

Structure and Properties of Electroactive Composites Based on Oligomers of Different Molecular Weight Doped with Lithium Perchlorate Salt

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Polymer mixtures are an important object of scientific and industrial interest and doping with salts is a common way to implement composite conductivity. The structure and properties of composites based on oligomers of different molecular weight, namely amorphous diglycidyl ether of poly(ethylene glycol) (DEG-1, $M_w = 372$ g/mol) and highly crystalline poly(ethylene glycol) (PEG, $M_w = 10,000$ g/mol), and Li^+ ions have been investigated. Polymeric organic-inorganic systems have been investigated by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS), and broadband dielectric spectroscopy. Using DSC and WAXS methods, it has been shown that composites with PEG have an amorphous-crystalline structure. The average crystallite size is 4.0 nm according to the study of WAXS. The DSC method revealed a decrease in the degree of PEG crystallinity in the composite due to the plasticizing ability of DEG-1 and the interaction of PEG with lithium perchlorate salt. Using the SAXS method, it has been established that there are regions of heterogeneity with a size of 95-130 nm in the volume of the studied composites. Studies of the electrical characteristics of polymer systems have shown that the doping of the composite with a lithium salt leads to an increase in the conductivity of the samples by two orders of magnitude. The temperature dependences of the conductivity at direct current for the studied composites do not obey the Arrhenius dependence and are analyzed using the Vogel-Tamman-Fulcher equation. The studied composites can be attributed to fragile.

Keywords: Epoxy oligomer, Poly(ethylene glycol), Lithium salt, Structure, Properties.

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1. INTRODUCTION

Significant efforts of researchers in the field of polymers are aimed at obtaining multifunctional materials [1] with lower cost, increased productivity and service life. Polymer mixtures are of great industrial importance because they have a wide range of electrical and mechanical properties compared to their individual components [2].

Epoxy polymers are of great interest because the chemistry of epoxy resins and a wide range of commercially available options allow them to be obtained with a very wide range of properties, such as high thermal insulation or thermal conductivity combined with high electrical resistance, optical transparency and heat resistance. Nitrogen-based (amines, imidazole) or anhydride-based compounds are mainly used as hardeners for epoxy systems [3].

Poly(ethylene glycol) (PEG) is a widely studied substance characterized by low lattice energy, high solvation capacity for alkali metal salts, flexible chain, high ionic conductivity in the amorphous phase, but poor mechanical properties and dimensional instability at high temperatures [4-6].

A wide variety of solid electroactive composites have been developed by combining different combinations of salts and polymer matrices [1]. Doping with lithium salts is an important criterion for realizing the conductivity of a composite, because they have high solubility, electrochemically and thermally stable, and also due to the specific properties of lithium ions (for example, their small size), which ensures the migration of Li^+

ions along the polymer chain [4].

Diglycidyl ether of poly(ethylene glycol) (DEG) and PEG have the same chain structure, thanks to which the oligomers are able to dissolve large concentrations of inorganic salts, including lithium salts. Also, they contain ether oxygen in the chain, which gives them an affinity for the ability to transport lithium cations.

Thus, the aim of the work is to study the structure of composites based on oligomers of different molecular weight and to study the influence of the dopant – positive lithium ions on the level of conductivity.

2. EXPERIMENTAL

To create composites, an aliphatic epoxy oligomer was used – diglycidyl ether of poly(ethylene glycol) (DEG-1, 90 %) with a molar weight $M_w = 372$ g/mol and polyethylene polyamine (PEPA) was used as a hardener (10 %). The content of lithium perchlorate salt LiClO_4 as well as PEG-10000 are 20 phr to 100 % of the polymer matrix.

Thermophysical characteristics have been studied by differential scanning calorimetry (DSC) on a TA Instruments DSC Q2000 device in a temperature range from -50 to $+160$ °C with a linear heating rate of 10 °C/min. Glass transition temperatures (T_g) were determined on DSC curves during the second heating.

