External impacts on structure and relaxation properties of thermotropic liquid crystal copolyester

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Abstract. The methods of thermally stimulated depolarization (TSD) and X-ray diffraction analysis were used to study the impact of electric and temperature fields on the relaxation properties, structure, and molecular mobility of a liquid crystal (LC) copolymer based on polyethylene terephthalate (PET) and n-hydroxybenzoic acid (n–HBA). It was shown that polarization in the LC state besides the main relaxation transition leads to the formation of additional high-temperature maximum on current thermograms of thermally stimulated depolarization (TSD). The data of X-ray diffraction analysis indicate a change in the orientation of mesogenic units after polarization in an electric field. The results were explained by the combined action of electric and temperature fields on the conformational structure of the liquid crystal copolyester, namely, a change in the degree of crystallinity of the studied copolyester under the influence of external fields.

1. Introduction

The interest of many researchers in thermotropic LC copolyesters with mesogenic structural units in the main chain is primarily due to their ability to form filaments from these units in thermoplastic matrix flowing into the melt, which leads to self-reinforcement of such materials after cooling down the melts. The ability of LCs to change properties depending on the external influences (temperature, pressure, electric and magnetic fields, radiation, etc.), a special structure, a combination of ordering in the arrangement of mesogenic structural units of macromolecules with high mobility make it possible to widely use liquid crystal materials in various industrial fields.

Therefore, recently, an intensive study of the influence of the electric fields on the structure and properties of thermotropic LC polymers is in progress. The results of research are summarized in a number of monographs by domestic and foreign authors [1–10]. However, a special attention of researchers was focused on the study of electrical and optical properties of liquid crystals in alternating electric and magnetic fields. It was explained by the fact that in constant electric fields, the processes of charge accumulation and injection of charge carriers, electric transport, and polarization of the liquid crystal phase make it almost impossible to obtain electrical and optical properties with optimal characteristics [11, 12]. The study of the listed properties of liquid crystals was apparently restrained, for the reasons related with certain experimental difficulties, especially when it comes to direct current [6, 13, 14].
On the other hand, in many electrical and optical effects, the above phenomena play a decisive role and can provide quite useful information about the structure and properties of liquid crystal polymers.

When analyzing the above-mentioned works, the following tendency is observed: firstly, the processes associated with the dielectric effect of Fredericks, electrohydrodynamic instability, and ionic conductivity are mainly considered; secondly, the questions related to the relaxation of structural units after the removal of a constant external electric field are not studied.

Given the foregoing, the aim of the work is to study the impact of constant electric and temperature fields on the relaxation and phase properties of thermotropic LC copolymers and to establish the relationship between them.

2. Methods and materials

A liquid crystal copolymer obtained by polycondensation of n-HBA and PET with a molar concentration of 65 mol% n-HBA and 35 mol% PET is one of the thermotropic LC complex copolyesters with nematic mesophase in the temperature range of $T \sim 190–320 \, ^\circ\text{C}$ [15–18].

The introduction of ethylene glycol residue with ether oxygen, which is a part of PET, into the HBA monomer provides possibility of rearranging the hard mesogenic fragments of copolymer macromolecules, this makes it possible to form an LC mesophase. As indicated above in [8, 17] by TSD method, it was shown that this copolymer passes into the nematic LC phase at a temperature of $T^* = 190 \, ^\circ\text{C}$.

Therefore, depending on the temperature range of studies, this copolymer can be considered in two different phase states: it is a partially crystalline copolymer below 190 $^\circ\text{C}$ [19]; accordingly, it is in a liquid crystal state above this temperature. Therefore, it seems interesting to study the impact of an external electric field on the copolymer properties of below and above the phase transition temperature.

The reaction of the copolymer to the action of electric and thermal fields was studied by TSD and X-ray diffraction analysis.

The copolymer samples with a thickness of 250 $\mu\text{m}$ were first heated to the polarization temperature and kept in a constant electric field of 0.6 kV/mm for 20 min, then, in the pores of the liquid nitrogen they were cooled to room temperature at a rate of 40 $^\circ\text{C}$/min without removing the field.

