

Thermotropic Liquid Crystalline Polymers

7. New Cooperative Structure Transition in Liquid Crystalline Polymers Induced by an Electric Field

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SUMMARY

Electro-optical behaviour of a liquid crystalline polymer- poly{1-[6-[4-N-(4-cyanophenyl)iminomethylphenoxy]hexyloxy carbonyl] ethylene}- is studied. A sharp change of the optical properties measured in crossed polarizers under the cooling of the preliminary oriented sample in an electric field is observed. The effect is explained from the viewpoint of the electric field induced cooperative structure transition.

Polymers of a comb-like structure containing mesogenic groups in side chains of macromolecules are known to have some properties being analogous to those of low molecular weight liquid crystals [1]. In particular a similarity in electro-optical phenomena takes place [2-8]. The orientational effects in an electric field are alike not only qualitatively but they are characterized by the similar mechanism [4]. In spite of the generality of phenomena mentioned liquid crystalline polymers form a special group of liquid crystals with specific properties. It arises from the chemical bonding of mesogenic groups forming the liquid crystalline phase by polymeric backbones.

In this paper one peculiar effect observed for the first time and unknown for low molecular weight analogues is discussed. This phenomenon has been discovered studying the electro-optical properties of po-

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ly{1-[6-[4-N(4-cyanophenyl) iminomethylphenoxy] hexyloxy-carbonyl]ethylene}. This polymer is characterized by a wide range of mesomorphic state: glass temperature $T_g=20^{\circ}\text{C}$ and clearing point $T_{cl}=154^{\circ}\text{C}$. There is only one diffused halo at wide angles (4,4 Å) on the X-ray pattern of the unoriented polymer. Taking into account the absence of small-angle reflexes the polymer should be considered as nematic-type of liquid crystals. The nitrile group at the free end of a mesogenic side chain provides a high positive value of the dielectric constant and as a result the ability of the polymer to the reorientation in an alternating electric field with $E= 10^5$ V/cm. The orientation process proceeds in the same way as in the CN-diphenyl derivative described in our previous papers[4,5]. It includes the orientation of side chains along the electric field direction and normally to the polymer film surface.

The electro-optical measurements were carried out in a thermostatic electro-optical cell according to the technique described in [4]. The direction of the external electric field coincides with the optical axis of the registration system. Therefore the orientation process is accompanied by the decrease of the optical transmittance measured with crossed polarizers practically down to zero (the observation is performed along the main chain of a birefringent single crystal) (Fig.1).

The effect properly said is the following: if the polymeric thin film preliminary oriented in an electric field at T_{cl} is cooled in that field the sharp increase of the optical transmittance takes place (polarizers are crossed) at the $T = T_1$ (Fig.2, curve 1). This effect also occurs if the electric field is switched off at the temperature above T_1 for

