Change of the structural organization in the polar elastomer film under the action of electrostatic field

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Abstract The effect of the electrostatic field on the structural organization of macromolecules of polar elastomers was studied using polychloroprene (PCP) as an example. The impact of the electrostatic field on thin films of polychloroprene in the process of their formation leads to the formation of a supramolecular structure that is different from that in films formed under similar conditions, but in the absence of a field. An analysis of the dielectric relaxation spectra of samples in an electrostatic field shows an increase in order in the arrangement of macromolecules (degree of crystallinity). The results of the evaluation of the increase in the degree of crystallinity of the films studied by the dielectric method are in good agreement with the estimate of this parameter by analyzing the IR spectra. The results obtained give grounds to conclude that there is an increase in orderliness in the arrangement of polar molecules in thin films of elastomers when they are formed and kept in an electrostatic field. Increasing the order in the arrangement of polar macromolecules leads to an increase in electrical conductivity in thin films of such a material. The work substantiates and uses a method for assessing the degree of crystallinity of an elastomer by analyzing the temperature dependence of electrical capacity.

1. Introduction
Regulation of the physical properties of polymeric materials expands the prospect of their use in developing areas of science and technology. The creation of polymer materials of new quality is possible not only through synthesis, chemical modification, doping, doping, but also when traditional materials are exposed to external physical fields (electromagnetic, electrostatic, etc.). This type of modification is determined by the fact that the properties of the polymer material depend not only on the chemical structure of macromolecules, but also on their configuration (conformation of macromolecules and isomerism), the location of the macromolecules relative to each other, their packing density, which results in the supramolecular structure of the material and its physical properties. The impact of physical fields can change the conformation of macromolecules and their supramolecular organization, and in the most severe conditions change the chemical structure of macromolecules (oxidation, dehydrochlorination under the influence of hard gamma irradiation, etc.). Polymeric materials are widely demanded in various branches of technology due to a wide range of their mechanical and physical properties, as well as the possibility of their modification in various ways and imparting properties other than inorganic compounds [1-3]. Thus, polymer films are widely used not only as high-voltage insulation in various electrical engineering, but also as semiconductor elements [4]. Films with high electrical conductivity, pseudometallic and semiconductor properties are widely demanded in the manufacture of light-emitting diodes and thin-film field-effect transistors. As a result of studies of conducting polymers with a high degree of orientation of polymer chains in a bulk sample (which makes it possible to use the characteristics of the quasi-one-dimensional structure of macromolecules), polymeric quasicrystalline materials with high anisotropy of electrical characteristics and high carrier mobility were obtained [5,6].

Of particular interest in terms of sensitivity to electromagnetic fields and the possibility of using as organic semiconductors are polymers whose macromolecules have polar groups. For such polymers, the density of the electron clouds, forming a bond between atoms, is asymmetrically distributed, and
The dipole moment of macromolecules depends on the polarity of the groups that make up the polymer, the frequency and symmetry of their arrangement along the molecule chain. Among the polar polymers is polychloroprene (PCP), the macromolecule of which includes the group C - Cl. PCP is an elastomer that is widely used for the manufacture of technical products.

The purpose of this work was to study the processes occurring in thin films of a polar polymer (polychloroprene) under the action of an electrostatic field and the influence of these processes on the electrophysical properties of this material.

2. Theoretical part

Polar polymers, being in an electrostatic field, can realize two types of polarization depending on their physical state [7]. In the glassy state, elastic-dipole and dipole-radical polarization occurs, and at temperatures when the polymer is in a highly elastic state, electron and dipole-elastic polarization is manifested. Both dipole-radical and dipole-elastic polarization are a kind of dipole-relaxation polarization. The difference lies in the fact that in the dipole-radical polarization there is a rotation not of the molecules as a whole, but of its individual segments or units (radicals). In the case of dipole-elastic polarization, entire segments (consisting of several molecules) are rotated [8], which is the case for elastomers. The result of the manifestation of polarization is a change in the position of individual parts of the macromolecules relative to each other with the appearance of local stresses that either relax under certain conditions or result in the destruction of the macromolecule [9].

