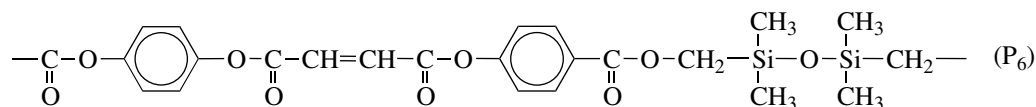


Scheme 1.

(where $n = 6$ and 10 , respectively),



The technique of dielectric relaxation of polymers in solution in an external orienting electric field has been tested for the linear flexible-chain polymers poly(methyl methacrylate) P_1 and poly(*p*-chlorostyrene) P_2 .

EXPERIMENTAL

Polymers P_1 and P_2 were synthesized by radical anionic polymerization; $M \sim 10^5$. The synthesis of polymers $\text{P}_3\text{--P}_6$ was described in [5–7]. The molecular mass of polymers $\text{P}_3\text{--P}_6$ did not exceed 10^5 . Polymers $\text{P}_4\text{--P}_6$ were characterized by LC properties in the bulk. Polymer solutions were placed in an external dc electric field over the entire period of dielectric measurements. A capacitor filled with a liquid (either solvent or solu-

tion) C_m and a blocking capacitor C_{bl} were in-series connected in the measurement circuit according to the standard procedure [8]. The strength of an external orienting field in the solution ($|E| \sim 10^4$ V/cm) was created by a VVC-1 dc voltage source. This value is several orders of magnitude below a breakdown strength of $\sim 10^{8-9}$ V/cm of all the solvents and solutions used. The dielectric permittivity ϵ' and the loss factor ϵ'' were measured at frequencies of $10^3\text{--}10^7$ Hz on a TESLA VM-484 bridge and a TESLA VM-560 Q-meter in the temperature range between the boiling and freezing points of the solvent. The error in the measurements of the loss factor was $\pm 2\%$.

Relaxation times of dipole polarization τ were determined from the temperature–frequency dependences of the loss factor according to the relationship

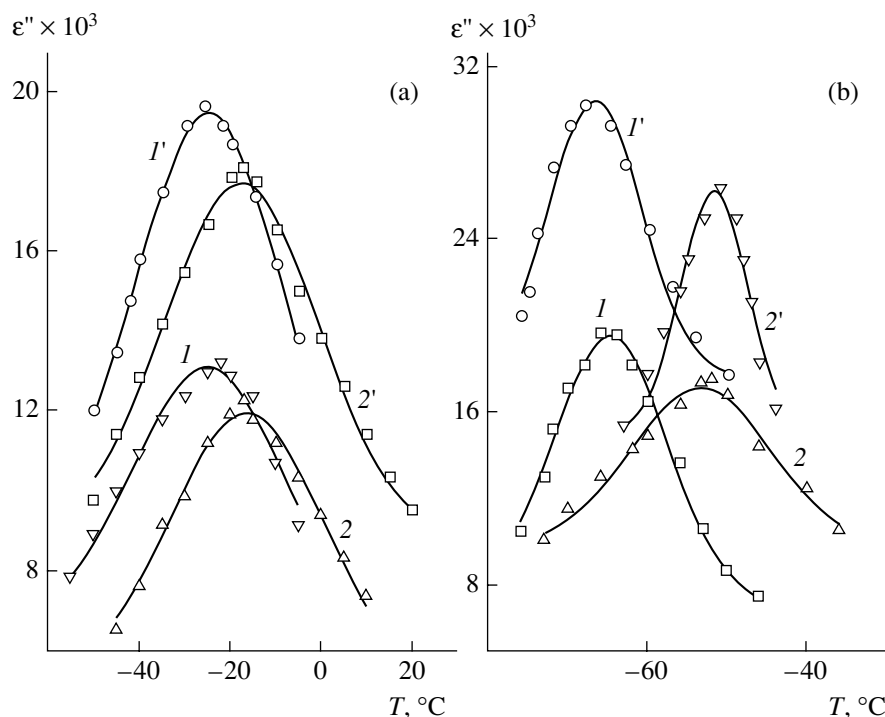


Fig. 1. Temperature dependence of the dielectric loss factor ϵ'' in toluene solutions of (a) P_1 ($w_2 = 3$ wt %) and (b) P_2 ($w_2 = 5$ wt %) at a frequency of (I, I') 0.15 and ($2, 2'$) 0.5 MHz; processes I' and $2'$ at $|E| = 10$ kV/cm.

