Relaxation of the Induced Orientational Order in the Isotropic Phase of a Nematic Polymer

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The orientational dynamics in the isotropic phase of a comb-like nematic polymer with mesogenic and functional side groups is studied using the Kerr effect and dielectric spectroscopy methods. For the first time, it has been found that, in contrast to low-molecular-weight mesogens, the relaxation of the electric birefringence of a melt above the temperature of the nematic–isotropic phase transition in a mesogenic polymer can be represented by a sum of several exponential processes, two of which play a decisive role. These processes replace each other in the temperature range of about 50°C. Dielectric spectroscopy also makes it possible to distinguish two orientational relaxation processes, one of which is due to the rotation of the side mesogenic groups, and the second is associated with the motion of the main chain segments.

The isotropic phase of liquid crystal substances is characterized by an increase in the short-range order near the phase transition temperature $T_c$ to the liquid crystal state. The short-range order plays a significant role in a number of physical phenomena observed in the isotropic liquid crystal phase, including static electric birefringence (or the Kerr effect) and relaxation of electric birefringence in a pulsed electric field [1–6]. The discussed effects are observed in the temperature range of several tens of degrees above $T_c$, with the exception of the immediate vicinity of the phase transition, where order fluctuations become very large. These effects are well studied, and the Landau–de Gennes theoretical model [7, 8], used to describe phase transitions in liquid crystals, has been successfully applied to analyze pre-transition phenomena in the isotropic phase of low-molecular-weight liquid crystals. According to the theory, the relaxation time of electric birefringence in an isotropic liquid crystal melt depends on the temperature as $\tau \sim \nu/(T - T^*)^{\gamma}$. Here, $\tau$ is the relaxation time, $\nu$ is the coefficient of viscosity, and $T^*$ is the temperature of an apparent second-order phase transition, which for the low-molecular-weight nematic is approximately 1°C higher than $T_c$. The exponent $\gamma$ in the theory is 1, which was experimentally confirmed for low-molecular-weight liquid crystals with the accuracy of up to 0.01 [9]. Liquid crystal polymers differ from low-molecular-weight liquid crystals in a significantly more complex molecular architecture. A few studies of isotropic melts of comb-shaped liquid crystal polymers showed that the temperature dependence of static electric birefringence in polymers is the same as for low-molecular-weight liquid crystals: the Kerr constant behaves as $K \sim 1/(T - T^*)^\gamma$, where $\gamma = 1$ [10–12]. At the same time, it turned out that the application of the Landau–de Gennes approach for describing the dynamics of electric birefringence in a polymer gives unexpected results. In particular, it was found that the relaxation time calculated from the rotational viscosity of the polymer in the liquid crystal phase differs by several times from $\tau$ measured in the experiment [11], and the exponent $\gamma$ reaches a value of 1.5 [13]. To clarify the origin of such deviations, we studied liquid crystal polymers with different molecular structures [14]. For all polymers, it was found that $\gamma > 1$, and the exponent increases up to 3 at the increase in intra- and intermolecular interaction owing to the introduction of functional (acidic) side groups into the polymer structure. It is important to note that other dynamic characteristics of polymer melts that are not related to short-range effects, such as viscosity, electrical conductivity, and frequency dispersion of the Kerr effect, are described in a classical way [14]. The results of this analysis allow us to propose a model of the orientational dynamics in liquid crystal polymers, which explains the anomalously large value of the exponent $\gamma$. According to this model,
this exponent is anomalously large because a temperature change in the correlation length is accompanied by the replacement of one mechanism of rotational relaxation involving polymer chains by another mechanism, where chains do not play a significant role. The model implies a complex nature of relaxation; for this reason, the aim of the present work is to analyze the relaxation spectrum of electric birefringence for distinguishing the contributions of various orientational mechanisms.

In this work, we studied the electro-optical properties of a melt of comb-like nematic polyacrylate Cop9.7 with cyanobiphenyl and carboxyl side groups [15, 16]. Cyanobiphenyl mesogenic groups are responsible for the formation of the nematic phase. The strongly polar end —CN group provides a sufficient electro-optical effect in the temperature interval necessary for measurements. The copolymer contains 9.7 mol % of functional acid groups —COOH, which form intramolecular hydrogen bonds and thereby affect the dynamics of the melt.

