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Perspective polyionens with special properties

Abstract: *New polyionens based on epoxy derivatives of 1,2-epoxy-4,7-dioxononen-8 and tetrahydro-1,4-oxazine were synthesized. The basic regularities of polyionen synhthesis were established. Systematic study of the physico-chemical, optical, thermal and viscosimetric properties of new polyionens was carried out. It was found that the obtained polyionens are capable of operating in the range from -54 to 140^{0}C. The ionic conductivity of synthesized polyionens are 10^{-2}-10^{-4} Cm·cm^1. Thus, the studied polyionens can be recommended for use as a component of liquid, polymeric lithium electrolytes, solar cells, condensers, as effective additives for cellulose triacetate compositions, as coagulants in the treatment of sewage.*
Keywords*: polyionen, ionic liquid, cellulose triacetate, coagulant*

1. INTRODUCTION

At present, the trends of polymer chemistry are aimed at finding ways to rational use of known polymeric materials with special properties. A promising direction for the development of chemistry of macromolecular compounds is the synthesis of polyionens based on epoxidized derivatives with given properties. The analysis of patent and scientific literature has shown the existence of several problems, namely the safety of polymers for the environment, reducing the cost of their production, expanding areas of polymers application.

The synthesis of environmentally safe polyionens, the study of their physico-chemical properties, ionic conductivity, coagulation capacity and application possibilities are relevant.

2. TEST METHODS

Previously, the direct synthesis of polyionens based on tetrahydro-1,4-oxazyne and epoxidized derivatives of 1,2-epoxy-4,7-dioxononen-8 (PITE) was conducted [1].

The structure of synthesized PITE was confirmed by elemental analysis, IR spectroscopy. The physical and chemical properties of PITE with functional groups were examined by potentiometric, argentometric, pycnometric and optical methods. The possibilities of PITE practical application as ionic liquids, effective modifiers of polymer materials based on cellulose triacetate, coagulants for sewage illumination were studied.

3. MATERIALS USED IN RESEARCH

The objects of the study are polyionens based on tetrahydro-1,4-oxazine (M = 87,12; d_{20} = 999 kg/cm^3; n_{D20} = 1,429; T_b = 128,9^{0}C) and epoxidized derivatives of 1,2-epoxy-4,7-dioxononen-8 (PITE). Their structure is presented in the fig.1 and the table 1.

For the synthesis of tertiary diamine, dihalogenide based on epoxidized derivatives of 1,2-epoxy-4,7-dioxononen-8 (1mol) was mixed with morpholine (2mol). The resulting tertiary diamines were purified by the addition of 40% saturated sodium hydroxide solution and vacuum distillation.

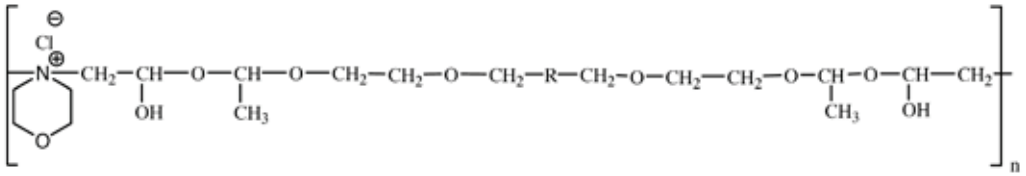
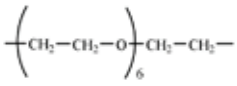
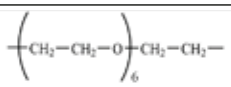
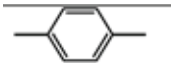
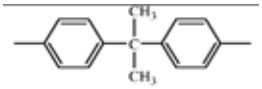
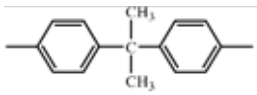


Fig. 1. The general formula of the synthesized polyionens

Table 1. Fragments of PITE polyionens structure

Polyionen symbol	R	R′
PI-1-1		
PI-1-2		
PI-1-3		
PI-1-4		
PI-2-2		
PI-3-3		
PI-4-4		

4. RESULTS OF THE RESEARCH AND THEIR DISCUSSION

The new PITE were synthesized by the Menshutkin reaction (Fig.2).

The reactions for obtaining dihalogenides based on epoxidized derivatives of 1,2-epoxy-4,7-dioxononen-8 and tertiary diamines based on tetrahydro-1,4-oxazine was carried out. The reaction was conducted at 50-60^{0}C for 25 hours, in the mixture of ethanol and water as a solvent, what allowed to dissolve used monomers and formed polymers.

The structure of synthesized PITE was studied by IR spectroscopy. The characteristic absorption bands in the PITE macromolecule correspond to the initial molecules of the monomers, excluding the final groups and quaternary nitrogen atoms.