$\tau = 1/(2\pi f_{\max})$, and the activation energy was calculated through the Arrhenius equation $\tau = \tau_0 \exp(U/kT)$.

RESULTS AND DISCUSSION

Effect of External Orienting Electric Field on Dipole Relaxation in Model Polymers $P_1, P_2,$ and P_3

As an illustration, Fig. 1 collates the temperature dependences of the loss factor ϵ'' for polymers P_1 and P_2 at $|E| = 0$ (curves $I, 2$) and at $|E| \neq 0$ (curves $I', 2'$) in toluene solutions at two frequencies. As can be seen, polymers P_1 and P_2 show one region of dipole polarization relaxation in both sets of experiments; at the same frequency, the temperature position of ϵ''_{\max} remains unchanged; the value of ϵ'' increases when the solution is exposed to an external field.

Figure 2 presents the relaxation times τ as determined from the $\epsilon''-T$ plots. For both polymers, the arrays of relaxation times τ in the absence and in the presence of external field are described by the same linear relationships $\log \tau - 1/T$, from which the activation energy of dipole polarization relaxation can be calculated. The parameters τ and U found to be 4–5 s and ~ 29 kJ/mol, respectively, are characteristic of small-scale processes, which are described by the Gaussian statistics of macrochains [9]. According to the theoretical concepts [9], dipole polarization relaxation in both polymers P_1 and P_2 is due to the reorientational motion

of polar side groups ($-\text{COOCH}_3$ and $-\text{PhCl}$) with a certain segment of the polymer main chain.

Figure 3a shows the temperature–frequency dependence of ϵ'' in polymer P_3 at $E = 10$ kV/cm in comparison with the data reported in [3]. As can be seen, this

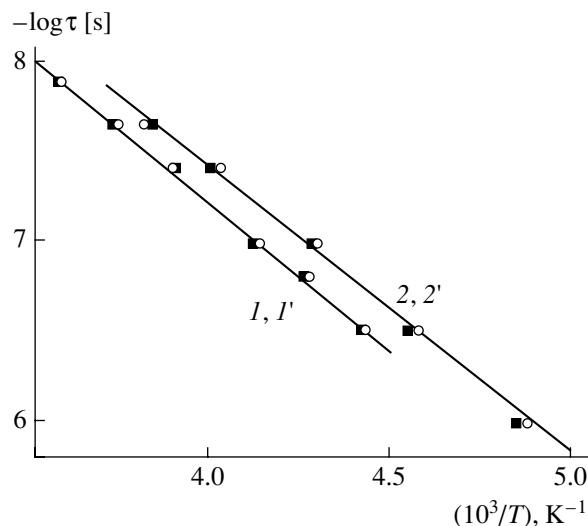


Fig. 2. Temperature dependences of the relaxation time τ in (I, I') P_1 and ($2, 2'$) P_2 in toluene ($w_2 = 3$ and 5 wt %, respectively). Processes I and 2 at $|E| = 0$ (closed circles) and $I', 2'$ at $|E| = 10$ kV/cm (open circles).

