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CONFORMATIONAL APPROACH TO DETERMINING THE POLARIZATION OF POLYETHYLENE OXIDE DURING MELT-CRYSTAL TRANSITIONS IN A NON-UNIFORM TEMPERATURE FIELD

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In connection with the widespread use of polyethylene oxide (PEO) in modern technologies, studies of the relationship between its supramolecular structure and properties by modeling methods have recently intensified. Usually, when modeling the thermopolarized effect, the supramolecular structure of flexible-chain polymers is represented by a set of linear one-dimensional crystals. This approach does not take into account the conformational features of the structure of polymers. Using the example of (PEO), the article substantiates a method for calculating the influence of the conformations of a polymer molecule on the temperature dependence of the averaged square of the dipole moment of its molecules. The problem solved in this work, as well as the proposed solutions and approaches, reflect the general fundamental problem of the thermodynamic stability of multicomponent systems in external fields.

Keywords: conformations of molecules, flexible-chain polymers, polyethylene oxide, supramolecular structure, thermopolarization effect, inhomogeneous temperature field.

Introduction

In recent years, there has been a shift in interest in condensed matter physics towards studies of various classes of disordered and incompletely ordered materials. This broad area of research includes both crystalline and amorphous or glassy materials: polymers, amorphous semiconductors and dielectrics, spin and dipole glasses, relaxors, etc. The reason for this interest is the fact that disordered phases of condensed media occur incomparably more often, and in practical terms, they are no less important than idealized single crystals.

Many of the disordered polymeric materials exhibit metastable polarization, i.e. such a polarization that can be induced by various external fields (electric, magnetic, and, as shown in the work, inhomogeneous temperature). This polarization can be maintained indefinitely under certain conditions. In some crystallizing partially ordered polymers, not only the creation of induced polarization is possible, but also the occurrence of spontaneous polarization in the absence of external fields.

Since the role of electrically active polar polymeric dielectrics in the formation of the latest areas of electronic, computer, and measuring technology is growing sharply, it is undoubtedly that for their more effective use it is necessary to study in detail the regularities and mechanisms of the occurrence of electric polarization and the features of the real structure of these materials.

In this regard, on the example of polyethylene oxide (PEO), which is widely used in the above areas, studies of the relationship between its supramolecular structure and properties by modeling methods have intensified. Usually, when modeling the thermopolarization effect, the supramolecular structure of flexible-chain polymers is represented by a set of linear one-dimensional crystals. Within the framework of such approaches, the conformational feature of the polymer structure cannot be taken into account.

In modern technologies, polyethylene oxide (PEO) is used in powder metallurgy, mechanical engineering, metalworking, oil refining, agriculture, textile, leather, rubber, paper, chemical, mining and other industries. Based on PEO, lubricants, cutting fluids, solvents, anti-caking additives for bulk materials are produced, and they are also used in the conservation of wet wood [1–4]. Therefore, the study of its supramolecular structure to create materials with certain properties does not lose its relevance [5-6].

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When constructing a model of the thermopolarization effect [7], the calculations are usually based on the assumption that the crystal structure is a set of linear one-dimensional crystals. It is clear that such a model cannot take into account the conformational features of the structure of flexible-chain linear polymers.

The paper proposes a method for taking into account the influence of conformations on the dependence of polarization on the temperature of a flexible-chain polymer. The proposed approach to the determination of polarization characteristics is considered on the example of polyethylene oxide (PEO), since the conformational structure of its macromolecule and the experimental values of polarization, pyroelectric coefficients, etc., obtained from thermograms of polarization and depolarization currents are known [8, 9].

When considering the conformational approach, we will use the following assumptions.

- The electric charge of the kinetic fragment of the macromolecule remains unchanged when the conformation of the chain changes.
- Any monomeric unit is considered electrically neutral.
- Interaction between macromolecules is not taken into account.

1. Theoretical part

It was shown in [10–11] that when a polymer (both synthetic and natural biopolymer) is introduced into an inhomogeneous temperature field, electric fields of thermal origin arise in it. As a result of orientational polarization at the interface with vacuum or metal, uncompensated bound charges of molecular nature appear on the polymer surface, the surface density of which coincides with the normal projection of the polarization vector:

$$\sigma_b = \pm P_n \tag{1}$$

If the polymer is at a constant temperature ($T = const$) in a state of thermodynamic equilibrium with an electric field whose strength is $\vec{E} = const$, the equilibrium value of polarization is determined by the thermal equation of state [12, 13]:

$$P_i = -n_0 \frac{kT}{Z} \frac{\partial Z}{\partial E_i} \qquad (i = x, y, z), \tag{2}$$

where $n_0 = \frac{\rho N_A}{\langle M \rangle}$ is the number of macromolecules per unit volume; ρ and $\langle M \rangle$ are the density and average molecular weight of the polymer, respectively; N_A is the Avogadro's number; k is the Boltzmann constant; Z is the integral of the states of an individual macromolecule in the field $\vec{E}$:

$$Z = \sum_l \exp\left\{-\frac{1}{kT}\left[\varepsilon_l^0 - (\vec{p}\vec{E})\right]\right\}. \tag{3}$$