The peculiarities of the orderliness of macrochain fragments according to their translation in the volume of polymer composites have been studied by the method of wide-angle X-ray scattering (WAXS) on a DRON-4.07 X-ray diffractometer, the X-ray optical scheme of which

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was made according to the Debye-Scherrer method for the passage of the primary irradiation beam through the investigated polymer sample, using monochromatized by a Ni filter $\text{CuK}\alpha$ -radiation ($\lambda = 1.54 \text{ \AA}$). As a source of characteristic X-ray radiation, a BSV27Cu X-ray tube operating in the mode of $U = 30 \text{ kV}$ and $I = 30 \text{ mA}$ was used. The research was carried out by the method of automatic step-by-step scanning in the range of scattering angles (2θ) from 2.6 to 40 degrees; the exposure time was 5 s.

The heterogeneous structure of composites (at the nanometer level) was studied via small-angle X-ray scattering (SAXS) with a CRM-1 camera having a slit collimator of the primary irradiation beam made via the Kratky method. The geometric parameters of the camera satisfied the condition of infinite height of the primary beam [7]. The intensity profiles were normalized to the volume of X-ray scattering and the attenuation factor of the primary beam of the test sample. All X-ray diffraction studies were performed in $\text{CuK}\alpha$ radiation monochromatized with a Ni-filter at $T = 20 \pm 2 \text{ }^\circ\text{C}$.

The study of the electrical and dielectric characteristics of the systems was carried out using a high-resolution broadband dielectric analyzer "Novocontrol Alpha" with the Novocontrol Quatro Cryosystem, equipped with a two-electrode circuit, in the frequency range of 10^{-1} - 10^7 Hz and a temperature range from -60 to $+180 \text{ }^\circ\text{C}$. The rate of heating and cooling was $2 \text{ }^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. The voltage applied to the sample was equal to 0.5 V . The studied samples were round in shape with a diameter of 30 mm and a thickness of 0.5 mm , on which an aluminum coating, which served as electrodes, was previously sprayed in a vacuum. The data were analyzed using the software "Novocontrol WinDETA" version 3.8.

3. RESULTS AND DISCUSSION

Analysis of the thermograms showed that the glass transition temperature of the DEG-1/PEPA polymer matrix (Fig. 1, curve 1) is $-10 \text{ }^\circ\text{C}$, and when 20 phr LiClO_4 is added to the composition of this polymer matrix (Fig. 4, curve 2), T_g increases to $25 \text{ }^\circ\text{C}$. Some polymer composites reported in the literature showed a similar trend when lithium salt was added [4, 8, 9], which can be explained by the formation of coordination complexes and a decrease in the segmental mobility of polymer chains in the formed complexes, which leads to an increase in the glass transition temperature T_g of the composites [10].

As can be seen from Fig. 1 (curves 3 and 4), when 20 phr of PEG is added to the composition of the DEG-1/PEPA matrix, an endothermic peak appears on the DSC curves, which corresponds to the melting of the PEG crystalline phase and indicates the amorphous-crystalline structure of the composites. The melting of PEG in the polymer (Fig. 1, curve 3) is manifested by the presence of two endothermic maxima with $T_{m1} = 61.8^\circ\text{C}$ and $T_{m2} = 64.5^\circ\text{C}$, respectively, which indicates the presence of two types of crystallites in its crystalline phase. From the analysis of curve 4 (Fig. 1), it can be seen that when 20 phr LiClO_4 is added to the DEG-1/PEPA/PEG system, one endothermic maximum at $T_m = 60.5 \text{ }^\circ\text{C}$ is responsible for the melting of PEG,

and this peak shifts to lower temperatures, indicating the interaction between the lithium salt and PEG [11].

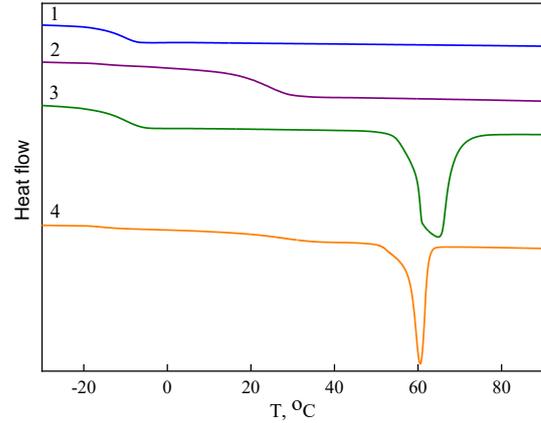


Fig. 1 – DSC curves of composites: DEG-1/PEPA (1), DEG-1/PEPA/ LiClO_4 (2), DEG-1/PEPA/PEG (3), DEG-1/PEPA/PEG/ LiClO_4 (4)