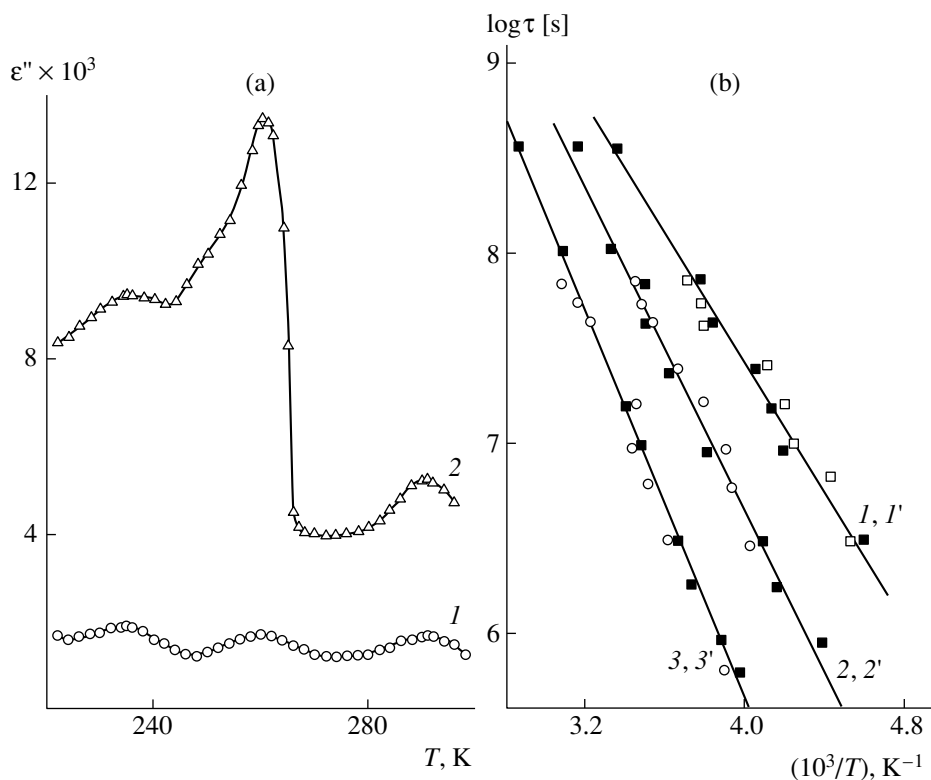


Fig. 3. Temperature dependences of (a) the loss factor ϵ'' and (b) the dielectric relaxation time τ in P_3 in toluene ($w_2 \sim 5$ wt %) at 2.6 MHz. (a): at $|E| = (1)$ 0 and (2) 10 kV/cm; (b) processes $1, 2, 3$ at $|E| = 0$ (closed circles) and $1', 2', 3'$ at $|E| = 10$ kV/cm (open circles).

polymer retains three regions of dielectric relaxation in the presence of an electric field as well. As in the case of P_1 and P_3 , the temperature position of ϵ''_{\max} in the $\epsilon''-T$ plots remains unchanged for polymer P_3 in an external electric field. The dielectric polarization relaxation times calculated from the $\epsilon''-T$ plots at $E \neq 0$ (Fig. 3b) agree well with the Arrhenius plots $\log \tau - 1/T$ obtained earlier for this polymer.

The nature of relaxation processes should be associated with certain kinetic fragments shown in the above structural formula for monomer unit of polymer P_3 , whose molecular structure is similar to that of linear LC polymers. The presence of internal rotation axes in fragment A suggests the reorientation of polar groups, namely, the chlorophenylene radical ClPh and ester groups conjugated with peripheral phenylene radicals and the silicon atom $-\text{COO}-\text{Ph}-\text{Si}-$. The parameters of processes 1 and 1' are $\tau = 4$ ns and $U = 33$ kJ/mol and, thus, appear to be close to those of the local process observed in P_2 . Therefore, it may be concluded that process 1 is associated with the reorientation of the chlorophenylene radical PhCl. At $E \neq 0$ (Fig. 3a, curve 2'), the rate of process 1 markedly increases: ϵ''_{\max} increases by a factor of ~ 5 . At the random initial arrangement of the chlorine atom on the phenylene ring, the dipole moment of groups Cl-Ph (~ 1.6 D)

acquires the direction aligned preferably with that of the external field, and dielectric polarization of solution increases.

It may be assumed that processes 2 and 2' are determined by the mobility of $\text{O}-(\text{C}=\text{O})-\text{Ph}-\text{Si}$ groups. This molecular group is bulkier and longer than the radical (PhCl), and its mobility is characterized by high values of τ and U , which are ~ 10 ns and 41 kJ/mol, respectively. At $E \neq 0$, ϵ''_{\max} for process 2' increases to the greatest extent, by a factor of ~ 7 . The higher values of ϵ''_{\max} for process 2' relative to process 1' are due to the two factors, a higher dipole moment of ketone groups $-(\text{C}=\text{O})-$ (2.8 D) and a higher molar concentration in the macromolecule. The pattern of the $\epsilon''-T$ plot for process 2' is nonsymmetric. The asymmetry may be a consequence of the uncertainty in the position of the chlorine atom in the central part of fragment A and by its inductive effect on the dipole moment of the ester group.