Electric birefringence was measured in a Kerr cell with electrodes 0.4 cm long and an interelectrode gap of 0.03 cm. Pulsed electric fields with a strength of up to 25 kV/cm were used, with an electric pulse decay time of less than 10−7 s. The measured effect was characterized by the Kerr constant \( K \), which is related to induced birefringence \( \Delta n \) and electric field strength \( E \) by the Kerr law \( K = \Delta n/E^2 \). The dynamics of the orientational macroscopic order arising in an isotropic-liquid medium in the form of a response to an external field is described by the equation \(-\frac{\partial F}{\partial S} = \nu \frac{\partial S}{\partial t}\). Here, \( F \) is the free energy, \( t \) is the time, and \( S \) is the orientational order parameter. It follows that the order relaxation after the switching off the field occurs exponentially \( S = S_0 \exp\left(-\frac{t}{\tau}\right) \) with the characteristic time \( \tau \). In the experiment, a change in the induced order was detected by the optical anisotropy of the sample \( \Delta n(t) = \Delta n_0 \exp\left(-\frac{t}{\tau}\right) \). The relaxation time was determined from the dependence \( \Delta n(t)/\Delta n_0 \) on \( t \) (inset of Fig. 1) as \( \tau = \int_0^t \frac{\Delta n(t)}{\Delta n_0} dt \).

The log–log plot of the temperature dependence of \( 1/\tau \) (Fig. 1) has the same anomalous character as that for previously studied liquid crystal polymers [13, 14]. The exponent \( \gamma \) exceeds a theoretical value of 1 and is in the range of 2.0–2.7. The reason for the abnormal relaxation may be the complex character of the relaxation process. In this case, the photocurrent decay curve \( f(t) \) can be described by a linear combination consisting of \( i \) exponential terms: \( f(t) = \sum_{i=1}^{N} a_i \exp\left(-\frac{t}{\tau_i}\right) \), where \( \tau_i \) are the partial relaxation times and \( a_i = f_i(0)/\Sigma f_i(0) \) are the partial amplitudes. It is known that the procedure for separating exponentials is a nontrivial task because of fundamental mathematical constraints, and in practice it is solved in various ways [17]. We used a widespread method in which experimental data are represented in semilogarithmic coordinates \( \ln[\Delta n(t)/\Delta n_0] \) versus \( t \). In this representation, a straight segment with the greatest partial time \( \tau_i \) is distinguished; then the data of this component are subtracted from the data array of the initial kinetic curve. Then, the procedure is repeated several times to separate other exponentials.

Separating the relaxation curve, we obtain several exponential processes (Fig. 2), for which the partial amplitudes differ significantly (Fig. 3). Obviously, the main contribution comes from two processes 3 and 4 whose characteristic times differ by almost an order of magnitude.

Near the transition and at temperatures close to \( T^* \approx T_c \), the slower process 4 completely dominates. Its contribution decreases with an increase in the temperature. At high temperatures, the fast process no. 3 becomes predominant. Such a behavior is well explained by the model proposed in [14]. The relaxation of the orientational order after switching off the field is associated with the disordering of nematic-type fluctuations. The fluctuation sizes are given by the correlation length \( r_c \) depending on the temperature as \( r_c = r_0[T^*/(T - T^*)]^{0.5} \). It is important that the composition of the molecular ensemble involved in fluctuations changes inevitably under the variation of \( r_c \). At low temperatures, fluctuations reach a size of \( \sim 100 \) Å [14]. This is noticeably larger than the distance...
between adjacent chains, which is approximately equal to the length of the mesogenic groups, 20 Å; therefore, the chain segments are included in the ensemble together with mesogenic groups. As a result, at low temperatures, the relaxation time is determined by the slow motion of the polymer segments together with the mesogenic groups (process 4). At high temperatures $K$, the correlation length becomes less than 20 Å. In this case, fluctuations are so small that they can involve only the orientational order carriers (mesogenic groups) that are hardly coupled to polymer chains because of $-(CH_2)_4-$ spacers. The motion of mesogenic groups corresponds to the faster basic process 3.

The dielectric relaxation times, both in the isotropic and in the liquid crystal phase, were also measured. The dielectric spectra were obtained on a Concept-21 Novocontrol Technologies dielectric spectrometer with an Alpha-ANB high-resolution frequency analyzer in the frequency range from $10^{-1}$ to $2 \times 10^6$ Hz and at temperatures from 20 to 200°C. The initial samples were films prepared by pressing at the temperature several kelvins higher than the isotropization temperature $T_c$. Brass disks were used as electrodes. The diameter of the upper disk was 20 mm. The sample thickness was set by 50 μm quartz fibers.