The degree of crystallinity (X_{cr}) of the composites was calculated according to the equation:

$$X_{cr} = \frac{\Delta H_m}{\Delta H_m^0} \cdot 100\%,$$

where ΔH_m is the melting enthalpy of the polymer determined experimentally from DSC; ΔH_m^0 is the melting enthalpy of 100 % crystalline polymer (for PEG with a molecular weight of $10,000 \text{ g/mol}$ $\Delta H_m^0 = 196.8 \text{ J/g}$ [12]).

Calculations showed that the degree of crystallinity of the DEG-1/PEPA/PEG system is 11.4 %, and when the composite is doped with 20 phr of LiClO_4 , it is 10.7 %. This indicates a decrease in the crystallinity degree of PEG in the system due to the plasticizing effect of DEG-1 and the interaction of PEG with LiClO_4 ; as well as an increase in the segmental movement of the polymer, which leads to better ion diffusion and, accordingly, to an increase in conductivity.

Analysis of a wide-angle X-ray diffraction pattern of an epoxy cross-linked polymer with *in situ* components, namely PEG and LiClO_4 salt (Fig. 2), showed that this polymer composite has an amorphous-crystalline structure. At the same time, the crystalline structure is manifested by PEG, and the amorphous structure is inherent to the epoxy polymer, which allows us to call this polymer system "semi-interpenetrating networks". This is indicated by the appearance against the background of an imaginary diffraction maximum of the diffuse type (amorphous halo), the angular position ($2\theta_m$) of which is about 20.2° , of two main intensity-based diffraction maxima of the discrete type ($2\theta_m = 19.4^\circ$ and 22.78°), which characterize the crystal structure of the PEG component. The relative level of crystallinity (X_{cr}) of the composite doped with LiClO_4 salt was evaluated according to the method of the authors of the paper [13]:

$$X_{cr} = Q_{cr} / (Q_{cr} + Q_{am}) \cdot 100\%,$$

where Q_{cr} and $(Q_{cr} + Q_{am})$ are the areas under the "crystalline" part and the entire X-ray pattern in the information interval of scattering angles 2θ (from 9.3° to 37.6°); it was found that $X_{cr} \approx 13$.

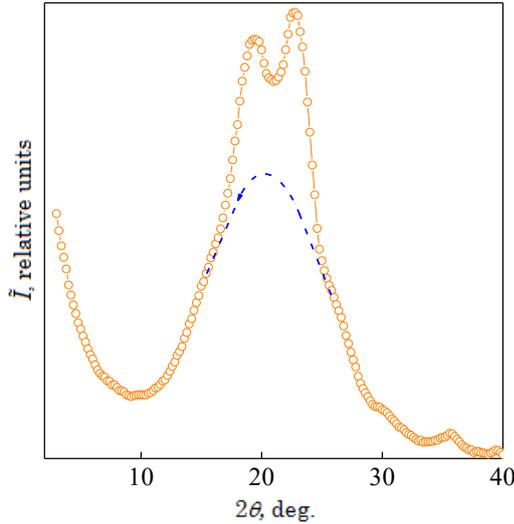


Fig. 2 – WAXS pattern of the DEG-1/PEPA/PEG/LiClO₄ composite (dashed line shows trace of amorphous halo)

In turn, the estimation of the average value of the crystallite size (L) of PEG (in the direction of $2\theta_m = 19.4^\circ$ and 22.7°) was carried out via the Scherrer method [14]:

$$L = K\lambda(\beta\cos\theta_m)^{-1},$$

where K is a constant ($K = 0.89$ if the shape of the crystallites is unknown), λ is the wavelength of characteristic X-ray radiation ($\lambda = 0.154$ nm), and β is the angular half-width of discrete-type singlet diffraction maxima; it was found that $L = 4.0$ nm.