Relaxation processes 3 and 3' are displayed on the temperature-frequency plots of the loss factor at higher temperatures. The relaxation time of processes 3 and 3' is ~ 50 ns and considerably exceeds the relaxation times of both processes 1, 1' and 2, 2'. A study of polymer P_3 with different molecular masses has shown that this process is not associated with the rotation of the mole-

cule as a whole, since the relaxation times turned out to be independent of the molecular mass [3, 10]. Relaxation times of $\tau \sim 10^{-8}$ s at an activation energy of $U \sim 50$ kJ/mol for processes 3 and 3' are characteristic of molecular rotation about the short axis in molecules of low-molecular-mass LC compounds [11]. Therefore, the origin of processes 3 and 3' in P_3 may be associated with the intrachain reorientational movement of rigid fragment **A** as a whole.¹ By their nature, processes 3 and 3' (intramolecular segmental mobility) should also be categorized with small-scale processes of molecular mobility. Scheme 1 presents two types of molecular motion in polymer P_3 : (a) the hindered rotation of polar groups in fragment **A** and (b) the segmental mobility of fragments **A** as a whole.

Thus, the measurements of dielectric polarization in model polymers P_1 , P_2 , and P_3 that do not display bulk LC properties show that dipole relaxation processes occur in dilute solutions, which proceed via the local mechanism and their parameters (τ , U) remain unchanged under the action of external orienting field. The external field has an effect on the intensity of dipole polarization ϵ''_{\max} , including the dependence on the direction of the dipole moment of kinetic fragments in macromolecule. The field effect allows the nature of relaxation processes to be revealed with a greater certainty.

Effect of External Orienting Electric Field on Dipole Relaxation in LC Polymers P_4 – P_6

As an illustration, Fig. 4 presents the temperature–frequency dependences of ϵ'' for LC polymer P_5 at two different frequencies. Figure 5 shows the Arrhenius plots of relaxation times for P_6 at $|E| = 0$ and 10 kV/cm. It is interesting that curves 1 and 2 do not contain the intermediate region of dielectric dispersion, which is detected in the corresponding dependences of ϵ'' at $|E| \neq 0$. This behavior is due to the fact that the reorientational motion of the central fragment, which is connected with the second relaxation region, has a low dielectric activity at $|E| = 0$ because of the compensation of oppositely directed dipole moments of COO groups [13]. At $|E| \neq 0$, the number of polar *cis*-conformers in the central fragment increases, and curves 1' and 2' manifest the occurrence of the corresponding process of dipole polarization relaxation.

¹ As was shown in [12], experimental and calculated (according to the theory of rotational isomerism) values of the dipole moment μ_A of low-molecular-mass compound **A** [1,4-bis-(phenylcarbonyloxy)chlorobenzene] and the dipole moment μ_{eff} of fragment **A** in the repeat unit of polymer P_3 are respectively 2.42 and 2.3 at 20°C. This implies that the Kirkwood factor is close to unity $g = (\mu_{\text{eff}})^2/(\mu_A)^2 = 2.3^2/2.42^2 = 0.92$ and, thus, suggests weakly correlated reorientational motion of fragments **A** along the chain of polymer P_3 .

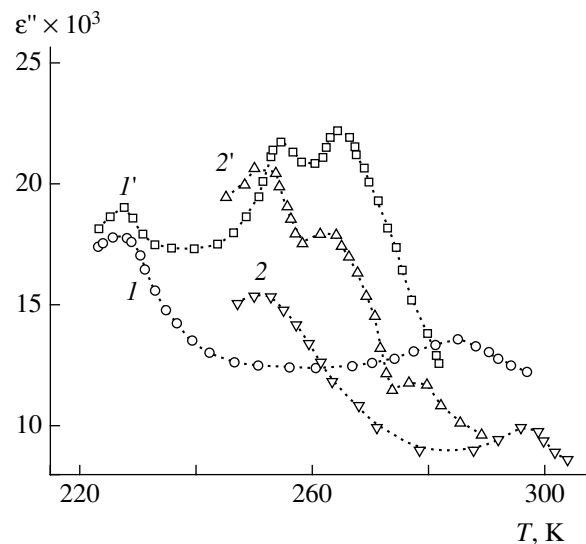


Fig. 4. Temperature dependences of the loss factor ϵ'' for P_4 in chloroform ($w_2 = 5$ wt %) at (1, 1') 0.5 and (2, 2') 1.5 MHz; processes 1' and 2' at $|E| = 10$ kV/cm.

