ISSN 0321-4095, Voprosy khimii i khimicheskoi tekhnologii, 2024, No. 6, pp. 101-109

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

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SYNTHESIS OF POLYMER IONIC LIQUIDS AND IONENE-TYPE IONIC LIQUIDS

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The synthesis of polymer ionic liquids and ionene-type ionic liquids has been optimized through the implementation of a rigorous scientific and methodical approach. The feasibility of utilizing an integrated «polymer—monomer» strategy for synthesizing polymer ionic liquids has been demonstrated. The concentration-dependent viscosity of ionene-type polymer ionic liquids in solutions was analyzed, and the influence of their chemical nature was elucidated. Practical recommendations have been developed to address the scientific and applied challenges associated with creating new ionene-type polymer ionic liquids that exhibit high ionic conductivity while maintaining a liquid state over a wide temperature range. These findings aim to solve pressing issues in chemical technology.

Keywords: polymer ionic liquids, ionic liquids, synthesis, viscosity, ionic conductivity.

DOI: 10.32434/0321-4095-2024-157-6-101-109

Introduction

In the light of the accelerated advancement of the ecological dimension as a core component of social development, the creation of novel polymer ionic liquids with an elevated degree of ionic conductivity has emerged as a pivotal area of focus. The most pressing issues in this field pertain to the stabilization of liquid states across a broad temperature range and the reduction of ionic liquid costs. Ionic liquids are currently employed in a multitude of applications, including as components of liquid and polymer electrolytes for electrochemical devices, extractants, solvents, and catalytic media in organic and polymer synthesis. Among the polymer materials of the modern industry of high molecular compounds, particular attention is directed towards polyionenes, which is due to their effective utilisation in a range of fields within the chemical sciences and chemical technology, including as ionic liquids.

Previous studies [1—3] have focused on addressing current scientific challenges, namely the development of novel polymer ionic liquids and ionene-type ionic liquids based on tetrahydro-1,4-oxazine with high ionic conductivity, which maintain a liquid state across a wide range of temperatures. This enables the expansion of the potential applications of such compounds. The studies yielded several noteworthy findings, among which the following are particularly noteworthy: In a novel development, new polymer ionic liquids and ionene-type ionic liquids based on tetrahydro-1,4-oxazine have been created. These have been found to exhibit markedly enhanced ionic conductivity ($\sim 10^{-1}-10^{-6}$ $Sm\cdot cm^{-1}$) at a considerably reduced melting temperature (-28^0C to -135^0C) in comparison to the previously documented global analogs based on polymeric ionic liquids obtained through radical polymerization of methacrylate monomers, specifically pyrrolidinium and imidazolium derivatives ($\sigma=10^{-6}-10^{-10}$ $Sm\cdot cm^{-1}$; $T_{mp}=-8\div80^0C$).

It is therefore reasonable to suggest that research aimed at establishing the regularities of the synthesis of new polymer ionic liquids of the ionene-type based on quaternary morpholinium salts with a low glass transition temperature and high ionic conductivity should be considered relevant. The implementation of the strategic direction of improving the scientific and methodological approach to obtaining polymeric ionic liquids and ionic liquids of a liquid aggregate state in a wide range of temperatures is carried out by using available raw materials of starting monomers

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with different functional groups, varying the structure and molecular weight of polymers, as well as a predicted assessment of the influence of the nature of radicals near the atom nitrogen macromolecules of polymer ionic liquids of the ionene-type on objects of synthesized ionic monomers with various organic cationic parts. Research aimed at establishing the dependences of the physicochemical properties of polymer ionic liquids and ionic liquids distinguished by the nature of the charge of their macromolecules, the type of cation, the degree of delocalization, and the size of anions, the mobility of ion centers, and external factors should also be considered relevant for the purpose of predicting the possibility of effectively solving urgent scientific problems and technical problems of chemical technology. The results obtained will facilitate the formulation of new hypotheses and theories that build upon existing ideas within the scientific field of ionic liquids.

Experimental

A review of the literature revealed that there is currently no consensus among researchers on the controlled synthesis of polymeric ionic liquids. Studies [4–8], conducted by domestic and foreign scientists, demonstrated this lack of consensus. All existing concepts provide a framework for understanding the relationship between the physical and chemical properties of polymer solutions, their structure, and the nature of the solvent. This understanding is crucial for developing polymer ionic liquids of the ionene-type, as it determines the conditions under which these liquids can be obtained.

