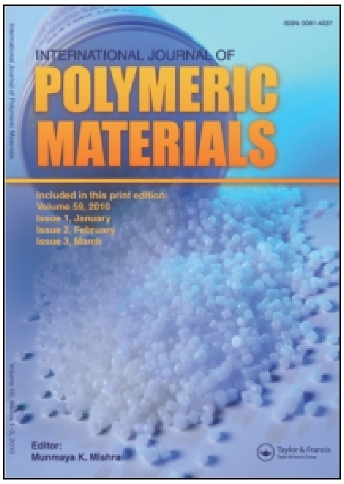

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Influence of the External (Electric or Mechanic) Field on the Dielectric Relaxation in Liquid Crystalline Side Chain Polymers

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The effect of orienting fields on the relaxation of dipole polarization in siloxane and methacrylate liquid crystalline polymers with cyanobiphenyl groups in side chains has been investigated.
The temperature-frequency dependences of dielectric losses of comb-like polymers with the main siloxane chain were studied in the mesomorphic state (in bulk). Two relaxation processes, α and δ, were established. They are related to the reorientation of the transverse and longitudinal components of the dipole moment of the mesogenic group. Similarity of the temperatures of the α- and δ-processes and of the glass transition are due to the dependence of the main chain segment motion on the interaction between side mesogenes, with the segmental mobility occurring only when the mesogenes move. The effect of the external orienting field leading to homeotropic orientation of mesogenic fragments results in the increasing intensity of δ-transition and the suppression of α-transition. The relaxation times and the activation energies of the δ-transition remain unchanged. On the basis of dielectric data the order parameter of mesogenic groups was evaluated. Three relaxation regions of dipole polarization were detected on the temperature-frequency dependences of dielectric losses in a comb-like polymer with the methacrylate main chain in a chloroform solution. Two of them were related to intramolecular mobility of polar kinetic elements in side chains, whereas the third region was associated with the cooperative mobility of mesogenic groups in the macromolecular coil. Only the third process was shown to be influenced by the external electric field.

KEY WORDS Dielectric relaxation, liquid crystalline polymer, order parameter, molecular alignment in the mechanic or electric field.

INTRODUCTION

Dielectric relaxation phenomena in comb-like thermotropic polymers including systems oriented by external orienting fields indicate the existence of transitions which are characteristic of the mesomorphic state alone. These are primarily relaxation processes related to molecular motion which induces changes of the structural order: those in the mesophases within the limits of the existence of the liquid crystalline (LC) state or the transition into the isotropic melt.[1,2] Besides, there are two relaxation processes denoted by α and δ in the range of glass transition[2–9] instead of a single relaxation process occurring in amorphous polymers. Relevant mechanisms of molecular mobility require further investigation. Useful information may be obtained by utilizing samples oriented in external fields.

The study of the dielectric polarization relaxation in oriented and unoriented comb-like LC polymers may be used as a direct quantitative method to determine the degree of orientation of mesogenic groups (order parameter).[3–6]

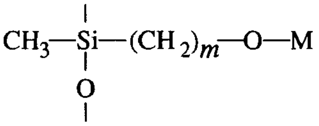
The present study considers dielectric transitions in initial thermotropic comb-like poly-

TABLE I
Dielectric characteristics of relaxation transitions (α and δ) for various polymers, clearing (T_c), and glass (T_g) temperatures

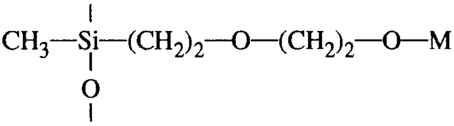
Polymer	U_α (kJ mol^{-1})	U_δ (kJ mol^{-1})	T_α (°C)	T_δ (°C)	T_g (°C)	T_c (°C)
1	188	205	20	36	36	142
2	218	140	11	17	21	168
3	230	150	16	21	21	92

mers with cyanobiphenyl mesogenic groups as well as those oriented by external electric or mechanical fields. They had the following structure:

polymer 1 ($m = 1$), polymer 2 ($m = 5$), polymer 3,

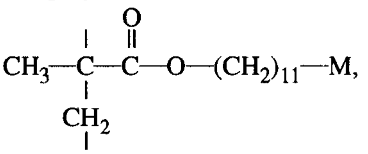


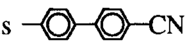
$$\mathrm{CH_3{-}\underset{\underset{|}{O}}{\overset{|}{Si}}{-}(CH_2)_m{-}O{-}M}$$



$$\mathrm{CH_3{-}\underset{\underset{|}{O}}{\overset{|}{Si}}{-}(CH_2)_2{-}O{-}(CH_2)_2{-}O{-}M}$$

and polymer 4



$$\mathrm{CH_3{-}\underset{\underset{|}{CH_2}}{\overset{|}{C}}{-}\overset{\overset{O}{\|}}{C}{-}O{-}(CH_2)_{11}{-}M}$$, where M is 