For a more complete characterization of the structure of the samples, the method of SAXS was used. Thus, when analyzing the profile of the intensity of SAXS of the composite, presented both as a dependence of \bar{I} on q (Fig. 3) and as a dependence of $s^3\bar{I}(s)$ on s^3 (Fig. 4), according to works [15, 16], where s is the value of the wave vector in the space of the inverse lattice ($s = \lambda^{-1}\sin\theta$), it was found that despite the amorphous-crystalline structure of this sample, the electron density contrast $\Delta\rho$ in its volume is rather small (Fig. 4). A fairly small value may be the result of a gradual decrease in volume density in the series: Li⁺ and ClO₄⁻ ions – PEG crystallites – amorphous nanosized PEG regions – amorphous epoxy polymer.

To estimate the effective size of the heterogeneity regions existing in the volume of the composite of the studied polymer systems, a structural parameter such as the range of heterogeneity l_p [17] was determined according to the method of W. Ruland [15, 16]. This parameter is directly related to the average diameter of the heterogeneity regions in the two-phase system ($\langle l_1 \rangle$ and $\langle l_2 \rangle$):

$$l_p = \varphi_2\langle l_1 \rangle = \varphi_1\langle l_2 \rangle,$$

where φ_1 , φ_2 are the volume fractions of the regions ($\varphi_1 + \varphi_2 = 1$). It was established that there are regions of heterogeneity in the volume of the composite, the size of which is 95-130 nm.

Fig. 5 shows the frequency dependence of the real part of the dielectric constant ε' (DEG-1/PEPA/PEG sample)

at different temperatures. At temperatures below the glass transition temperature, the dielectric constant has low values and almost does not change with frequency. As the frequency increases, the value of ε' decreases, which is due to the contribution of the phase separation boundary and a decrease in electrode polarization. A shift of relaxation toward higher frequencies is observed with increasing temperature due to the segmental movement of polymer chains. An increase in the relaxation frequency with increasing temperature means that the relaxation of polymer chain segments in the composite occurs faster.

Fig. 5b shows the isotherms of the real part of the complex electrical conductivity (σ) of the DEG-1/PEPA/PEG sample obtained in the temperature range from -20 to 180 °C. Two regions are observed on the curves: the conductivity increases with increasing frequency, which describes the phenomena of electrode polarization, and the conductivity, which does not depend on the frequency (plateau on the graph), is associated with direct current conductivity (DC conductivity).

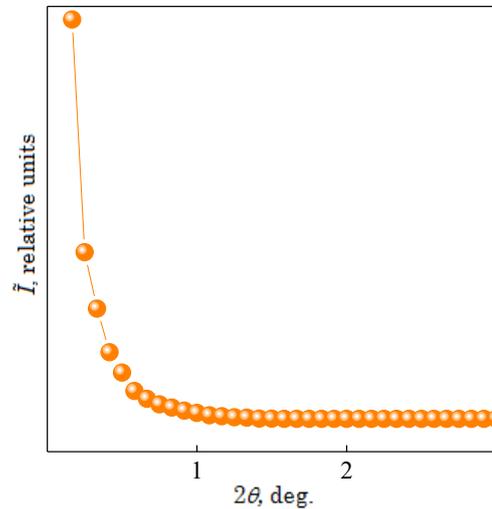


Fig. 3 – SAXS intensity profile pattern of DEG-1/PEPA/PEG/LiClO₄ composite

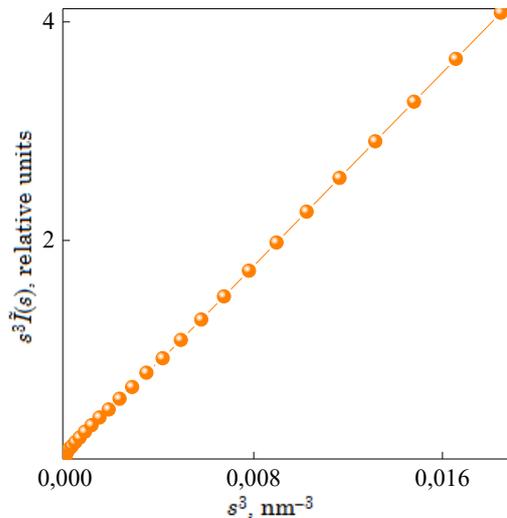


Fig. 4 – SAXS intensity profile pattern of DEG-1/PEPA/PEG/LiClO₄ composite presented in the coordinates of W. Ruland [15, 16]