In the course of the work, a novel class of mono-, dimeric, and polymer ionic liquids of the ionene type, based on quaternary morpholinium salts, was developed.

Halogen derivatives based on monofunctional epoxidized compounds of the EX-121 (HD-1), EX-142 (HD-2), EX-146 (HD-3) (Fig. 1) and dihalogen derivatives based on difunctional epoxidized compounds of the EX-211 brand (DH-1), EX-252 (DH -2), EX-721 (DH -3), EX-920 (DH -4), EX-931 (DH -5) (Fig. 2) were obtained by the interaction of epoxy compounds with concentrated hydrochloric acid according to the well-known method given in ref. [9]. The reaction was conducted at room temperature for a period of two hours. In the initial, rapid and reversible phase, epoxy compounds are protonated by the oxygen atom, resulting in the formation of an oxonium ring. In the second slow stage, a nucleophilic attack by a halide ion of the protonated form of epoxy compounds occurs. Paken [9] demonstrated and validated the reaction of the epoxy group with hydrogen chloride through the analysis of PMR spectra of epoxy resin and its products at varying ratios of reagents. Their findings confirm that this interaction has been extensively studied and occurs with definitive outcomes.

Halogen derivatives based on monofunctional epoxidized compounds of the brands EX-121 (HD-1), EX-142 (HD-2), EX-146 (HD-3) were used as starting monomers for the synthesis of tertiary amines and as monomers for the synthesis of dimeric ionic liquids of ionene-type Dihalogen derivatives based on difunctional epoxidized compounds of the brands EX-211 (DH-1), EX-252 (DH-2), EX-721 (DH-3), EX-920 (DH-4), EX-931 (DH-5) 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.

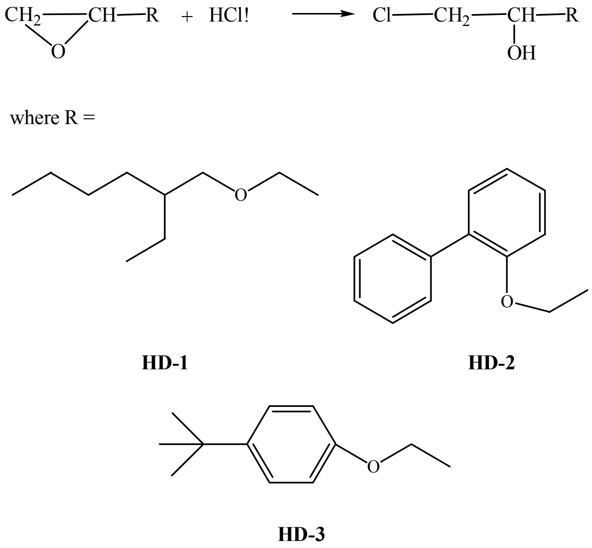

Fig. 1. Synthesis scheme of halogen derivatives based on monofunctional epoxidized compounds

The starting tertiary amines (Fig. 3) and tertiary diamines (Fig. 4) were obtained through the interaction of tetrahydro-1,4-oxazine with dihalogen derivatives based on difunctional epoxidized compounds. The synthesis (in the case of obtaining a tertiary amine with an equimolecular amount of tetrahydro-1,4-oxazine, and a tertiary diamine – with a two-fold excess) was carried out at a temperature of 50–60^{0}C for 6–8 hours. The reactivity of mono- and dihalogen derivatives based on epoxidized compounds is determined by the large negative charge of chlorine in the carbon–chlorine group. Concurrently, a partial negative charge is observed on the chlorine atom, while a positive charge is evident on the carbon atom, resulting in bond polarization. The reactions take place according to the mechanism of nucleophilic substitution of chlorine atoms for nitro groups by opening the epoxy ring under the action of nucleophilic reagents due to electrophilic action [10].