The mesogenic groups of these polymers are separated from the main chain by at least five simple bonds, the main siloxane chain exhibiting high kinetic flexibility. Therefore, one may expect that the motions of mesogenic groups and the main chain are relatively independent of each other, which favors the formation of LC order. At the same time, a strongly polar nitrile group with dipole moment 4.05 D directed along the axis of the mesogene is present at the end of the mesogenic fragment, ensuring thereby a considerable orientational effect. In oriented samples of polymers and low molecular weight liquid crystals with cyanobiphenyl groups the anisotropy of dielectric permittivity was shown to be positive[10] and equal to 7.5.

EXPERIMENTAL

Polymer samples studied in this work were kindly supplied by Prof. V. P. Shibaev (Moscow University).

Siloxane polymers 1, 2, and 3 were studied in bulk, and methacrylatic polymer 4 was investigated in a dilute solution. Table I gives the clearing temperatures T_c determined with the aid of a polarizing microscope, glass transition temperatures T_g, obtained by the DSC method, the temperatures of dielectric transitions T_α and T_δ at 1 Hz and the activation energies for these processes of dielectric relaxation.

Dielectric measurements were carried out for polymer films 3–100 μm thick and 1–2 cm in diameter. The films were obtained by pressing at a temperature higher than T_c. The tangents of dielectric loss angles and capacitance of polymer films were measured in

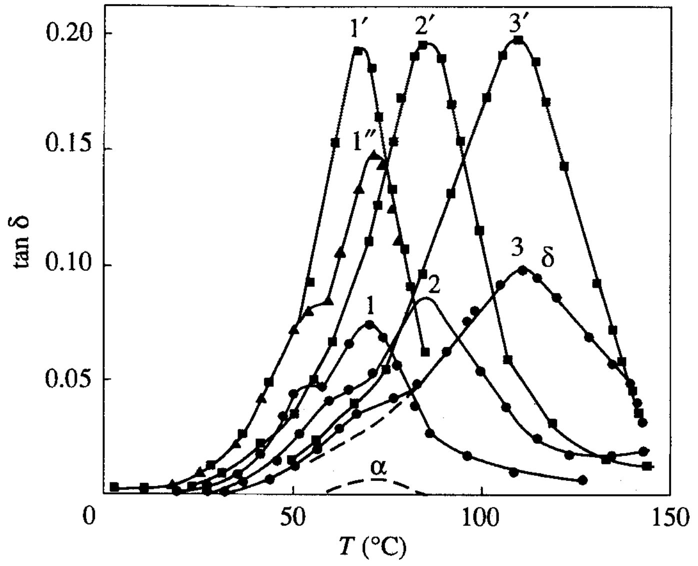


FIGURE 1 Temperature dependences of dielectric loss tanδ for polymer 1 unaligned (curves 1–3) and aligned by mechanic field (curves 1′–3′) or by electric field (curve 1″) at frequencies 1 kHz (curves 1, 1′, 1″), 10 kHz (curves 2, 2′), and 100 kHz (curves 3, 3′). Dashed lines indicate, as an example, the separation of α- and δ-processes for curve 3.

a frequency range from 0.03 to 1000 kHz and at temperatures ranging from 0 to 200°C.

Polymer samples were oriented in electric and mechanical fields. For orientation in the electric field, the sample was heated in a measuring cell at temperature exceeding T_c by several degrees, kept for 15 min in the field of 50 Hz frequency and 130 V and subsequently cooled below T_g, thereafter the orienting field was switched off. Orientation in a mechanical field was carried out by a horizontal displacement of the upper electrode with respect to the lower one at a temperature higher than T_g but lower than T_c.