The polarization temperature varied in the range of 100–250$^\circ\text{C}$. The TSD currents of polarized samples were measured using an U5-9 electrometric amplifier with the recorded measurement results on H306 two-coordinate recorder. The linear heating and linear cooling at a speed of 2 deg/min was provided by the BTP-78 thermal programmer. The constant electric field was set by the source B5-50. The measurements were carried out in a standard cell with clamping electrodes, where a sample with ground electrodes made of aluminum foil was placed.

X-ray diffraction patterns at large diffraction angles were recorded on an IRIS-3.0 setup (Cu K$\alpha$, Ni-filter, flat cartridge) at 20 $^\circ\text{C}$.

3. Results

Depending on the polarization temperature, several peaks are observed in the thermograms of the TSD currents due to different levels of molecular organization. The maximum at 80$^\circ\text{C}$ manifests itself regardless of the polarization temperature, a peak at a temperature of 65–70 $^\circ\text{C}$ occurs only at polarization temperatures $T_p < 120 \, ^\circ\text{C}$, and corresponds to the glass transition temperature of amorphous PET.

If the samples are polarized in the LC state when $T_p > T^*$, where $T^*$ is the phase transition temperature, then on the thermograms of the TSD currents there is one more maximum of the currents at a temperature of 120 $^\circ\text{C}$ and a shoulder in the temperature range of 190–220 $^\circ\text{C}$ (Figure 1).
This result is unexpected, since, according to the existing theory of relaxation spectrometry, maxima in thermograms with certain values of $T_{\text{max}}$ should appear at any polarization temperature $T_p > T_{\text{max}}$. The appearance of this maximum after the impact of constant electric field on the copolymer in the LC state indicates that the influence of the field on it is determined by its phase state, which is determined by the temperature.

The main relaxation process at $T_{\alpha_{\text{max}}}= 80 \, ^\circ\text{C}$ is apparently responsible for the dipole-segmental mobility in the crystalline region of PET fragments oriented during stretching. A similar process was observed by the authors of [13], where a special study of the impact of crystallinity on this maximum was carried out. However, the work does not mention the presence of high-temperature relaxation at a temperature of 120 $^\circ\text{C}$, which manifests itself for crystalline PET.

Any further increase in the polarization temperature leads to a decrease in the intensity of the main relaxation process. This indicates a limitation of the mobility of the kinetic units responsible for this process, which is apparently related both to an increase in the degree of crystallinity of PET with increasing temperature and to the orientational action of the electric field. The increase in the half-width of the peak of the TSD currents from 10 to 20 $^\circ\text{C}$ associated with this factor indicates redistribution of the spectrum of relaxation times.

However, upon transition to a liquid crystalline state, the intensity of the described process increases sharply, and the peak responsible for the relaxation $\alpha$-process becomes similar to monorelaxation process. The temperature position of the peak of $\alpha$-relaxation does not change. If the copolyester is polarized at temperatures above the temperature of the phase transition temperature $T^*$, then the maximum of the $\alpha$-relaxation process will be shifted towards high temperatures.

The results can be explained if to assume that the copolymer below the phase transition temperature is a polymer system with a heterophaseic structure with three phases: a partially crystalline phase of PET that has not reacted with n-HBA; pure crystalline phase of n-HBA and mesomorphic copolyester obtained by copolycondensation of PET and n-HBA.

The following arguments speak in favor of this phase separation. It is known [1–3, 8, 15] that the copolymer macromolecule consists of hard fragments of n-HBA, terephthalic acid and flexible spaces of ethylene glycol and essential oxygen bound to them. Since the copolymer under study has a molar
concentration of components of 65 mol% n-HBA and 35 mol% PET, even with perfect and complete copolymerization, local regions of its components cannot but remain. Consequently, the mechanisms of relaxation peaks in the thermograms of TSD currents become clear: the relaxation process in the temperature range 65–70°C is apparently responsible for the dipole and segmental mobility in amorphous PET.