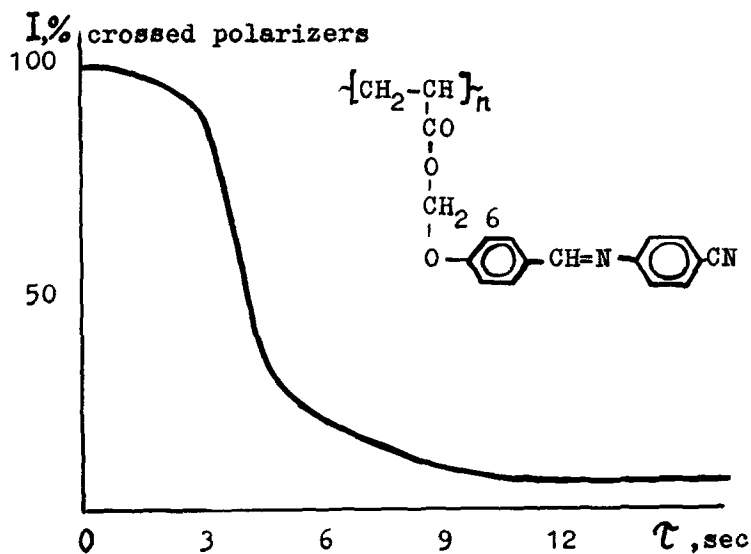


FIG. 1 Optical transmittance as a function of time

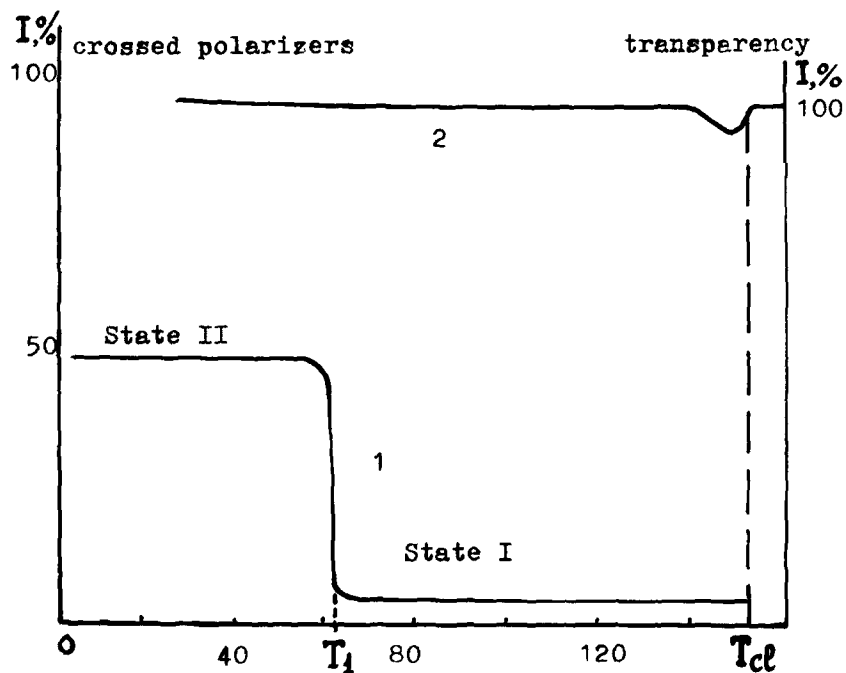


FIG. 2 Change of optical properties of the polymer with temperature.

example at $T=80^{\circ}\text{C}$ and the cooling is carried out in absence of the field. The transparency of the oriented film at this transition is not falling down (Fig. 2, curve 2). Thus it can be concluded that the effect under study is not related to the depolarization of the scattered light and is a result of birefringency change measured in crossed polarizers. The preferred orientation along the field applied earlier of the side chains at this transition is mainly preserved as it can be seen from the X-ray pattern of the oriented film cooled down below T_g .

A long annealing of the sample at the different points of the temperature range near the transition temperature T_1 shows that the oriented State I is stable enough. These data as well as the narrow transition temperature interval permit to suppose that the change of optical properties with the cooling is related with the cooperative structure transition. It should be pointed out that under subsequent heating of the polymer in the absence of an electric field State II remains stable in a wide temperature range, i.e. under these conditions the transition is irreversible (Fig.3, curve 1).

One can try to explain the results obtained in a following way:

1. The orientation of the side groups chemically bonded with the backbone of the macromolecule in the electric field direction initiates the deformation of the main chain and its transition into a new conformational state.
2. A new conformation seems to be stabilized due to the appearance of the strong interaction between the oriented side chains.
3. At the temperature T_1 the conformational state of the system as a whole becomes thermodynamically

unstable. That leads to the transition of the main chain into another conformational state possibly the former one and as a result the rupture of the stabilizing bonds between side chains.

According to the explanation suggested it is the rupture of stabilizing bonds that causes the distortion of the side chains orientation and is accompanied by the observed change in optical properties. The repeated reestablishment of these bonds, i.e. the transition from State II into State I is possible only under the action of a newly applied electric field. Such effect can be actually observed if an external field is applied for a certain period of time to the sample in the State II heated up to 64°C (Fig. 3, curve 2).

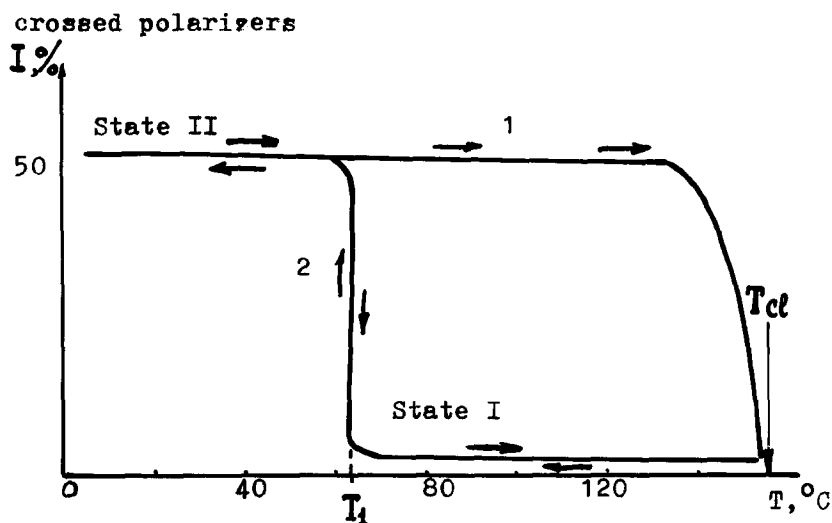


FIG. 3 Influence of an electric field on a reversibility of the cooperative transition : 1- $U=0$, 2 - 200 V.

The possibility of the experimental observation of this effect depends on whether the position of T_1 is above or below T_g . We suppose that in our case unlike the described one in [4] it is not possible to freeze the oriented structure into a glassy state, i.e. here T_1 is higher than T_g .

The exact explanation of this new effect is not possible yet at present and the molecular mechanism of that phenomenon is not clear. But the phenomenon itself seems to be rather unusual and interesting to attract attention of polymer physicists.

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