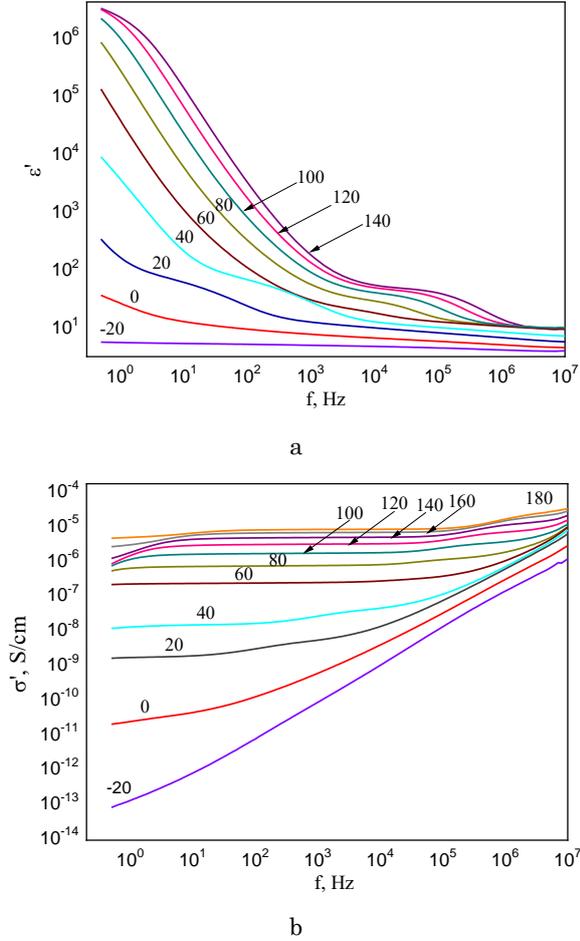


Fig. 5 – Frequency dependences of the dielectric constant ε' (a) and the real part of the complex electrical conductivity σ' (b) of the DEG-1/PEPA/PEG sample at different temperatures (numbers near the curves)

The dependences of conductivity at direct current for the studied composites are presented as a function of temperature ($1000/T$, K^{-1}) in Fig. 6. The curves deviate from the Arrhenius behavior, and the resulting bending of the curves can be explained by the concept of free volume. Therefore, for further analysis, the obtained experimental values require interpretation according to the following nonlinear Vogel-Tamman-Fulcher (VTF) equation [18]:

$$\sigma = \bar{\sigma}_0 \exp\left(-\frac{D \cdot T_0}{T - T_0}\right),$$

where $\bar{\sigma}_0$ is the preexponential constant, D is the fragility parameter, and T_0 is the Vogel temperature.

Using the approximation of experimental results, it was calculated that the fragility parameter for the DEG-1/PEPA system is 5.3, for the system with LiClO_4 it is 6.6, and for the system with PEG and LiClO_4 it is 8.3. According to the obtained values of the fragility parameter, the composites can be classified as fragile, i.e., the charge transfer process is significantly affected by the free volume. The most fragile are materials that show

the largest deviations from the Arrhenius law, corresponding to small values of D (as a rule, $D < 10$) [19].

It can be seen from the given data (Fig. 6) that the numerical value and nature of the σ_{dc} curves depend on the content of LiClO_4 , PEG, as well as on the measurement temperature. Thus, at a temperature of 60°C , the conductivity of the DEG-1/PEPA/ LiClO_4 composite is at the level of the conductivity of the DEG-1/PEPA and DEG-1/PEPA/PEG samples and is $1.5 \cdot 10^{-7}$ S/cm. However, when the temperature increases, there is a rapid increase in the electrical conductivity (DEG-1/PEPA/ LiClO_4 sample) due to the destruction of aggregates, which is accompanied by the release of charge carriers, namely lithium cations Li^+ [10]. An increase in the conductivity of the DEG-1/PEPA/PEG/ LiClO_4 system (Fig. 6, curve 4) is observed due to an increase in the mobility of PEG macromolecular chains above the melting temperature, and the facilitation of the lithium cations movement along the polymer chain with the participation of ether oxygen. The maximum values of conductivity are achieved for the DEG-1/PEPA/PEG/ LiClO_4 composite, and at 60°C σ_{dc} is $1.4 \cdot 10^{-5}$ S/cm, and at 180°C it is $7.2 \cdot 10^{-4}$ S/cm.