The result of structural transformations in the film of polychloroprene under the influence of a constant electric field is reflected in changes in the temperature dependences of the dielectric constant and the tangent of the dielectric loss angle of samples compared to similar dependencies for samples that have not been subjected to such an impact. An analysis of the corresponding dependences makes it possible to determine the change in the degree of macromolecular ordering (quasicrystallinity) under the action of electrostatic fields on thin elastomer films.

Following the principle of superposition of relaxation processes in completely crystalline and fully amorphous polymer samples, formulas were obtained that establish the dependence of the dielectric properties of polymers on the degree of crystallinity (κ) [9]:

\[
\varepsilon = \kappa \varepsilon_{1c} + \frac{\varphi}{1 + \omega^2 \tau^2} + (1 - \kappa) \varepsilon_{2c} + \frac{\varphi}{1 + \omega^2 \tau^2},
\]

where subscripts 1 and 2 refer to fully crystallized and fully amorphous samples, \( H(\tau) \) is the density of the dielectric relaxation time spectrum, \( \tau \) is the relaxation time, and \( \omega \) is the circular frequency of the alternating electric field. Since most of the volume of the elastomer refers to the amorphous phase, the second term significantly exceeds the first term, then the expression takes the form

\[
\varepsilon \approx (1 - \kappa) \varepsilon_{2c} + \frac{\varphi}{1 + \omega^2 \tau^2}.
\]

From the presented relation it follows that the dielectric constant decreases with increasing degree of crystalline. If the crystalline phase is destroyed, then \( \kappa = 0 \), and the expression (2) takes the form

\[
\varepsilon_{am} \approx \frac{\varphi}{1 + \omega^2 \tau^2}.
\]

The ratio of the dielectric constant of the partially crystallized polymer (\( \varepsilon \)) to the dielectric constant of the completely amorphous polymer (\( \varepsilon_{am} \)) can be represented as \( \varepsilon / \varepsilon_{am} = (1-\kappa) \), from where the degree of crystallinity can be estimated by the ratio

\[
\kappa = 1 - \varepsilon / \varepsilon_{am}.
\]

In the process of heating the PCP sample, the crystalline phase melts in the region of 333 K [10]. This argument was the basis for determining the degree of crystallinity and analyzing its change in the process of heating the sample by the dielectric method. Since the degree of crystallinity decreases with
increasing temperature, this should be reflected in an increase in dielectric constant. On the other hand, as the sample temperature changes, the dielectric constant also changes. The Debye equation for dielectric constant is

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2}$$  \hspace{1cm} (5)

where $\varepsilon_0$ is the static low-frequency value of $\varepsilon$, $\varepsilon_\infty$ is the value of $\varepsilon$ as $\omega \to \infty$. According to the Onsager, Fröhlich, Debye theory [9] for polar molecules, $\varepsilon_0 - \varepsilon_\infty = A / T$, where $A$ is a constant, $T$ is temperature.

After substitution of this relation into equation (5)

$$\varepsilon - \varepsilon_\infty = \frac{A}{T(1 + \omega^2 \tau^2)}$$  \hspace{1cm} (6)

Since the relaxation time $\tau$ depends exponentially on the temperature and activation energy [17]

$$\tau = \tau_0 \exp \frac{U}{kT}$$  \hspace{1cm} (7)

the transformation of equations (6) and (7) leads to the dependence

$$\frac{1}{\varepsilon - \varepsilon_\infty} = \frac{T(1 + \omega^2 \tau_0^2)}{A} - \frac{2U}{Ak} \omega^2 \tau_0^2$$  \hspace{1cm} (8)

If we take into account that $\varepsilon < \varepsilon_\infty$ (with an increase in the frequency $\omega$, the value of $\varepsilon$ decreases [13]), then in the first approximation we can assume that $\varepsilon - \varepsilon_\infty \approx \varepsilon$. Then the ratio between the dielectric constant and temperature will take the form

$$\frac{1}{\varepsilon - \varepsilon_\infty} = \frac{T(1 + \omega^2 \tau_0^2)}{A} - \frac{2U}{Ak} \omega^2 \tau_0^2$$  \hspace{1cm} (9)

In the theories of Fröhlich and Buckingheim [8], the dependence of the dielectric constant relations under different conditions on temperature is also inversely proportional.

