненів на основі похідних тетрагідро-1,4-оксазину, удосконалено методи регулювання молекулярної маси синтезованих полімерів шляхом варіювання природи та складу розчинника, концентрації вихідних мономерів для створення нових перспективних матеріалів. Вперше встановлено вплив температури, природи і складу розчинника, хімічної будови і концентрації полііоненів на основі похідних тетрагідро-1,4-оксазину на їх поведінку у водних і водно-етанольних розчинах, форму макромолекул у різних розчинниках. Синтезовані полімерні іонні рідини та іонні рідини іоненового типу з іонною провідністю $\approx 10^{-2}$ – 10^{-5} См/см у діапазоні температур склування -150°C – 15°C мають на п'ять-шість порядків більшу іонну

провідність у порівнянні з відомими світовими аналогами.

Ключові слова: полімерні іонні рідини, іонні рідини, іонна провідність, температура склування, синтез.

SYNTHESIS OF POLYMER IONIC LIQUIDS OF THE IONENE TYPE

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New regularities have been discovered in the synthesis of polymer ionic liquids and ionene-type ionic liquids based on polyionenes derived from tetrahydro-1,4-oxazine. The methods for regulating the molecular weight of the synthesized polymers have been improved by varying the nature and composition of the solvent, as well as the concentration of the starting monomers. These improvements have resulted in the creation of new and promising materials. For the first time, we investigated the effects of temperature, solvent type and composition, chemical structure, and concentration of polyionenes derived from tetrahydro-1,4-oxazine on their behavior in water and water-ethanol solutions, as well as the shape of macromolecules in different solvents. Newly synthesized polymeric ionic liquids and ionene ionic liquids with an ionic conductivity of $\approx 10^{-2}$ – 10^{-5} S·cm⁻¹ and a glass transition temperature range of -150°C – -15°C exhibit five to six orders of magnitude higher ionic conductivity compared to known analogues.

Keywords: polymeric ionic liquids; ionic liquids; ionic conductivity; glass transition temperature; synthesis.

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