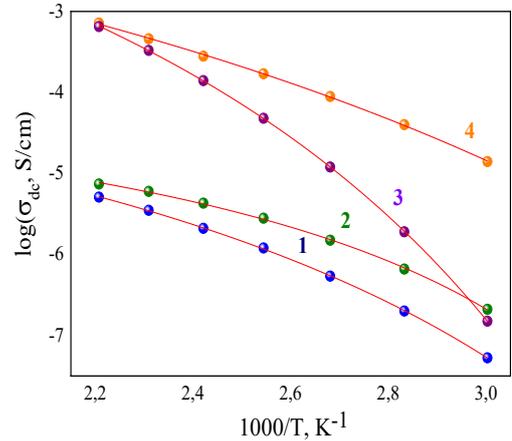


Fig. 6 – Temperature dependence of direct current conductivity for composites: DEG-1/PEPA (1), DEG-1/PEPA/PEG (2), DEG-1/PEPA/ LiClO_4 (3), and DEG-1/PEPA/PEG/ LiClO_4 (4). The red lines are approximations of the data using the VTF equation for each system

4. CONCLUSIONS

The conducted studies showed that DEG-1/PEPA/PEG/ LiClO_4 composites have an amorphous-crystalline structure with an average crystallite size of 4.0 nm. It was established that LiClO_4 salt does not show its crystalline structure in the composite, which indicates its manifestation in the ionic form. The value of the degree of crystallinity of the DEG-1/PEPA/PEG polymer system is 11.4 %, and when this sample is doped with 20 phr LiClO_4 , it is 10.7 %, which indicates a decrease in the degree of PEG crystallinity in the system due to the interaction of PEG with LiClO_4 . The maximum values of conductivity are observed for the DEG-1/PEPA/PEG/ LiClO_4 composite, and at 60°C σ_{dc} is $1.4 \cdot 10^{-5}$ S/cm, and at 180°C it is $7.2 \cdot 10^{-4}$ S/cm.

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Структура та властивості електроактивних композитів на основі олігомерів різної молекулярної маси, допованих сіллю перхлорату літію

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Полімерні суміші – важливий об'єкт наукових і промислових інтересів, а легування солями – поширений спосіб для реалізації провідності композиту. В роботі досліджено особливості структури та властивостей композитів на основі олігомерів різної молекулярної маси, а саме аморфного дигліцидилового етеру поліетиленгліколю (ДЕГ-1, $M_w = 372$ г/моль) і висококристалічного поліетиленгліколю (ПЕГ, $M_w = 10.000$ г/моль), та іонів Li^+ . Полімерні органо-неорганічні системи досліджено методами диференціальної скануючої калориметрії (ДСК), ширококутового розсіювання рентгенівських променів (ШРРП), малокутового розсіювання рентгенівських променів (МРРП) та широкосмуговою діелектричною спектроскопією. За допомогою методів ДСК та ШРРП показано, що композити з ПЕГ мають аморфно-кристалічну структуру. Згідно дослідження ШРРП середній розмір кристалітів складає 4,0 нм. Методом ДСК виявлено зменшення ступеня кристалічності ПЕГ в композиті за рахунок пластифікуючої здатності ДЕГ-1 та взаємодії ПЕГ з сіллю перхлорату літію. Методом МРРП встановлено, що в об'ємі досліджуваних композитів існують області гетерогенності розміром 95-130 нм. Дослідження електричних характеристик полімерних систем показали, що доповання композиту сіллю літію приводить до збільшення провідності зразків на два порядки. Температурні залежності провідності за постійного струму для досліджених композитів не підкоряються залежності Арреніуса та проаналізовані за допомогою рівняння Вогеля-Тамана-Фальчера. Досліджені композити можна віднести до фрагільних.

Ключові слова: Епоксидний олігомер, Поліетиленгліколь, Сіль літію, Структура, Властивості.