Dielectric measurements in solution were carried out in a frequency range from 1.5 kHz to 70 MHz in the temperature range from −60 to −50° C. A previously described dielectric cell[11] made of glass and platinum was modified, the capacitance of an empty condenser being 4.5 pF at a filling volume of 0.5 cm^3. The orientation of mesogenic groups in solution was achieved by applying a constant external electric field of strength in the interelectrode space $E_{ext} = 3\,\mathrm{kV\,cm^{-1}}$.

DISCUSSION OF RESULTS

Figures 1–3 show the temperature dependences of tanδ for samples 1, 2, and 3 at different frequencies. It is clear that two overlapping ranges of dielectric relaxation, processes α and δ (the latter taking place at a higher temperature), are observed in unoriented films near T_g in the LC state of the polymer. When necessary, the processes α and δ were graphically separated as is shown by curve 3 in Figure 1.

The Arrhenius dependences $\lg f_m = \varphi(1/T)$ for α- and δ-processes are shown in Figure 4. By extrapolating $\lg f_m = \varphi(1/T)$ to $\lg f_m = 0$ (f_m is the frequency at which tanδ passes through a maximum at a given temperature) the temperatures of dielectric

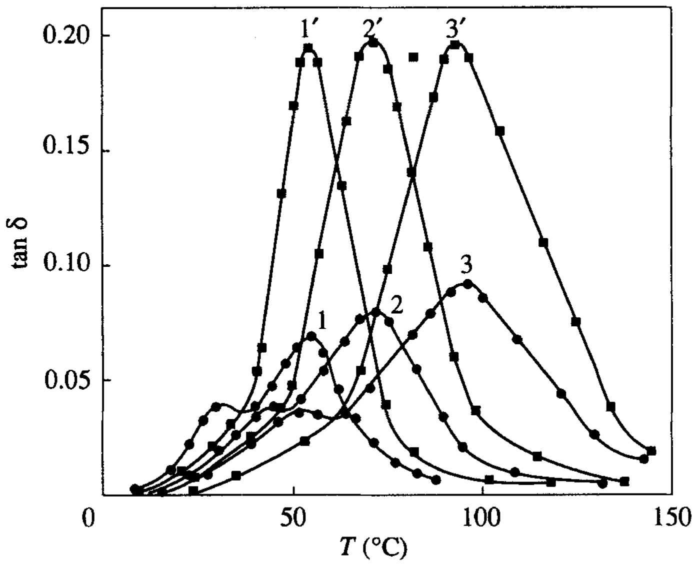


FIGURE 2 Temperature dependences of dielectric loss tanδ for polymer 2 unaligned (curves 1–3) and aligned by mechanic field (curves 1′–3′) at the frequencies 1 kHz (curves 1, 1′), 10 kHz (curves 2, 2′), and 100 kHz (curves 3, 3′).

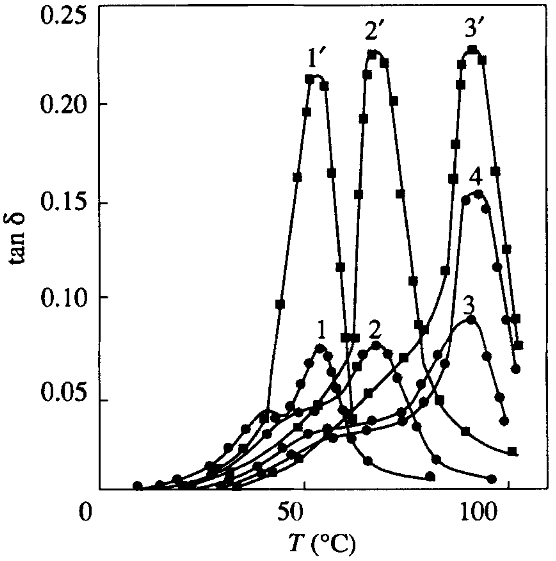


FIGURE 3 Temperature dependences of dielectric loss tanδ for polymer 3 unaligned (curves 1–4) and aligned by the mechanic field (curves 1′–3′) at the frequencies 1 kHz (curves 1, 1′), 10 kHz (curves 2, 2′), 100 kHz (curves 3, 3′), and 200 kHz (curve 4).

transitions, T_α and T_δ were determined. They were close to T_g values found by DSC (Table I). The activation energies of dipole polarization were calculated from the tangent of the slope angle of the Arrhenius dependences. For polymers 1, 2, and 3 they ranged from 140 to 230 kJ mol^{-1} (Table I). High values of activation energies indicate that the