In (7), the parameter $U$ represents the activation energy of the structural rearrangement process or the energy barrier of the transition of the system from one state to another. Since the applied electrostatic field contributes to the process of such a transition, reducing the energy barrier, the activation energy of the transition process will decrease due to the energy contribution of the electrostatic field: $W = U_{es}C/2$, where $U_{es}$ is the voltage or potential difference of the electrostatic field, $C$ is the electrical capacity. Then the activation energy of the process can be represented as

$$U = U_0 - \gamma U_{es}$$  \hspace{1cm} (10)

where $\gamma$ is the coefficient characterizing the degree of reduction of the initial activation energy by the applied voltage of the electric field, $U_0$ is the initial potential barrier in the absence of an electric field. The joint solution (9) and (10), taking into account that $C = \varepsilon_0 S/d$ ($S/d$ - geometric parameters of the film), with the necessary mathematical transformations make it possible to obtain a relation characterizing the influence of various factors on the dielectric constant of the film, having the form

$$\varepsilon = \left(\frac{b^2 + 2aAkU_{es}^2}{aU_{es}^2}\right)^{1/2} - b$$  \hspace{1cm} (11)

where $a = 2 \frac{S}{d} \gamma \varepsilon_0 \omega^2 \tau_0^2$ is the parameter that is determined by the geometric dimensions of the sample; $b = k[1 + \omega^2 \tau_0^2] - 2 \frac{U_0}{k} \omega^2 \tau_0^2$ - temperature dependent parameter. Substitution of equation (11) into expression (4) makes it possible to obtain an expression for the degree of crystallinity of the form
From expression (12) it follows that with increasing voltage of the electrostatic field, the degree of crystallinity increases in a linear relationship, and with increasing temperature, the degree of crystallinity also decreases linearly. Thus, an idea of the influence of temperature and an electrostatic field on the ordering process of the structure of polar macromolecules has been obtained.

3. Materials and methods.
The object of the study was polychloroprene rubber brand Neopren (Neopren WD, DuPont). The proportion of the crystalline phase of this polymer at room temperature ranges from 8 to 30%. The dipole moment of the macromolecule PCP calculated on the monomer unit is 1.45 D (4.8 $10^{-30}$ k $\cdot$ m). The viscosity average molecular weight, determined in a benzene solution, was 151,300. A sample in the form of a film for the study was prepared by pouring a solution of polychloroprene in carbon tetrachloride on a polyamide substrate. The choice of substrate was determined by the absence of oxidative processes at the sites of contact of polychloroprene-polyamide and the possibility of separating the film of PVC from the surface of such a substrate without breaking down to form a fairly high-quality and uniform surface. The process of film formation during solvent evaporation was carried out at a temperature of 303 K for 24 hours. The control of solvent removal was carried out by weighing on an analytical balance (until a constant weight of the sample was reached). The thickness of the films was measured with a micrometer with an accuracy of 1 $\mu$m, they ranged from 150 to 250 $\mu$m.

The polychloroprene film formed during the drying of the solvent was removed from the substrate and placed on a copper cathode, to which a constant voltage in the range from 5 to 30 V was connected, for further morphology formation. The cathode was chosen as an electrode, since according to the data of [12], the greatest change in the properties of a polychloroprene film (change in conductivity) occurs precisely at the cathode.

Measurement of ac conductivity, dielectric loss tangent and electrical capacitance of the material between two steel electrodes was carried out on a Hewlett-Packard 4284A digital LCR meter in an equivalent circuit of parallel-connected resistor and capacitor at 1 kHz in a thermostat with a controlled heating temperature with an accuracy of 2 $^\circ$ in the range of 290-423 K. The temperature of the samples was monitored with a thermocouple chromel-copel. To determine the dielectric constant of the film, the measured electrical capacitance (C) of the measuring cell was recalculated from the relation

$$\varepsilon = \frac{Cm}{\varepsilon_0 \rho S^2},$$  

where $m$ is the mass of the sample between the electrodes, the $\rho$-density of this sample, $S$ is the area of the electrodes of the measuring cell. If the change in the sample density in the temperature range of the study between two electrodes $(5 \times 10^{-4} \text{ m in diameter})$ is neglected, then the relationship between the measured electrical capacity (C) and $\varepsilon$ can be represented by the dependence $\varepsilon = 0.2353 \times 10^{14} \text{C}$ $\cdot$ m, $\Phi^{-1}$ $\text{kg}^{-1}$.