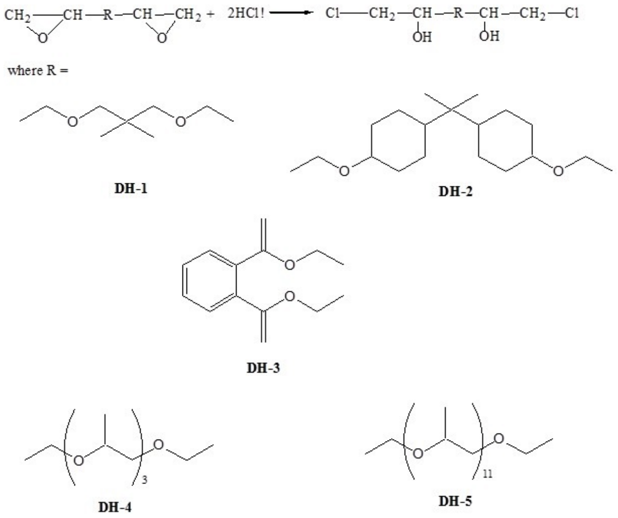

Fig. 2. Scheme of the synthesis of dihalogen derivatives based on difunctional epoxidized compounds

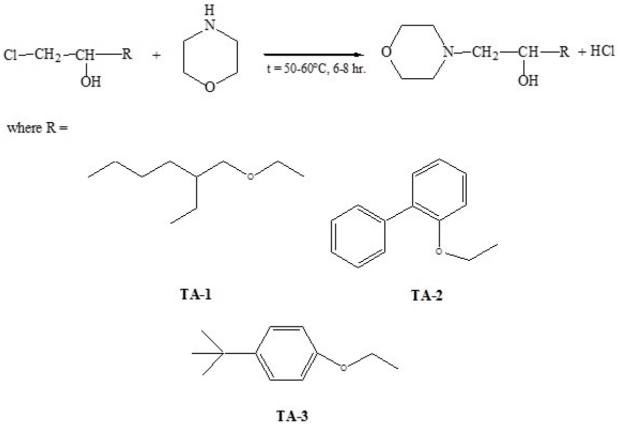

Fig. 3. Scheme of the synthesis of tertiary amines based on tetrahydro-1,4-oxazine and epoxidized compounds

For the synthesis of ionic liquids with high yields, tertiary amines based on tetrahydro-1,4-oxazine and monofunctional epoxidized compounds of the brands EX-121 (TA-1), EX-142 (TA-2), EX-146 were selected as starting monomers (TA-3). For the synthesis of polymeric ionic liquids and for the synthesis of dimeric ionic liquids with high yields, tertiary diamines based on tetrahydro-1,4-oxazine and difunctional epoxidized compounds of the brand were isolated EX-211 (TDA-1), EX-252 (TDA-2), EX-721 (TDA-3), EX-920 (TDA-4), EX-931 (TDA-5).

The synthesis of ionene-type ionic liquids was achieved through the interaction of tertiary amines based on tetrahydro-1,4-oxazine with halogen derivatives. The general synthesis schemes are illustrated in Fig. 5. The reaction of obtaining ionic liquids of the ionene-type was carried out at a temperature of 50–60^{0}C for 10–12 hours. At the stage of formation of target ionic liquids of the ionene-type, quaternization of tertiary amine with halogen derivatives was carried out. It was established that monomeric ionic liquids of the ionene type are formed with high yields ~75–98%.

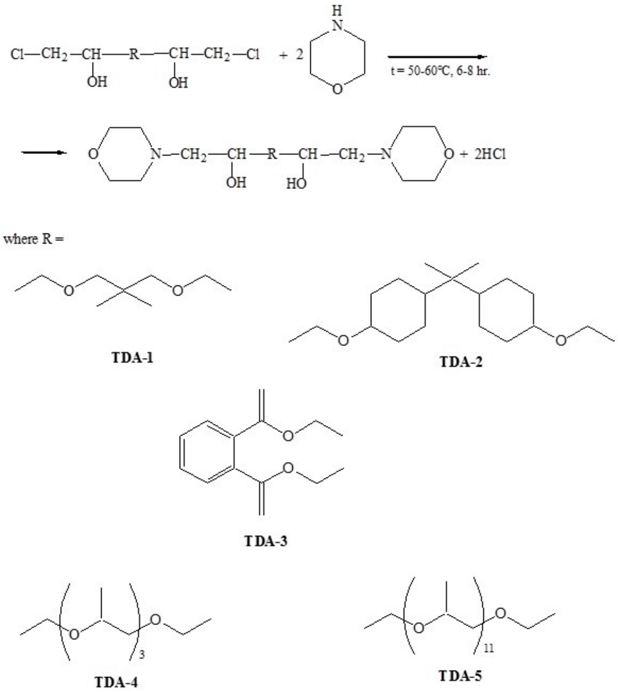

Fig. 4. Scheme of the synthesis of tertiary diamines based on tetrahydro-1,4-oxazine and epoxidized compounds