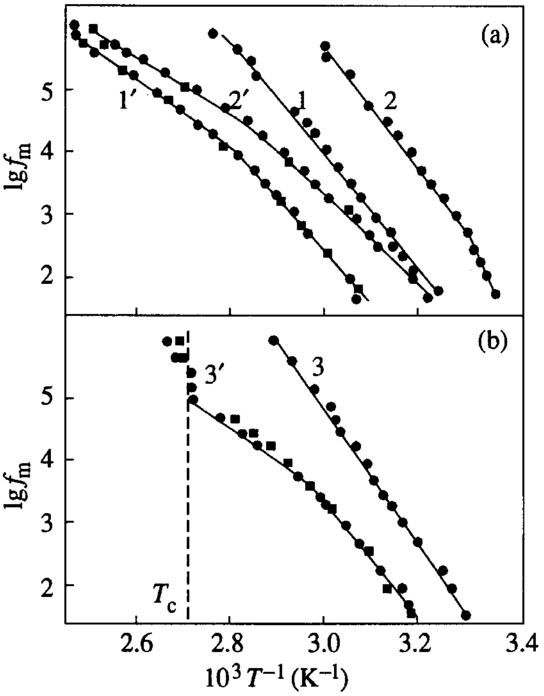


FIGURE 4 Temperature dependences of f_m for (a) polymers 1, 2 and (b) polymer 3. α-processes, (curves 1–3); δ-processes, (curves 1'–3').

molecular motion responsible for these processes is of a cooperative character (for local forms of molecular mobility, the activation energy of dielectric relaxation processes is usually 15–45 kJ mol^{-1}. When the spacer length increases from 3 to 5 methylene groups (polymers 1 and 2), the values of T_α and T_δ decrease in agreement with the data in Reference 10.

The comparison of curves 1', 2', 3', 1'' with 1, 2, and 3 in Figures 1–3 shows that as a result of orientation in the electric and mechanic fields the values of tanδ_m for the δ-transition increase markedly, the α-process disappearing partially or completely. The temperature-frequency coordinates of the δ-transition do not change during orientation.

The comparison of curves 1' and 1'' in Figure 1 shows that the value of tanδ_m for the δ-process in sample 3 oriented in an electric field is lower than that for a sample oriented in the mechanical shear field. Hence, under these conditions the mechanic orienting field appears to be more effective than the electric field, since the latter cannot lead to maximum orientation in a polymer sample. Figure 5 shows the dependences of tanδ_m in the range of the δ-transition at different frequencies on inverse temperature for the initial sample of polymer 3 (curve 1) and for that oriented by the mechanical field (curve 2). It can be seen that near T_c the orientation effect disappears because the values of tanδ_m for oriented samples decrease and attain the values corresponding to those for initial samples. Hence, Figure 5 clearly shows that the dielectric measurements provide a simple and direct method for fixing phase transitions, which illustrates the transition from the oriented into the unoriented state or from the mesophase into the isotropic state. The relaxation time

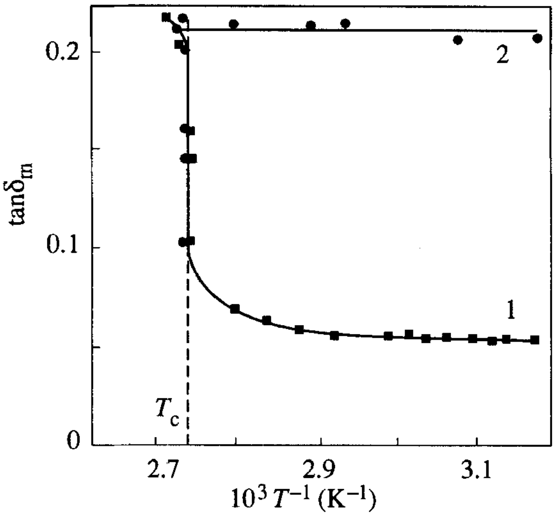


FIGURE 5 Temperature dependences of $\tan\delta_m$ for polymer 3 for unaligned (curve 1) and aligned by mechanic field (curve 2) in the range of the δ-process.