Analysis of the degree of crystallinity and the content of cis and trans isomers in the polymer was evaluated by the IR spectra obtained on a Perkin Elmer Spectrum FTIR - FT spectrometer 100 at 295 ± 2K in the range of 4000$\leq n \leq$ 450 cm$^{-1}$ in transmitted light.

4. Experimental results and discussion.
Figure 1 shows the temperature dependence of the dielectric constant of the original polychloroprene film. This dependence has a stepped nature, the jumps of which reflect changes in the arrangement of macromolecules as a result of structural transitions [9]. An increase in $\varepsilon$ with an increase in temperature characterizes the dipole orientational polarization. Moreover, an increase in $\varepsilon$ is observed in the region of the maximum tangent of the dielectric loss angle (D).
Figure 2 shows the temperature dependence of the dielectric loss tangent of polychloroprene films at a frequency of 1 kHz. The kinks in the temperature dependence of the dielectric constant correspond to the temperatures of the maxima of the tangent of the dielectric loss angle (D) in Fig. 2 (curve 1).

![Figure 1. Temperature dependence of the dielectric constant of the original polychloroprene film.](image)

In the range of melting points of the crystalline phase (60 °C or 333 K), clear peaks are found in the samples studied, which should be associated with morphological transformations in the film. Comparison of the temperature of the dielectric loss of the sample after exposure to an electric field with the original sample (Fig. 2, curves 1 and 2) shows that the influence of an electric field leads to a shift of the maxima of the tangent values of the dielectric loss angle D in the temperature range from 45 °C to 90 °C higher temperatures and an increase in these values. The relaxation spectra reflect phase and structural transitions with a change in temperature at a constant frequency of an electric field or with a change in the frequency of a field at a constant temperature. The mechanism of phase transitions suggests a change in the cooperativity of thermal molecular mobility in polymer systems [11].

Upon annealing in amorphous-crystalline polymers, a liquid-liquid phase transition occurs, leading to the manifestation of mobility of various types of macromolecules of the intercrystallite layer and macromolecules of amorphous regions [13]. The melting of the crystal structure of polymers occurs in a finite temperature range and is associated with a decrease in crystallite size and a gradual transition into the amorphous phase of the intercrystallite layer [14]. For PCP, the temperature range for the melting of the crystalline phase coincides with the temperature of the transition from the highly elastic state to the viscous flow [10].

At temperatures above 310 K, an increase in the tangent of dielectric loss angle is due to the manifestation of the cooperativeness of the thermal molecular motion. The elimination of conformational restrictions imposed on parts of the macromolecules of the intercrystalline layer during the melting process leads to a decrease in D. The mobility of parts of the macromolecules of the intercrystalline layer is limited by fixing in crystals. This fact determines the cooperativeness of molecular motions and the growth of D at lower temperatures than amorphous elastomers [10]. As a result, in the melting temperature range of the crystalline phase, the tangent of the dielectric loss angle and the dielectric constant has the maximum value. The temperatures of their maxima coincide. In the range of melting points of the crystalline phase (310–353 K), the maxima of D appear. The more perfect the structure of crystallites, the higher the D value and less ε, but their maxima are shifted toward higher temperatures than for samples with a less perfect structure [9]. The presence of several maxima in the temperature range from 45 to 90 °C is determined by the fact that the destruction of the
crystalline (ordered) phase is accompanied by segmental movement of macromolecules (dipole-segmental polarization), as well as with an increase in the mobility of polar groups (dipole-group polarization). In the process of exposure to a constant electric field, the polar groups of the polymer acquire a certain orientation, contributing to greater orderliness in the arrangement of the macromolecules. Therefore, the observed change in the temperature dependence of the dielectric loss tangent occurs.