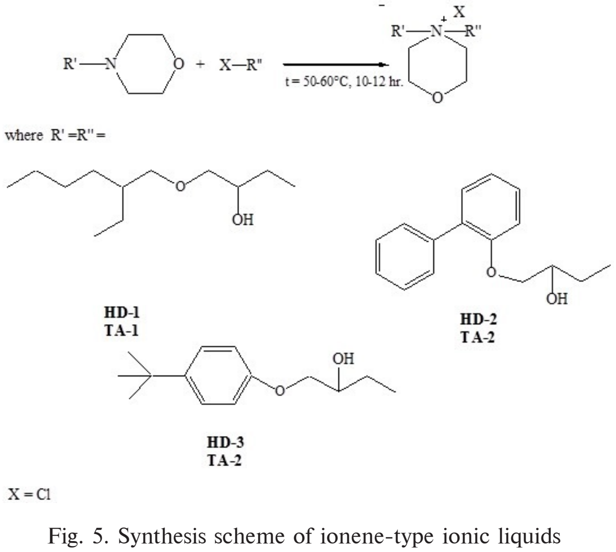

Fig. 5. Synthesis scheme of ionene-type ionic liquids

The synthesis of ionene-type dimeric ionic liquids was conducted by reacting equimolecular amounts of tertiary diamines based on tetrahydro-1,4-oxazine derivatives with halogen derivatives based on monofunctional epoxidized compounds at a temperature of 50–60^{0}C for a period of 10 hours. The syntheses were conducted in accordance with the general scheme depicted in Fig. 6. It was demonstrated that dimeric ionic liquids of the ionene-type are formed with high yields ~68–97%.

The synthesis of polymer ionic liquids of the ionene type was carried out (Fig. 7) according to the Menshutkin reaction, which according to ref. [15] occurs according to the (S_N2) mechanism of bimolecular nucleophilic substitution in various solvents.

Results and discussion

A distinctive feature of the study of the synthesis of mono- and dimeric ionic liquids of the ionene-type based on quaternary morpholinium salts was the determination of the possibility of obtaining ionic liquids without the use of solvents in which the reaction is carried out. The investigation of this phenomenon has revealed the potential for the synthesis of ionic liquids that can maintain a liquid aggregate state across a broad temperature range through the application of green chemistry principles.

The effect of the concentration of initial monomers, temperature and reaction time of the interaction of tertiary diamines and dihalides on the molecular weight of the synthesized polymer ionic liquids of the ionene-type was investigated in the paper. In a previous study [11], it was demonstrated that the synthesis of polyionenes in a solvent of variable ethanol–water composition at an initial ratio of 70:30 at a temperature of 55–60^{0}C for 18–20 hours results in the formation of sufficiently large molecular weight polymer ionic liquids of the ionene-type. Additionally, the optimal concentration of the initial monomers was found to vary from 0.4 to 0.6 mol/l, depending on the structure of the monomers.

It was revealed the correlation between the reduced viscosity of polymer ionic liquids of the ionene-type and the reaction temperature of tertiary diamines with dihalides. It was demonstrated that the maximum viscosity of polymer ionic liquids of the ionene-type is attained at a temperature of 50^{0}C. This suggests that the initial increase in the reduced viscosity of polymer ionic liquids with rising temperatures during the initial stages of the synthesis process is linked to acceleration in the growth rate of the polymer macromolecule chain. Conversely, the subsequent decline in reduced viscosity of polymer ionic liquids with further temperature increases is attributed to the occurrence of side reactions involving the chloromethyl groups of dichlorides.