distribution parameter according to Fuoss and Kirkwood (β_{FK}) depending on temperature and orientation was calculated for polymer 3 from the frequency dependences $C\tan\delta$ (C is the sample capacitance). To calculate β_{FK}, the processes α and δ were graphically separated, the result of this separation for the unoriented sample being shown in Figure 6b. The parameter β_{FK} was obtained from the equation $\beta_{FK} = 1.14/\Delta \lg f$, where $\Delta \lg f$ is the width of the curve $C\tan\delta = \varphi(f)$ at the half-height of the maximum. For the α-process (50–70°C) the value of $\beta_{FK} = 0.38$ was obtained. It is characteristic of the glassy state of the polymers. In oriented and unoriented samples at the same temperatures the δ-process has $\beta_{FK} = 0.76$. With increasing temperature β_{FK} rises attaining values close to unity, i.e. to those characteristic of the highly elastic state of the polymer. The molecular mechanisms of the α- and δ-processes in comb-like LC polymers with mesogenic end groups in side chains have already been considered.[3–8] From these studies follows that the source of the α- and δ-processes of dielectric relaxation was the reorientational mobility of perpendicular $\mu_\perp$ and parallel $\mu_\parallel$ components of the dipole moment of the polar mesogenic group. In the homeotropic orientation by an external field, i.e. when the mesogenic groups are oriented mainly normally to the surface of the film polymer sample, the main contribution to dielectric losses is provided by the reorientating motion of the parallel component of the dipole moment of mesogenic groups. As a result, the intensity of the δ-process increases with the degree of orientation. In this case the relative contribution of the transverse component of the dipole moment decreases until the indications of the α-transition disappear completely.

In the side chains of polymers investigated in the present paper, the mesogene is the polar cyanobiphenyl end group. For polymers 1, 2, and 3, the longitudinal component of the dipole moment of the mesogene is determined by the polarity of the CN group and is 4.05 D, as was already mentioned. The transverse component of the dipole moment of the mesogenic group is due to the presence of the ether bond adjoining the cyanobiphenyl group. The dipole moment of the ether group is almost perpendicular to the long axis

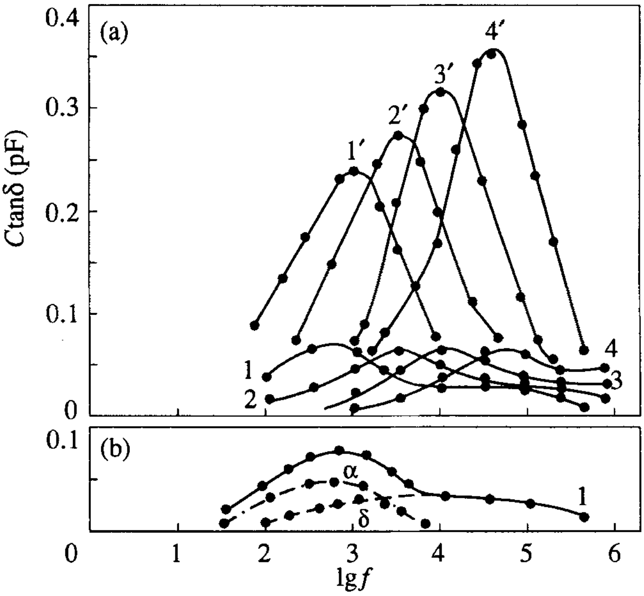


FIGURE 6 (a) Frequency dependences $C\tan\delta$ of polymer 3 for unaligned (curves 1–4) and mechanically aligned films (curves 1′–4′) at temperatures 50°C (curves 1, 1′), 60°C (curves 2, 2′), 70°C (curves 3, 3′) and 80°C (curves 4, 4′). (b) Separation of α- and δ-processes at 50°C.

of the mesogene[10] and is 1.22 D. It should be noted that the siloxane backbone of the macromolecule of these LC polymers has a much lower dipole moment per monomer unit (0.95 D) than that of the mesogenic group.[10] Hence, the motion of the main chains provides only a relatively weak contribution to dielectric polarization.

Consequently, the α- and δ-processes of dielectric relaxation observed for polymers 1, 2, and 3 should be related to the mobility of the transverse and longitudinal components of the dipole moment of the mesogenic group, respectively.