This temperature region is typical of amorphous PET and corresponds to the glass transition temperature of the latter. At a temperature of \( T_g = 80 \) \(^\circ\)C, the \( \alpha_1 \)-relaxation process is responsible for similar mobility in crystalline PET. However, it is possible for the process to describe molecular mobility in the copolyester, the structure of which has sufficient thermodynamic affinity with the structure of PET. It can be seen from the TSD current curves that it is a fraction of monorelaxation process typical of pure polymers. It involves several types of kinetic units with a wide spectrum of distribution of relaxation times. The apparent activation energy calculated for this process is \( U = 0.6 \) eV and is typical of polyesters. This confirms that the ideas presented are correct.

Thus, it was shown that in the copolymer there are local regions of crystalline PET that did not react with n-HBA. The conclusion made is consistent with the results of [13], where crystallization of amorphous PET during polarization was noted; however, in our opinion, the attention is not not pay to the fact that during thermopolarization of a sample, the changes occurring in it are associated not only with the polarization temperature, but also with the orienting action of the electric field. It is obvious that the TSD peak current at 80°C is responsible for the segmental mobility in these areas. Or it points to the same mobility in the hard mesogenic unit of copolymer.

To clarify the influence of thermal field on the structure and physical properties of the liquid crystal copolyester, the sample was subjected to heat treatment at different temperatures corresponding to different phase states. The results obtained in this case do not indicate noticeable changes in the structural and phase properties. An analysis of the current curves of the TSD shows that in the glassy state of PET can exist both in amorphous and crystalline phase states. In this case, the transitions from one state to another are determined by the temperature.

In particular, at a temperature of \( T \approx 50 \) °C PET transitions to an elastic state, while the mobility of some parts of macromolecules (segments) increases, but there is still no mutual movement of macromolecules. Therefore, a notable crystallization process has not yet been observed. Active crystallization begins at \( T \approx 100 \) °C and ends at \( T \approx 150 \) °C with the formation of a clear crystalline structure consisting of folded lamellas.

Consequently, the crystallization rate of amorphous regions increases significantly with the simultaneous electric and thermal fields. In our opinion, the thermal field defrosts the mobility of the kinetic units of copolymer responsible for crystallization, while the electric field directs them, thereby contributing to the ordering of the structure. This conclusion is confirmed by the absence of a low-temperature maximum responsible for thawing the molecular mobility of amorphous PET on the thermogram of the TSD currents of samples of copolymer polarized in the LC state and indicates a modification of the structure of copolyester under the influence of external influences.

Based on the foregoing, it can be argued that crystallization in the thermotropic LC copolymer can be achieved by the simultaneous action of thermal and electric fields.

It is known [8, 11] that the interaction energy of the dipole moment of a macromolecule with an external electric field is tens of thousands of times less than the energy of thermal motion of molecules. Therefore, the electric field practically does not affect the degree of ordering of copolymer macromolecules in true crystalline states.

The reaction of copolymer to an electric field in a liquid crystalline state similarly to the low molecular weight of LCs [3], in our opinion, will be collective in nature, therefore an external electric field applied to the LC layer, even of low intensity, will lead to the redirection of all mesogenic units, since the director’s redirection is accompanied by a spatial redistribution of a charge.

Considering the foregoing, the appearance of the second maximum during the polarization of copolymer in the LC state and its absence when the copolymer is polarized at temperatures can be explained in the following way:
The copolymer under consideration in the LC state, due to the molding conditions (extrudates were placed parallel to the substrate plane) has a planar orientation. When exposed to an electric field on the copolymer in the LC state, the mesogenic units with non-zero dipole moments are oriented perpendicular to the electrode plane, that is, they are polarized. In this case, a double electric layer appears at the insulator-electrode interface, the sign of which, due to injection of a homo-charge is opposite to the sign of the electrode. The surface density of a homo-discharge depends on the polarization temperature, the higher the $T_p$, the more dipoles are oriented along the field, and the higher the surface charge density. On the thermograms of TSD currents this circumstance is reflected as an increase in the intensity of the second maximum with an increase in the polarization temperature (Figure 1). At the temperatures $T_p$ lower than the phase transition temperatures, this orientation is excluded. In addition, the injection of a homo-charge does not take place. In this regard, even at the temperatures $T_p > 120 ^\circ C$, but lower than the phase transition temperature, the process under discussion cannot be implemented.