As previously established in ref. [11], the optimal time for the synthesis of polymer ionic liquids of the ionene-type with maximum viscosity is within 18–20 hours. A similar regularity of the change in reduced

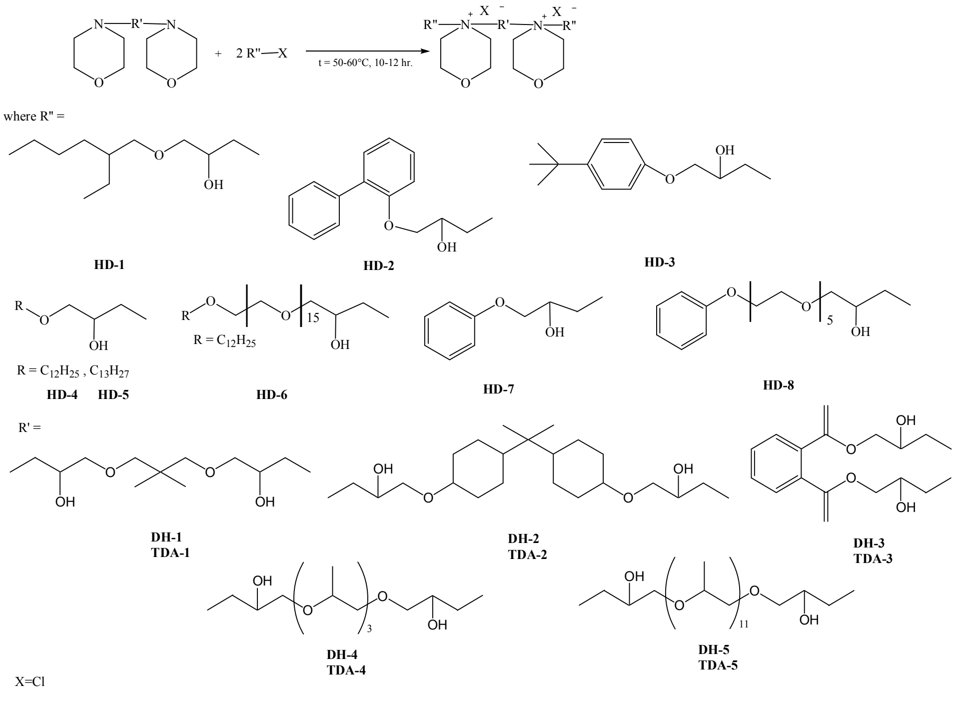

Fig. 6. Synthesis scheme of ionene-type dimeric ionic liquids

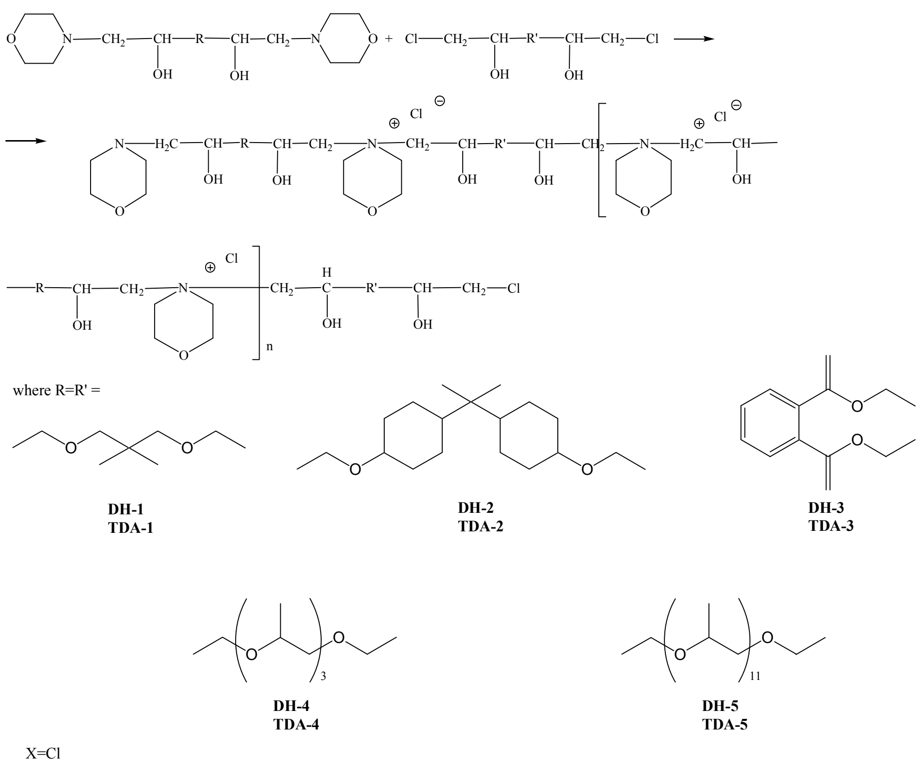

Fig. 7. Scheme of the synthesis of polymer ionic liquids of the ionene type

viscosity is characteristic of the studied polymer ionic liquids of the ionene-type with a maximum at the same duration of the reaction of tertiary diamine with dichloride, which is 20 hours.