The content of chlorine and nitrogen atoms in the new PITE macromolecule was determined by argentometric and potentiometric methods. It was established that the PITE with aliphatic structure had a higher refractive index and a lower density than aromatic PITE.

It was shown that PITE could be concerned as heat-resistant compounds in the range 50-140^{0}C. According to thermographic analysis PITE characterized by thermal stability up to 50^{0}C (PI-1-1 and PI-2-2); 75^0 C (PI-1-2). It should be noticed that PI-1-2 is more resistant to thermooxidative degradation. Almost the same correlation for PITE was observed during autocatalytic decomposition. At the final stage of thermooxidative destruction PITE was not fully decomposed - formed a mass balance.

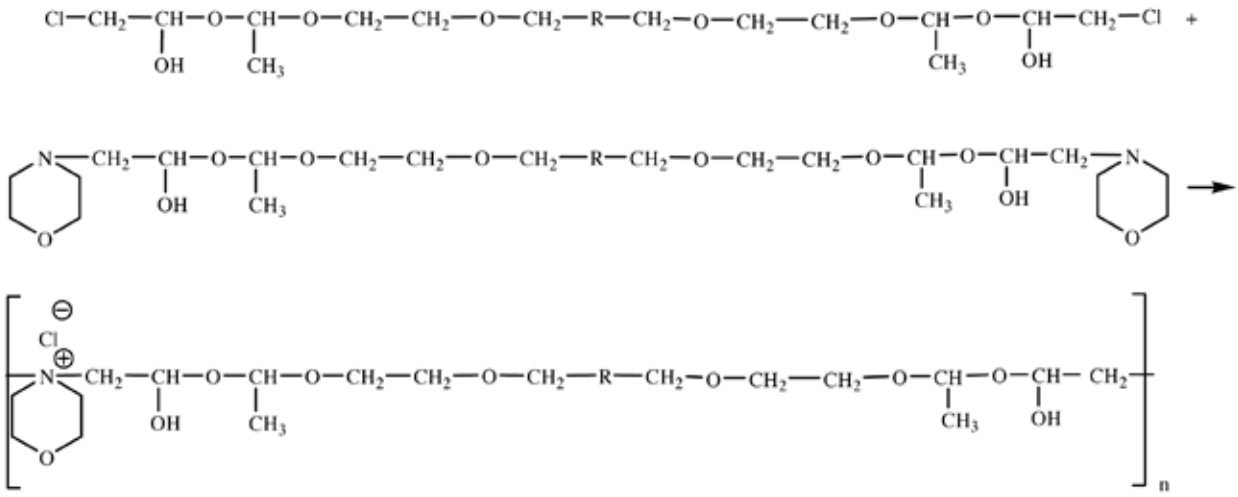


Fig. 2. Scheme of polyionen synthesis

In this work the reduced viscosity of aqueous solutions of synthesized PITE was investigated. It was found that a decrease of the concentration of PITE in water led to an increase of the reduced viscosity, what indicates a decrease of polymer-polymer interactions. Further reduction of the concentration of synthesized PITE solutions led to a sharp increase of the reduced viscosity.

During evaluation of the reduced viscosity of PITE aqueous solutions it was found that PI-1-2 was characterized by the highest values of reduced viscosity, and PI-4-4 possessed the smallest values of the reduced viscosity.

The specific and molar ionic conductivity of PITE have high values (10^{-2}-10^{-4} Cm·cm^{-1}) (fig.3 and 4) [2]. A systematic study of the effect of temperature, nature and symmetry of cation-radical, the distance between the atoms of quaternary nitrogen macromolecule ionic conductivity of PITE were conducted. It was

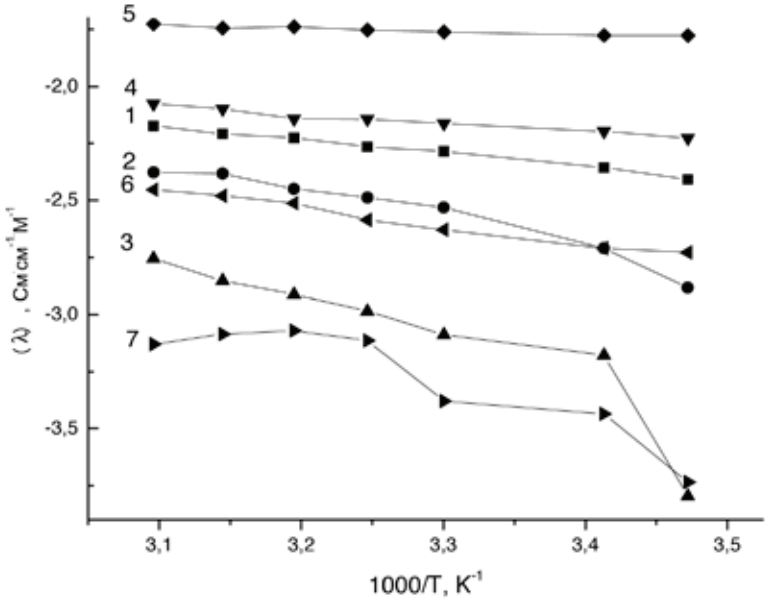


Fig. 3. Temperature (1000/T) dependence of polyionens ionic conductivity (logσ): 1 –PI-1-1; 2 – PI -1-2; 3 – PI -1-3; 4 – PI -1-4; 5 – PI -2-2; 6 – PI -3-3; 7 – PI -4-4