The analysis of the obtained X-ray confirms everything mentioned above. Two types of X-ray diffraction patterns were obtained for each sample (initial and polarized at 170 and 250 $^\circ C$): the first pattern indicated that the primary beam was directed perpendicular to the plane of the sample in the direction of the electric field vector (shooting in the plane), and the second pattern indicated that the shooting was carried out in the direction perpendicular to the electric field vector (shooting at the end).

The pattern of the intensity distribution substantially depends on the region of the sample chosen for the study, which indicates morphological heterogeneity, as well as the anisotropy that arose during the formation of this sample. It can be argued that the predominant orientation of mesogenic units or larger macromolecule formations found in the initial sample, mechanically incorporated, is retained and even enhanced at a polarization temperature above 170 $^\circ C$ (Figure 2a, 2a').

An increase in grain-orientation during thermal treatment below phase transition temperatures was also observed by the authors of [13].

The combined actions of the temperature and the electric fields lead to the orientation effects indicated above and can be explained on the basis of the Fredericks effect, which is a characteristic of nematic LCs placed in a constant electric field. This conclusion is confirmed if we analyze the X-ray patterns obtained for the samples polarized in the mesophase at $T_p = 250 ^\circ C$. When shooting at the end, the X-ray diffraction pattern almost coincides with that for the initial sample and polarized at 170 $^\circ C$; however, when shooting at the plane, the orientation ordering is not observed (Figure 2a'). In this case, the pattern of the intensity distribution substantially depends on the region of the sample chosen for the study, which indicates morphological heterogeneity, as well as the anisotropy that arose during the formation of this sample. It can be argued that the predominant orientation of mesogenic units or larger macromolecule formations found in the initial sample, mechanically incorporated, is retained and even enhanced at a polarization temperature above 170 $^\circ C$ (Figure 2a).
case, the pattern of the intensity distribution when shooting at the end, with the primary beam perpendicular to the vector of the intensity of polarizing field, substantially depends on the selected region of the sample. Based on this, it can be argued that as a result of the Fredericks effect we observe the regions of different director orientations.

It is important to note that when the electric field is removed and the sample is heated as a result of a decrease in polarization, the copolyester texture is more ordered. This is evidenced by the results obtained from a repeated study of samples that were in the LC phase in an electric field at the temperatures below the phase transition temperature. As a result of such actions, the relaxation properties were stabilized. At high polarization stresses, periodic ordering deformation was observed in nematic liquid crystals [17–19].

4. Conclusion
1. The relaxation mechanisms of the thermotropic LC copolyester based on n-HBA and PET do not fit into the classical theory of relaxation spectrometry due to the heterophaseic structure of the copolymer; as a result of the Fredericks effect, the regions with different director orientations are observed.

2. Apparently, a flow induced by constant electric field arises in copolymer in a nematic state. At the same time, mesogenic units oriented at different angles in the XOY plane acquire the same orientation, that is, the structure of the nematic is arranged in better way. This leads to an increase in the elastic coefficients of the liquid crystal copolyester, as a result of which the intensity of the α-relaxation process in the thermograms of the TSD currents decreases.

3. The combined action of a constant electric and thermal fields leads to an increase in the degree of ordering of the structure of the liquid crystal copolymer and changes its structure at the morphological level. The discovered fact of the influence of external fields on the structure of copolymer makes it possible to control it and obtain materials with various electrical and physical properties.

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