It should be noted that it is possible to synthesize polymer ionic liquids of the ionene-type at a temperature of 25^0C to the boiling point of the solvent, but the duration of the reaction will be more than 100 hours.

The paper presents the results of the study of the effect of the concentration of the initial monomers on the value of the reduced viscosity of the synthesized polymer ionic liquids of the ionene-type. It is important to note that the optimal concentration of initial monomers for obtaining polymer ionic liquids of the ionene-type, which contain radicals of an aliphatic structure with maximum viscosity, corresponds to the maximum on this dependence at a concentration of initial monomers higher than 0.3 mol/l, and for polymeric ionic liquids of the ionene-type, which contain radicals of the alkylaromatic structure (0.6 mol/l). In other words, the polymer macromolecule undergoes a collapse, which is caused by an increase in the number and strengthening of intra- and intermolecular interactions between the products of polymer chain growth in the reaction mixture. Additionally, it has been observed that the position of the maximum on the dependence of the reduced viscosity of the synthesized polymers on the concentration of the initial monomers is determined by the structure of polymer ionic liquids. This is due to the influence of the orderliness of the structure of the polymer on the conformation of the growing chain of its macromolecule and, accordingly, on the activity of the final functional groups.

Despite the large number of works [12] dedicated to the study of the influence of the solvent on the reaction rate of the formation of polyionenes according to the Menshutkin reaction, in each individual case, depending on the structure of the initial monomers, it is necessary to establish the effect of the solvent on the reaction rate of the formation of the polymer, taking into account the solubility of the initial monomers and polymers, as well as conformational factor of the growing chain of the polymer macromolecule in the reaction medium.

According to literature sources [12], it was established that the synthesis of polyionenes in solvents of various nature and variable composition is the most promising method. This is explained by the fact that the original monomers are soluble in organic solvents, and polyionenes are soluble in water and partially in aprotic solvents.

In works [1,12], it was demonstrated that it is unfeasible to synthesize a polyionene with an adequate molecular weight in an acetone—water mixture. This is due to the fact that the addition of a considerable quantity of water to the reaction mixture results in a notable decline in the solubility of monomers and the products of polymer chain growth and hydrolysis of the latter, as well as dihalides. The conducted studies [12] of the influence of the solvent on the reaction rate of polymer formation demonstrated that the dielectric constant in the ethanol—methanol, acetone—ethanol mixture is lower than in the ethanol—water mixture. Consequently, the rate of polymer formation in the ethanol—water mixture is higher.

The results of the study of the effect of the nature and composition of the solvent in which the synthesis was carried out on the viscosity of polymer ionic liquids of the ionene-type are shown in Table. The data obtained allows for the estimation of the impact of solvent nature on the molecular weight of the synthesized polymers, which is a crucial step in the further improvement of the synthesis methodology of polymeric ionic liquids of the ionene type.

It was established that in the acetone-organic solvent mixture polyionenes are synthesized with minimal viscosity and low yield of the polycondensation product, which is due to the effect of the dielectric constant of the solvent on the reaction rate of polyionene formation. The addition of water to the solvent mixture in a different ratio of acetone-water components leads to obtaining polymers with higher viscosity and the yield of the polycondensation product. This phenomenon can be attributed to the fact that the addition of a considerable quantity of water to the reaction mixture results in a notable decline in the solubility of monomers and the products of polymer chain growth and hydrolysis of the latter, as well as dihalides. The elevated viscosity and yield values of the synthesized polymers in the acetone—water reaction medium across varying ratios of components substantiate the prevailing concepts. The dielectric constant in the acetone—ethanol, ethanol—methanol mixtures is observed to be inferior to that of the ethanol—water mixture, thereby indicating that the rate of polymer formation in the ethanol—water mixture is superior. It is important to note that the enhancement of the quality of the solvent for polymer ionic liquids of the ionene type is only observable when the ethanol content of the ethanol—water mixture exceeds 50—70 vol.%. In the light of the aforementioned considerations, it is imperative to provide a concise overview of the following. It is possible to obtain an ionene-type polymer ionic liquid with a higher viscosity and polycondensation product yield. This can be achieved by preparing polymer ionic liquids containing aliphatic radicals (e.g., ethanol and water in a solvent of variable composition at a ratio of 50:50) and alkylaromatic radicals (e.g., ethanol and water in a solvent of variable composition at a ratio of 70:30).