In expression (3), the summation is carried out over all conformational states of each macromolecule with energy ε_l^0.

$$\vec{p}_n = \sum_n q_n \vec{r}_n, \tag{4}$$

where $\vec{p}_n$ is the dipole moment of a particular macromolecule with its node number n; q_n and $\vec{r}_n$ are the charge and radius-vector of this molecule in K_0 coordinate system. The coordinate system K_0 is chosen in the way that the *OZ* axis is parallel to the field.

As an example let's consider the structure of the PEO chain the structural formula of which is $-\left[\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}\right]_n-$ [14]. The conformational structure of PEO is a repeating unit consisting of three bonds (Fig. 1).

As is known, molecular conformations represent different states of a molecule with an unequal arrangement of atoms in space, arising from changes in the internal geometric parameters of the molecule, in particular, rotation angles around chemical bonds and bond angles (see, for an example, [15]). So, let's introduce into consideration the coordinate system K_1 associated with the rotating fragments of the molecule using the Euler angles. Let the axes OX_1 and OX is directed parallel to the first $\mathrm{C}-\mathrm{O}$ valence bond and the OZ_1 axis is parallel to the direction of the dipole moment of the molecule in the given conformation.

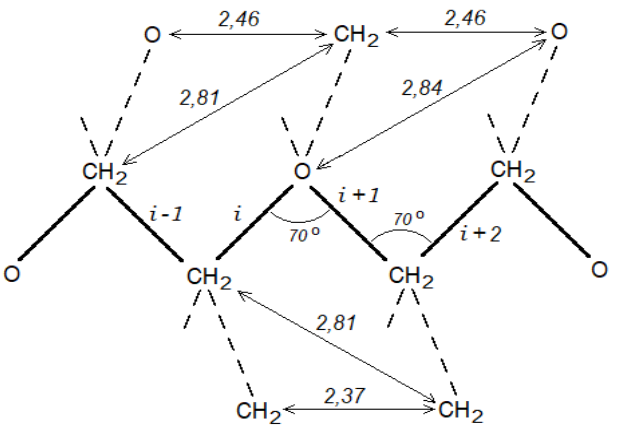

Fig.1. Conformational structure of the polyethylene oxide chain [15]. The $C-O$ and $C-C$ bond lengths are 1.43 Å and 1.53 Å, respectively; the angles complementary to valence are about 70º.

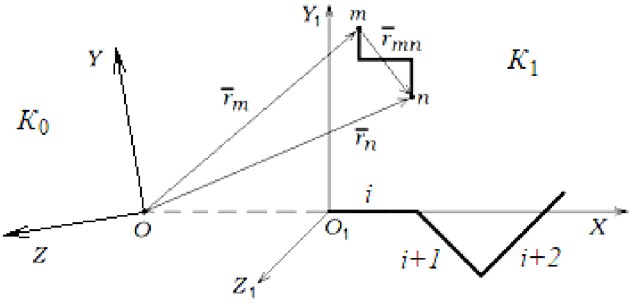

Fig.2. The orientation of coordinate axes.

Then the relationship between the system coordinates K$_1$ and K$_0$ is defined as follows [13] ($\varphi_1 = 0$, $\varphi_2 \in [0, \pi]$, $\varphi_3 \in [0, 2\pi]$):

$$\begin{aligned} x_1 &= x\cos\varphi_3 - y\sin\varphi_3 \\ y_1 &= x\cos\varphi_2\sin\varphi_3 + y\cos\varphi_2\cos\varphi_3 - z\sin\varphi_2 \\ z_1 &= x\sin\varphi_2\sin\varphi_3 + y\sin\varphi_2\cos\varphi_3 + z\cos\varphi_2 \end{aligned} \tag{5}$$

Let us write the state integral (3) in the system K$_1$:

$$Z = \sum_l \exp\left\{-\frac{1}{kT}\left[\varepsilon_l^0 - E\cos\varphi_2 \sum_n q_n z_{1n}\right]\right\}, \tag{6}$$

where q_n is the charge of the n-th kinetic fragment of the macromolecule and dipole energy of the n-th kinetic fragment is

$$\varepsilon_p^n = Ep_n\cos\varphi_2 = E\cos\varphi_2 \sum_n \left(x\sin\varphi_2\sin\varphi_3 + y\sin\varphi_2\cos\varphi_3 + z\cos\varphi_2\right)_n . \tag{7}$$

To calculate the polarization using formula (2), it is necessary to average over all possible orientations of the first valence bonds of all macromolecules located in a unit volume of PEO, i.e. integrate over the Euler angles. Let us first estimate the ratio of the dipole energy to the thermal energy at $T \approx 300$ K and $E \approx 10$ V/cm, i.e. for a group of atoms with a size of ~10 valence bonds. This allows at considering polymers not having electret properties [16] to expand $\exp\left(\frac{\varepsilon_p^n}{kT}\right)$ into a series and restrict ourselves to the first non-vanishing terms.