In References 7, 8, and 12 a somewhat different treatment of the α- and δ-processes has been proposed: the α-transition is considered to be related to the segmental motion of the main chain, and the δ-transition is ascribed to the rotation of the mesogenic group about the backbone of the macromolecule which for this type of motion is the rotation axis. The latter statement does not seem very convincing since the side chain which contains both the mesogene and the spacer is not a rigid rod which could rotate about the main chain.

As was mentioned above, the α- and δ-transitions in these polymers with the siloxane main chain are localized near the glass transition range. Polysiloxanes exhibit high kinetic flexibility: glass transition is usually observed at temperatures about 100°C lower than the room temperature.[13] Hence, relatively high T_g obtained for these polymers can be explained by strong interactions between mesogenic groups in the side chains, which hinder the motion of the main chain. The mobility of the mesogenic fragments actually eliminates the hindrance of main chain motion by side chains in each of its monomer units thereby making the segmental motion possible. Hence, it may be assumed that the temperatures of the α- and δ-transitions are directly related to the glass transition range of these polymers.

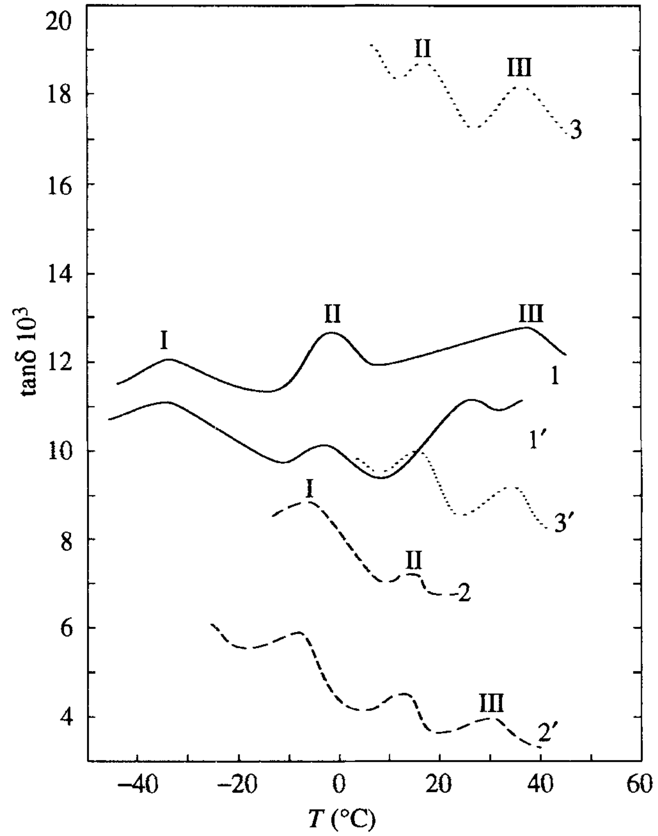


FIGURE 7 Temperature dependences of dielectric loss $\tan\delta$ for polymer 4 in chloroform solution (w = 2 wt %) at frequencies 0.15 MHz (curves 1, 1′), 1.5 MHz (curves 2, 2′), and 7 MHz (curves 3, 3′). $E_{\text{ext}} = 0$ (curves 1–3) and $E_{\text{ext}} = 3\ \text{kV cm}^{-1}$ (curves 1′–3′).

Dielectric data for oriented samples of the polymers investigated here made it possible to evaluate the order parameter P. The authors of References 3–6 have derived a simple equation for the calculation of P by using the maximum values of the factor of dielectric losses for oriented, ϵ''_{or}, and unoriented, ϵ''_{u}, samples

$$P = \frac{1}{2}\left(\frac{\epsilon''_{\text{or}}}{\epsilon''_{\text{u}}} - 1\right).$$

The value of ϵ''_{m} is related to the tangent of dielectric loss angle by the equation $\epsilon''_{\text{m}} = (\tan\delta_{\text{m}})(C/C_0)$. Hence, P may be evaluated from the values $C\tan\delta_{\text{m}}$ instead of ϵ''_{m}. The values of $C\tan\delta_{\text{m}}$ (at 1 kHz) for polymers 1, 2, and 3 oriented by the mechanic field and for polymer 1 oriented by the electric field are 16.6, 21.6, 23, and 11.8 pF, respectively, and the corresponding values of $C\tan\delta_{\text{m}}$ for unoriented films of polymers 1, 2, and 3 are 7.1, 7.6, and 8.5 pF, respectively. Therefore, for mechanically oriented samples 1, 2, and 3, the values of the order parameter P are 0.67, 0.91, and 0.95, respectively. For electrically polymer 1 oriented films $P = 0.33$. In spite of some assumptions in calculating the order parameter which can lead to its values being slightly excessive, these P values show that