The findings of the conducted research are applicable from a practical standpoint, providing a rationale for enhancing the methodology for synthesizing polymer ionic liquids of the ionene type with high ionic conductivity while maintaining their liquid state across a broad temperature range. The synthesis of polymer ionic liquids of the ionene type is achieved through the interaction of the obtained tertiary diamines and dihalides. The synthesis of polymer ionic liquids of the ionene type was conducted in a solvent of variable ethanol—water composition, with an initial ratio of 70:30, at a temperature of 50^0C for 20 hours. The reaction was conducted in a homogeneous medium, specifically an ethanol—water mixture with an ethanol content of 30 vol.% for ionene-type polymer ionic liquids with a lower charge density in the polymer chain and 50 vol.% for ionene-type polymer ionic liquids with a higher charge density in the polymer chain. Taking into account the essential role of the conformation factor of the growing chain of the polyionene macromolecule in the reaction medium, these actions must be repeated until the polymer deposition stops. According to the existing ideas: in the case when the polymer precipitates in the reaction mixture, its macromolecule is in the state of a ball, that is, as the degree of reaction conversion increases, the solubility of the polymer chain growth product and their reactivity decrease; upon addition of an ethanol—water mixture (the dielectric constant of the reaction medium increases), in which the polymer is dissolved, its macromolecule is in an unfolded state, active terminal functional groups are on the surface of the polymer coil and are available for the polymer chain growth reaction, i.e. to increase the rate of the polymer formation reaction with a higher molecular weight. The initial concentration of the initial monomers for obtaining polymer ionic liquids of the ionene type with the highest molecular weight, which contain radicals of the aliphatic structure, is 0.3 mol/l, and for polymer ionic liquids of the ionene type with the largest molecular weight, which contain radicals of the alkylaromatic structure, it is 0.6 mol/l.

According to the results of IR spectroscopy of the synthesized polymer ionic liquids of the ionene-type, a strong broad band of 3600—3100 cm^{-1} appears, which corresponds to fluctuations of chemically bound moisture (water of crystallization) and indicates the hydrophilicity of the synthesized polymers (a property

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

Cipher code of tertiary diamine	Cipher code of dichloride	Solvent (ratio)	Specific viscosity, η_s	Polymer solubility	Yield, %
DA-14	DC-14	acetone–water (70:30)	0.72	well soluble	86.56
		acetone–water (60:40)	0.61	insoluble or partially soluble	81.25
		acetone–water (50:50)	0.52	insoluble or partially soluble	78.63
		acetone–water (50:50 variable composition)**	0.48	insoluble or partially soluble	86.67
		acetone–ethanol (50:50)	0.88	well soluble	75.75
		acetone–methanol (60:40)	0.43	well soluble	73.38
		ethanol	0.95	insoluble or partially soluble	79.86
		methanol	0.88	well soluble	75.34
DA-11	DC-11	ethanol–water (70:30)	1.81	well soluble	97.45
		ethanol–water (60:40)	1.86	insoluble or partially soluble	95.94
		ethanol–water (50:50)	2.06	insoluble or partially soluble	94.62
		ethanol–water (50:50 variable composition)**	2.95	insoluble or partially soluble	90.45
		acetone–ethanol (30:70)	0.93	well soluble	74.51
		acetone–ethanol (50:50)	0.99	well soluble	79.55
		acetone–methanol (60:40)	0.75	well soluble	76.28
		acetone–water (70:30)	1.49	well soluble	83.98
		acetone–water (60:40)	1.66	insoluble or partially soluble	86.79
		acetone–water (50:50)	1.54	insoluble or partially soluble	83.33
		acetone–water (60:40 variable composition)	1.78	insoluble or partially soluble	79.99
DA-13	DC-13	ethanol–water (70:30)	1.48	insoluble or partially soluble	95.58
		ethanol–water (60:40)	1.36	well soluble	95.45
		ethanol–water (50:50)	1.28	insoluble or partially soluble	92.67
		ethanol–water (50:50 variable composition)**	1.30	insoluble or partially soluble	93.59
		acetone–ethanol (60:40)	0.83	well soluble	89.17
		acetone–methanol (60:40)	0.77	well soluble	77.31
		ethanol	1.07	well soluble	88.85
		methanol	0.27	well soluble	73.79
		acetonitrile	0.48	well soluble	82.55
DA-12	DC-12	ethanol–water (70:30)	1.73	well soluble	97.52
		ethanol–water (60:40)	1.85	insoluble or partially soluble	89.53
		ethanol–water (50:50)	1.99	insoluble or partially soluble	98.67
		ethanol–water (50:50 variable composition)**	2.65	insoluble or partially soluble	94.31
		acetone–ethanol (30:70)	0.86	insoluble or partially soluble	86.27
		acetone–ethanol (50:50)	0.93	well soluble	84.28
		acetone–methanol (60:40)	0.79	well soluble	85.49