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Having carried out the necessary calculations and having made the indicated expansion into a series, after integrating over the angles φ_2 and φ_3, we obtain:

$$P_n = \alpha(T)E\,, \tag{8}$$

where

$$\alpha(T) = -\frac{n_0}{kT}\frac{\sum p_l^2 \exp\left(-\frac{\varepsilon_l^0}{kT}\right)}{\sum \exp\left(-\frac{\varepsilon_l^0}{kT}\right)} = \frac{n_0}{3kT}\left\langle \vec{p}^{\,2}\right\rangle\,,$$

$$p_l^2 = q_l^2(x^2+y^2+z^2)_l\,. \tag{9}$$

It can be seen from (9) that the value of $\alpha(T)$ is proportional to the square of the dipole moment of an individual macromolecule, averaged over all its conformations in the K_1 system, without taking into account the external electric field with strength E. Expressions (8) and (9) are outwardly similar to the corresponding expressions in [17] for dielectrics of any nature, the molecules of which, even in the absence of an external electric field, have a nonzero dipole moment. However, for PEO $\left\langle \vec{p}^{\,2}\right\rangle$ is not a constant value and with a change in temperature leading to a change in conformation it changes.

2. Results and discussion

Thus, the calculation of the surface density of bound charges in an inhomogeneous temperature field reduces to averaging over all possible conformations of the squared dipole moment of one macromolecule in the K_1 coordinate system rigidly connected to the first valence bond of the macromolecule:

$$\sigma_b = \frac{N_A\rho E}{\langle M\rangle kT}\left\langle \vec{p}^{\,2}\right\rangle. \tag{10}$$

Since the surface charge density determines the polarization, i.e. $\sigma_b = P_n$, the expression (10) takes the form:

$$\left\langle \vec{p}^{\,2}\right\rangle = \frac{3k\langle M\rangle}{N_A\rho E}PT\,. \tag{11}$$

The value $a = \frac{3k\langle M\rangle}{N_A\rho E} = 1.7\times10^{-49}$ Qm^4/K is a constant for a given polymer, where all input values (for PEO-15) are taken from tables and other data presented in the work [11]. Expression (11) and the data from [11] for the temperature dependence of polarization make it possible to graphically represent the character of the dependence $\left\langle \vec{p}^{\,2}\right\rangle$ on temperature (Fig. 3).

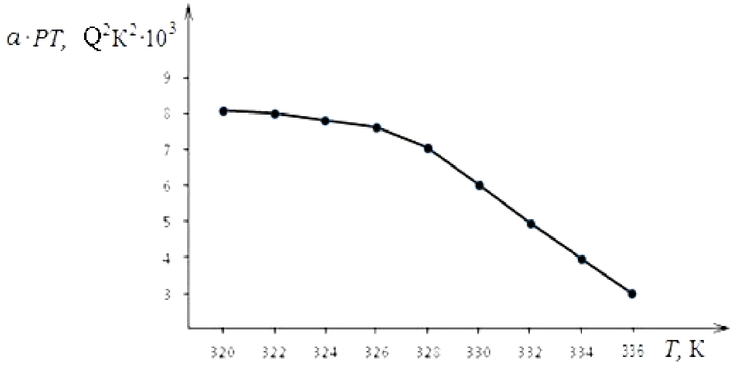

Fig.3. Dependence of the mean square dipole moment of PEO-15 on temperature.

The decrease $\left\langle \vec{p}^{\,2} \right\rangle$ shown by the graph with increasing temperature is due to the fact that the surface charge density decreases as a result of an increase in thermal motion

Conclusion

In conclusion, we note that many of the disordered dielectric materials have a metastable polarization, that is, a polarization that can be induced by various external fields, including an inhomogeneous temperature field. The experimental value of the polarization is determined by integrating the thermograms of the polarization currents, and the theoretical value is determined by using the model of a one-dimensional linear crystal. This model is rather simplified, since it does not take into account the conformation of the chain of the macromolecule. In this work, using the example of PEO, we show the possibility of determining the polarization taking into account the geometry of the kinetic fragments of the PEO macromolecule chain.

Comparison of the polarization determined by the formula (10) $P = 12$ μC/m^2 showed good agreement with experimentally data presented in the early works. The square of the dipole moment determined in this work is a very informative element of the polymer price structure. It depends on the mobility of its kinetic charge fragments, which form supramolecular structures. This is the most important factor for further investigation of the mechanisms of extended chain crystallization and folded chain crystallization using the mean square dipole moment of a particular polymer as a function of its molecular weight.

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