In the studied temperature and frequency range, dielectric spectra, i.e., the frequency dependences of the dielectric loss factor ε'' = φ(f), indicated the presence of two regions of the maximum ε'' denoted as processes α and δ. They are caused by dipole polarization relaxation processes. This is confirmed by the shift of the maxima with increasing temperature toward high frequencies. Dielectric spectra are described by the empirical Havriliak–Negami (HN) equation [18]. The characteristic relaxation times $\tau_{\text{max}}$ were determined from the frequency position of $\varepsilon''_{\text{max}}$ by the formula [19]

$$\tau_{\text{max}} = \tau_{\text{HN}} \left[ \frac{\sin \left( \frac{\pi(\alpha_{\text{HN}})\beta_{\text{HN}}}{2(\beta_{\text{HN}} + 1)} \right)}{\sin \left( \frac{\pi(\alpha_{\text{HN}})}{2(\beta_{\text{HN}} + 1)} \right)} \right]^{-1/(\alpha_{\text{HN}})}$$

The $\tau_{\text{max}}$ values calculated from the Havriliak–Negami equation in the region of processes α and δ are given in Fig. 4.

The temperature dependence $\log \tau_{\text{max}} = \varphi(1/T)$ is linear above $T_c$ and is described by the Arrhenius equation $\tau(T)_{\text{max}} = \tau_0 \exp \left( \frac{E_a}{RT} \right)$, where $\tau_0 = \tau_{\text{max}}$ at $T \rightarrow \infty$, $E_a$ is the activation energy, and $R$ is the gas constant. The parameters are $-\log \tau_0 = 22 \pm 2$ and $E_a = (23 \pm 3)$ kcal/mol. The temperature dependences of $\log \tau_{\text{max}}$ for α and δ processes are nonlinear below $T_c$ and are described by the empirical Vogel–Fulcher–Tammann–Hesse equation $\tau_{\text{max}} = \tau_0 \exp \left( \frac{B}{T - T_0} \right)$, where $\tau_0$, $B$, and $T_0$ are temperature-independent parameters.

The nonlinearity of temperature dependences of $-\log \tau_{\text{max}}$ is characteristic of cooperative forms of the molecular mobility, when the activation energy varies with temperature. The cooperative form of the molecular mobility includes, first of all, the segmental mobility associated with the transition to a highly elastic state. Comb-shaped liquid crystal polymers, as well as the polymer studied in this work, above the glass transition temperature demonstrate two cooperative

![Fig. 2](image-url) (Color online) Temperature dependence of partial relaxation times $\tau_i$; $i = 1–5$. The processes are marked in the plot with numbers. Large dots highlight the main processes 3 and 4.

![Fig. 3](image-url) (Color online) Partial amplitudes $q_i$ versus the relative temperature for processes 1–4 in the isotropic melt of the Cop-9.7 polymer.
processes $\alpha$ and $\delta$ rather than one (as in most polymers of other classes) [20–23]. The cooperativity of relaxation, as well as the complexity of the molecular architecture of comb-like liquid crystal polymers, leads to difficulties in interpreting the molecular mechanisms of the dielectric relaxation. Usually, the process $\alpha$ is associated with segmental mobility, i.e., the motion of individual kinetically independent sections of the chain (segments) consisting of several monomer units. The reorientation of the mesogenic group around the long axis also contributes to the process $\alpha$. The process $\delta$ is related to the cooperative rotation of the side mesogenic groups around the short axis.

Cooperative relaxation processes reflect the motion of relatively large parts of the molecule. The parameters of this motion are most sensitive to the chemical and morphological features of the polymer. It is clear from the aforesaid why the character of the relaxation changes so much during the nematic–isotropic phase transition. Figure 4 shows that the segmental motion (process $\alpha$) disappears in the isotropic phase, and the temperature dependence of the process $\delta$ becomes linear. In the liquid crystal phase in the presence of a long-range orientational order, the motion of the side groups is strongly cooperative; in addition, there is a strong dynamic relationship between the mesogenic fragments and the main chain. With the disappearance of the long-range order, mesogenic groups become more independent of each other and of the main chain.

Thus, both dielectric spectroscopy and, for the first time, the electric birefringence method reveal the presence of two main relaxation processes in the orientational dynamics of the comb-shaped liquid crystal polymer, which is in good agreement with our fluctuation model of the phenomenon [14]. One process is the motion of side mesogenic groups around a short axis, while the other is due to the orientation of the main chain segments together with its environment. According to dielectric spectroscopy, the long-range nematic order favors the cooperative nature of the relaxation motion in the liquid crystal phase. The Kerr effect is indicative of the strong effect of short-range order on the dynamics of the isotropic phase.

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