Figure 2. The dependence of the dielectric loss tangent of a polychloroprene film on temperature: 1-original sample; 2- the sample was held at the cathode at a voltage of 20 V for 120 minutes.

The ordering created by the field in the supramolecular structure of the elastomeric film can most likely be characterized as an increase in the degree of crystallinity or local ordering and can be estimated using relation (5). Processing the dependences of ε on temperature for samples aged for 6000 s in a constant electric field at different values of its magnitude makes it possible to obtain a dependence of the degree of ordering (crystallinity) of the system of macromolecules in a polychloroprene film. Figure 3 presents the dependence of the degree of ordering of macromolecules of polychloroprene, determined from the analysis of the temperature dependences of the dielectric constant of samples kept in an electric field of various sizes. The dependence is linear, the degree of order (local crystallinity) linearly depends on the voltage of the electric field, in which the structure of the elastomer film was formed by the ratio

\[ \kappa = 0.0014U + 0.1376 \]  

Relation (14) indicates the structural changes occurring in the polychloroprene film under the action of an electric field. The dependence of the temperature of the maximum of the tangent of dielectric loss angle in the region of melting temperatures for samples sustained at a voltage higher than 10 V depends on the voltage applied to the electrode squarely (fig. 4), which corresponds to the expression

\[ D = \frac{\alpha \tau U_{es}^2}{\delta^2} \]  

where α is the value that determines the properties and structure of the polar molecule, \( U_{es} \) is the value
of the voltage of the electrostatic field in which the polymer film was formed, the δ-thickness of the film, the τ-time of stress relaxation in the polymer chain, depending on temperature.

![Graph](image)

**Figure 3.** The dependence of the degree of crystallinity of films of PCP, aged in an electric field, on the magnitude of this field. The calculation of κ was carried out according to the relation (4).

![Graph](image)

**Figure 4.** The dependence of the maximum of the tangent of the dielectric loss angle (D) in the region of melting temperatures of polychloroprene films on the voltage of the electric field. The exposure time of samples in an electrostatic field is 3600 s.

When comparing the IR spectra, a change in the intensity of absorption in the region of 780 cm⁻¹ of PCP films held in an electric field for 3600 s at a voltage of 25 V and a temperature of 30 °C with respect to films kept outside the field was established. The intensity of absorption in this region is associated with the presence of crystalline structures [15]. The change in the degree of crystallinity in these films is estimated from the ratio of the absorption intensities: the degree of crystallinity increases 1.2 times when exposed to an electric field under the specified conditions. Comparison of changes in the degree of crystallinity, determined by the dielectric method (fig. 3), when exposed to a field of 25
V also leads to similar results: the degree of crystallinity increases 1.22 times. This fact confirms the possibility of estimating the degree of crystallinity of PCP films from the temperature dependence of the electrical capacitance, which reflects the temperature dependence of the dielectric constant of materials of this type. Analysis of the IR spectra made it possible to estimate the change in the ratio of structural isomers in the PCP film as a result of an electric field. By absorption in the region of 1180 cm\(^{-1}\) [15], it was determined that when an electric field is applied to the film of polychloroprene, the proportion of trans-structures increases 1.2 times. This fact gives grounds to believe that an increase in the degree of crystallinity occurs due to an increase in the content of trans-isomers under the action of an electric field.

Changes in the structure of polychloroprene entail a change in the electrical properties of the films of this material. An increase in the degree of ordering and orientation of macromolecules under the action of an electric field leads to an increase in the conductivity of polar polymer films. Figure 5 shows the temperature dependence of the polychloroprene film formed without the participation of the field. Figure 6 presents a similar relationship for a film formed under the influence of an electric field of 25 V. It can be seen from the figures that during the formation of the film under different conditions, the nature of the temperature dependence of the conductivity changes. For a film formed under the influence of a field, conductivity in a wide range of temperatures is more stable and an order of magnitude higher than for a film obtained in the absence of a field.

Figure 5. The dependence of the conductivity of the film of polychloroprene on temperature. O-A-B-C - heating at a rate of 6 deg. / min; C-D-E-G-F-K - cooling at a speed of 2.4 deg / min.
Figure 6. Temperature dependence of the resistivity of a polychlore film obtained from a solution by formation at the cathode. A-B-C-D – heating with a speed of 6 deg. / min; D-G-K - cooling at a speed of 2.4 deg. / min.