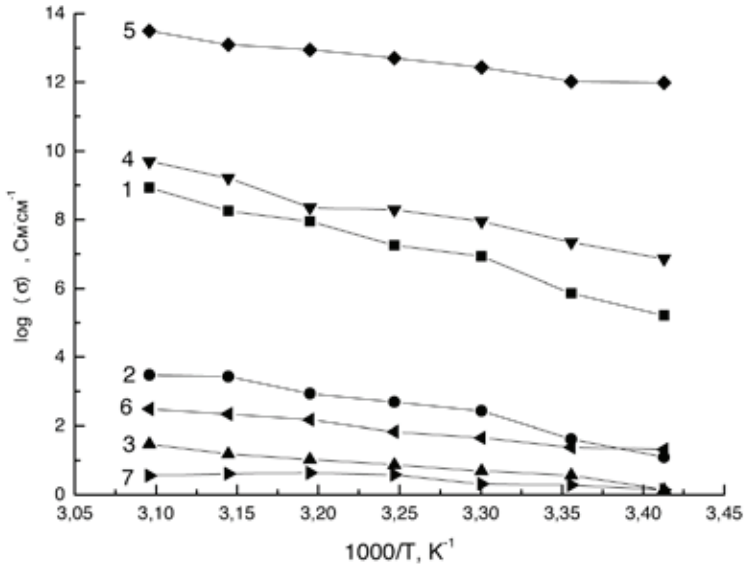


Fig. 4. The Arrhenius curves of molar ionic conductivity (λ) of polyionens: 1 – PI-1-1; 2 – PI-1-2; 3 – PI-1-3; 4 – PI-1-4; 5 – PI-2-2; 6 – PI-3-3; 7 – PI-4-4

found that specific and molar ionic conductivity of PITE increased with increasing temperature. It was revealed that PITE with symmetric radicals had higher ionic conductivity than PITE with asymmetrical radicals. It was established that the ionic conductivity decreased for PITE with increasing distance between atoms in the macromolecule quaternary oxide.

Synthesized PITE are promising ionic liquids of a new type. Therefore new PITE can be recommended for use as a component of liquid polymer electrolytes for new type of electrochemical devices (in lithium batteries, capacitors, solar batteries etc.).

A systematic study of the possibility of using PITE as an effective additive of cellulose triacetate compositions was made. The relative hardness of polymeric films based on cellulose triacetate was determined. Also the tensile strength and relative elongation at breakage of film polymeric materials based on cellulose triacetate were tested by using break-down machine type FP-10. The coefficient of light transmission of prepared films was evaluated on a photometer KFK-3. It was found that the most effective modifier of cellulose triacetate compositions was PITE with one aromatic radical in the o-position and one binuclear radical used in the amount of 0,01% by weight of cellulose triacetate.

The influence of structure and concentration of investigated PITE on the velocity and completeness of precipitation of bentonite clay was studied. The coagulability of epoxidized polyoxyens and tetrahydro-1,4-oxazine was determined by the speed and completeness of bentonite clay precipitation and by measuring the turbidity of a clay solution on a KFK-3 photometer. It was found that precipitation of a bentonite clay suspension did not occur due to self-coagulation. The new type of PITE can be successfully applied in the treatment of sewage and household water.

5. CONCLUSIONS

New polyionens based on epoxy derivatives of 1,2-epoxy-4,7-dioxononen-8 and tetrahydro-1,4-oxazine were successfully synthesized. The basic regularities of synthesis of new polyionens were studied. The viscosimetric properties of new polyionens in aqueous and water-ethanol solutions were investigated at different

temperatures. The physical-chemical, optical and thermal properties of synthesized polyionens were studied. It was found that the obtained polyionens were capable of operating in the range from -54 to 140^0C. The synthesized polyionens have high ionic conductivity in the range 10^{-2}-10^{-4} Cm·cm^{-1}. PITE are promising ionic liquids and can be recommended for use as a component of liquid polymer electrolytes for electrochemical devices of new type. A systematic study of the possibility of using new polyionens as effective additives of cellulose triacetate compositions was made. The possibility of using new polyionens as coagulants in the treatment of sewage was established.

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