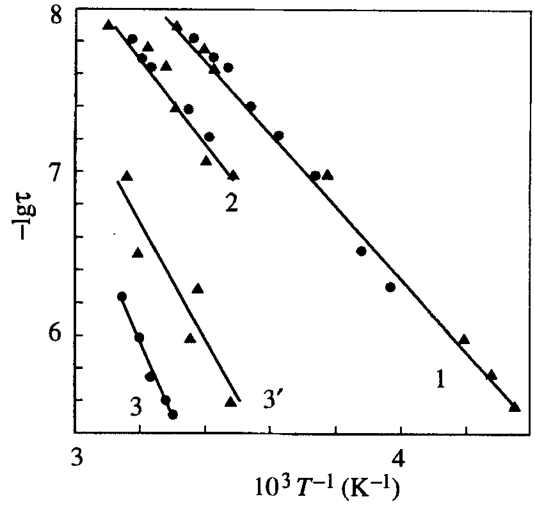


FIGURE 8 Temperature dependences of relaxation times for polymer 4 in solution for process I (curve 1), process II (curve 2) and process III (curves 3, 3′). ●, $E = 0$ and ▲, $E = 3$ kV cm^{-1}.

high order is attained in the arrangement of mesogenic groups when the polymer melt is oriented by the mechanical shear.

The effect of the orienting field on the molecular mobility of the LC polymer with a comb-like structure in a dilute solutions has some specific features because the macromolecules in solution are very flexible. Therefore, the orientational effects in the relaxation of dielectric polarization in solution can be studied only in the presence of an external orienting direct electric field E_{ext}.

Figure 7 shows the temperature-frequency dependences of tanδ for polymer 4 in a chloroform solution ($w = 2\%$ weight) in the absence of E_{ext} (curves 1, 2, and 3) and under the influence of E_{ext} (curve 1′, 2′, and 3′). Figure 7 shows that three regions of dielectric relaxation (I, II, and III) are observed in the dependences $\tan\delta = \varphi(T)$. The relaxation times of the processes corresponding to these regions determined from the equation $\tau_m = \pi f_m$, depending on temperature are shown in Figure 8. The activation energies were calculated for all three relaxation processes of dielectric polarization from the slopes of these dependences.

As is seen from Figures 7 and 8, the temperature position of tanδ for processes I and II is not affected by E_{ext}. The relaxation times and energies of processes I and II are 13 ns and 36 ns (at 30°C), respectively, and $U_{\text{I}} = U_{\text{II}} = 45$ kJ mol^{-1}. The values of these parameters point to the local character of intramolecular mobility, namely the mobility of polar groups within the monomer unit. These are the ester groups adjoining the main chain and cyanobiphenyl—a polar mesogenic fragment. The autonomic mobility of the mesogenic end group in the side chains of the macromolecular coil is ensured by a flexible spacer consisting of 11 methylene groups. When E_{ext} acts on the solution of a LC polymer, process III is displaced toward lower temperatures. In this case the activation energy decreases from 92 to 60 kJ mol^{-1}, and relaxation time reduces from 8000 to 2500 ns.

It has been shown previously[14] that the process of dielectric relaxation in solution which is characterized by these high relaxation times and activation energies is related to the cooperative form of motion of mesogenic polar fragments in their aggregates. It may be assumed that in this case the range of dielectric losses contains contributions of longitudinal and transverse components of the dipole moment of the mesogenic group. The orientational order of mesogenic fragments increases under the influence of E_{ext} and, hence, the contribution of parallel components of the dipole moments decreases. As a result, the contribution of perpendicular components having shorter relaxation times becomes predominant and, therefore, in the presence of E_{ext} process III is displaced toward lower temperatures. As stated above, for bulk polymers under the conditions used the external field leads to homeotropic orientation and suppresses the transition related to the perpendicular component of the dipole moment of the mesogenic groups. In contrast, the decrease in relaxation times in solution demonstrates experimentally the degeneration of the transition due to the parallel component of the dipole moment. Moreover, the effect of the external field is manifested only in the fraction of mesogenes which forms molecular aggregates.

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