Notes: * — the synthesis of polymer ionic liquids of the ionene type was carried out at a temperature of 50^0C for 10 hours. The concentration of initial monomers is 0.5 mol/l; ** — the initial ratio of ethanol—water or acetone—water in a mixture of variable composition 70:30.

characteristic of high molecular quaternary ammonium compounds); 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—CH$_3$ 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 oscillations of the benzene fragment in the region of 1620–1520 cm^{-1} (for alkylaromatic polymer ionic liquids of the ionene-type). The structure of the synthesized polymer ionic liquids of the ionene type was confirmed using elemental analysis.

Conclusions

1. New regularities of the influence of synthesis conditions on the structure of polymer ionic liquids and ionic liquids of the ionene-type based on quaternary morpholinium salts were revealed, the technique of regulating the molecular weight of synthesized polymers by varying the temperature and duration of synthesis, the nature and composition of the solvent, as well as the concentration of the initial monomers New approaches to the synthesis of mono- and dimeric ionic liquids of the ionene-type have been found, which consist in carrying out the reaction without solvents. Polymeric ionic liquids of the ionene-type with the highest molecular weight are formed at an initial concentration of initial monomers of 0.3–0.6 mol/l and using an ethanol–water solvent of variable composition at a temperature of 50^{0}C for 20 hours.

2. The theoretical foundations of the synthesis of new polymeric materials and their monomer analogues, ionic liquids based on quaternary morpholinium salts, have been developed by predicting the «synthesis–structure–properties» relationship, which is the basis for creating a methodology for obtaining materials with a high level of properties.

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Received 13.08.2024

СИНТЕЗ ПОЛІМЕРНИХ ІОННИХ РІДИН ТА ІОННИХ РІДИН ТИПУ ІОНЕНІВ

О.С. Свердліковська, М.О. Потапчук

Синтез полімерних іонних рідин та іонних рідин типу іоненів було оптимізовано шляхом застосування строго наукового та методичного підходу. Продемонстровано можливість використання інтегрованої «полімер–пономерної» стратегії для синтезу полімерних іонних рідин. Досліджено концентраційно-залежну в'язкість полімерних іонних рідин типу іоненів у розчинах та з'ясовано вплив їх хімічної природи. Розроблено практичні рекомендації для вирішення наукових і прикладних завдань, пов'язаних зі створенням нових полімерних іонних рідин типу іоненів, що характеризуються високою іонною провідністю при збереженні рідкого стану у широкому температурному діапазоні. Отримані результати спрямовані на вирішення актуальних проблем хімічної технології.

Ключові слова: полімерні іонні рідини; іонні рідини; синтез; в'язкість; іонна провідність.

SYNTHESIS OF POLYMER IONIC LIQUIDS AND IONENE-TYPE IONIC LIQUIDS

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The synthesis of polymer ionic liquids and ionene-type ionic liquids has been optimized through the implementation of a rigorous scientific and methodical approach. The feasibility of utilizing an integrated «polymer–monomer» strategy for synthesizing polymer ionic liquids has been demonstrated. The concentration-dependent viscosity of ionene-type polymer ionic liquids in solutions was analyzed, and the influence of their chemical nature was elucidated. Practical recommendations have been developed to address the scientific and applied challenges associated with creating new ionene-type polymer ionic liquids that exhibit high ionic conductivity while maintaining a liquid state over a wide temperature range. These findings aim to solve pressing issues in chemical technology.

Keywords: polymer ionic liquids; ionic liquids; synthesis; viscosity; ionic conductivity.

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