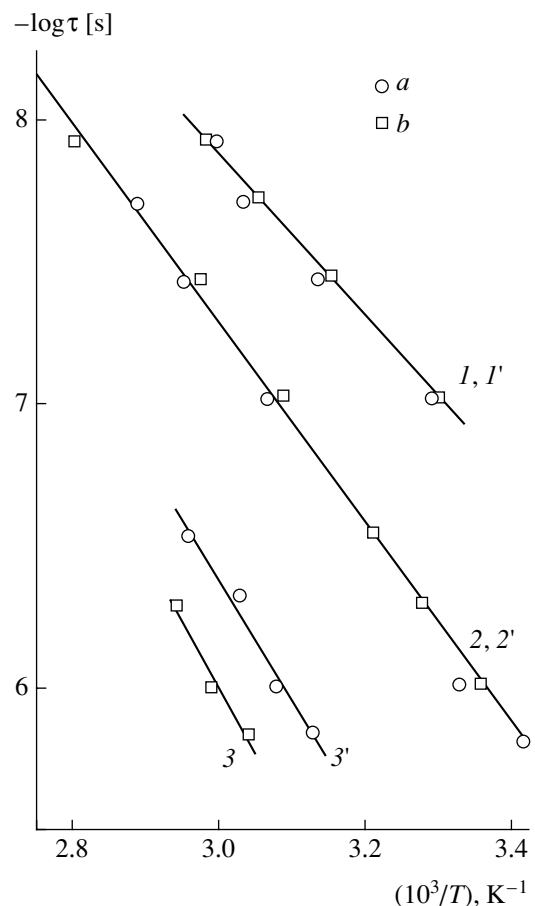


Fig. 5. Temperature dependence of the relaxation time τ for P_6 in toluene ($w_2 = 3$ wt %) for (a) processes 1–3 at $|E| = 0$ and (b) processes 1'–3' at $|E| = 10$ kV/cm.

For test LC polyesters P_4 – P_6 , the $\log \tau - 1/T$ plots are linear and are common for processes 1 , $1'$ and 2 , $2'$ at $|E| = 0$ and at $|E| \neq 0$. At $|E| \neq 0$, the relaxation times of process 3 are shifted toward lower temperatures (process $3'$). According to the structural formulas of polymers P_4 – P_6 , processes 1 and $1'$ observed at low temperatures are due to the mobility of peripheral ester groups. These groups are more mobile because they are attached to the kinetically flexible spacers [10]. In this case, τ and U are ~ 14 ns (P_6) or 17 ns (P_4 , P_5) and ~ 54 kJ/mol (P_4 – P_6), respectively. As compared with processes 1 and $1'$, the relaxation times of processes 2 and $2'$ are longer, ~ 42 ns (P_6) and 70 ns (P_4 , P_5) at 60°C , and the activation energy is higher, ~ 66 kJ/mol (P_4 – P_6), values that indicate a hindered reorientational rotation of COO groups bound to the nonpolar CH=CH group in the central part of the mesogenic fragment. By their parameters, processes 1 , $1'$ and 2 , $2'$ are small-scale processes. Along with the local modes of motion, process 3 can occur in polymers P_4 , P_5 , and P_6 ; at 60°C , the relaxation times of this process are almost two orders of magnitude above those of processes 1 and 2 : $\tau \sim 1.5 \times 10^{-6}$ s. In [10], it was also shown that the parameters of process 3 are independent of the polymer molecular mass. According to NMR and dielectric spectroscopy data [14, 15], process 3 in these polymers is caused by the cooperative mode of reorientational motion of polar mesogenic fragments in their associates according to Scheme 1c.

As in the case of a cyanobiphenyl-containing comb-shaped LC polymer [16], we assume that a decrease in the relaxation time of a large-scale process to $\tau \sim 4.3 \times 10^{-7}$ s (P_6) and 6×10^{-7} s (P_4 , P_5) at 60°C in the absence of external field is associated with the enhancement of orientational order in the associates of mesogenic fragments in macromolecules. In the given case, the orientational mobility of perpendicular components of dipole moments of ester groups in fragments **A** with shorter relaxation times becomes predominant.

The experimental results and their analysis show that the use of the dielectric technique in an external orienting electric field for studying internal rotation and molecular mobility in various polymers gives additional information on the specifics of the mechanism of

molecular motion and allows reliable identification of the nature of relaxation processes. The effect of an external dc electric field on the parameters of the cooperative process of dipole polarization relaxation in LC polymers in solutions was revealed for the first time in our studies.

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