5. Conclusions

Based on the conducted research on the effect of the electrostatic field on the process of ordering the macromolecular structure of polar elastomers using the example of polychloroprene, we can conclude:

1. When finding and forming thin films of such a polar elastomer as polychloroprene, ordering occurs in the arrangement of the macromolecules due to the elastic-dipole and dipole-radical polarization. This fact is confirmed by the results of dielectric spectroscopy, the temperature dependences of the dielectric constant and dielectric loss tangent. This changes the ratio of the cis- and trans-conformation of macromolecules in favor of the latter. The degree change in the order of macromolecules (local crystallinity) corresponds to the change in the ratio of the cis and trans conformation of macromolecules PCP.

2. The obtained and theoretically justified dependences of the increase in the degree of local crystallinity (orderliness) in PCP films on the voltage of the electrostatic field and temperature, under the action of which the structure was ordered, were confirmed experimentally. An increase in the order (local crystallinity) in the films studied increases linearly with an increase in the electric field voltage in which the supermolecular structure of the films is formed.

3. With an increase in the order in the arrangement of macromolecules of polar polymers, an increase in the conductivity of thin films of this material occurs.

4. The dependence of the maximum temperature in the melting temperature region for samples aged at a voltage higher than 10 V depends on the voltage applied to the electrode, rather than linear, but quadratic, indicating several processes (changing the conformation of macromolecules, changing the arrangement of segments and parts of macromolecules, changing the size of macromolecules with an increase in the mobility of individual structural units), proceeding with the ordering of the structure of a polar elastomer under the action of an electrostatic field.

Thus, the electrostatic fields applied to the films of polar elastomers can modify the morphology of these films and change their properties.
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References
[1] Takeda Y, Andrew T L, Lobez J M, Mork A. J and Swager T M 2012 An Air-Stable Low-Bandgap n-Type Organic Polymer Semiconductor Exhibiting Selective Solubility in Perfluorinated Solvents Angew. Chem. 51 36 9042–46.
[2] Hadziioannou G, Malliaras G G Semiconducting Polymers: Chemistry, Physics and Engineering 2007 2nd ed. (Weinheim: Wiley-VCH) p 321
[3] Wi H L and Yeong D P Organic Semiconductor Insulator Polymer Blends for High-Performance Organic Transistors 2014 Polymers 6 1057-73
[4] Bässler H Charge transport in organic semiconductors 2012 Top. Curr. Chem 312 1–66.
[5] Drobny J G 2012 Polymers for Electricity and Electronics: Materials, Properties, and Applications (New Jersey: John Wiley and Sons) p 332
[6] Hummel R E 2011 Electronic Properties of Materials (Springer) p 481
[7] Blythe A R, Blythe T and Bloor D 2005 Electrical properties of polymers. (Cambridge University Press) p 480.
[8] Nalwa H S 1997 Handbook of Organic Conductive Molecules and Polymers: Conductive polymers : synthesis and electrical properties (John Wiley & Sons Inc) p 888
[9] Perepechko I I 1978 Introduction in physics of polymers (Moscow: Khimiya) p 312
[10] Mashuryan A M , Gasparyan K A and Ovanesov G T Molecular Relaxation of Polychloroprene around its melting point 1985 Pol. Sci. USSR 27 8 1862-65
[11] Bartenev G M and Barteneva A G Relaxation Properties of Polymers (Khimiya, Moscow, 1992) p 384
[12] Komova N N Conductivity at alternating current of thin films of polychloroprene formed in electric field 2018 Fine Chemical Technologies 13 1 75-91.
[13] Mark J E Physical Properties of Polymers Handbook 2007 (New York Springer) p1073
[14] Gul’ V E and Kuleznev V N 1992 The Structure and Mechanical Properties of Polymers (Moscow: Khimiya) p 248
[15] Dechant J 1972 Ultrarotspektroskopische Untersuchungen an Polymeren (Berlin: Akademie-Verlag) p 516