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VISCOELASTIC PROPERTIES OF THERMOTROPIC LIQUID CRYSTAL
POLYMERS FROM ANALYSIS OF DYNAMICAL CHARACTERISTICS

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The rheological properties of liquid-crystal polymers with side-chain mesogenic groups are studied by means of small-amplitude periodic deformations in the mesophase and in the isotropic melt.

Thermotropic liquid-crystal polymers have been studied intensively in recent years in connection with their structure and behavior [1]. Therefore it is important to be able to describe their behavior in the different physical states, in particular, the viscous fluid state. The rheological approach to the study of the physical-chemical and physical-mechanical properties of liquid-crystal polymers is very fruitful and highly informative, since the viscoelastic parameters depend strongly on the structure and phase-aggregate state of the system.

Examination of the literature shows that in the majority of papers devoted to discussions of the rheological properties of liquid-crystal systems, only the viscous characteristics of the systems are considered. This is true both for thermotropic linear polymer systems [1, 2] as well as for polymers with a comblike structure [3]. However it is well known that the most complete rheological behavior of a system reflects its viscoelastic characteristics, which have not been studied extensively for liquid-crystal polymers, and have been limited to only a few systems [4-7].

The rheological behavior of liquid-crystal polymers with lateral mesogenic groups connected directly to the principal chains is of significant interest, for the following reasons. First, in polymers systems of this type the principal chain actively participates in the formation of the liquid-crystal phase, and hence the mesophases of these systems are true polymers. In addition, the macromolecules of these polymers are characterized by low equilibrium and high kinetic rigidity of the principal chain [8]. Finally polymers of this type have a layered structure which develops reversibly with increasing temperature [9, 10]. The features of the layered ordering depend on the structure of the monomeric unit and affect the thermodynamic, relaxational, and other properties of the polymers. In particular, for the series poly-n-methacryloiloxyphenyl ether n-H-alkyloxybenzoic acid (PMB-n), the methods of differential scanning calorimetry and linear thermodilatometry show that the parameters of the

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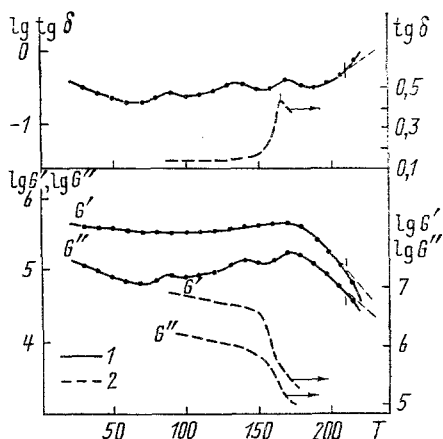


Fig. 1

Fig. 1. Dependence on temperature of the dynamical elastic G' and loss G'' moduli and the mechanical loss tangent $\tan \delta$: 1) PMB-9 at frequency $\omega = 10 \text{ sec}^{-1}$, 2) polypropylene [15]. T , $^{\circ}\text{C}$.

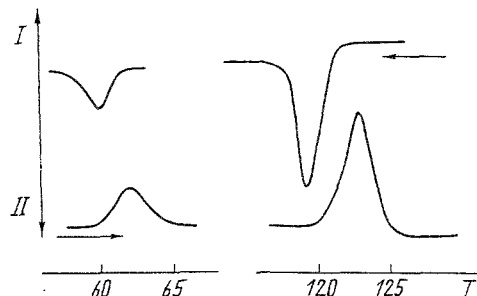


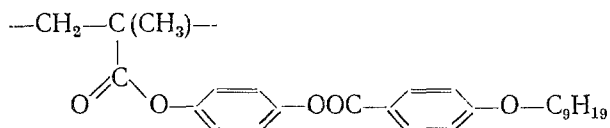
Fig. 2

Fig. 2. Thermogram of PM-10, 4 deg/min.

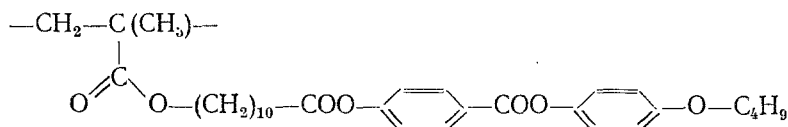
mesophase-isotropic melt phase transition and the temperatures of the principal relaxation transitions change in a nonmonotonic way as the length of the aliphatic substituent is increased [11, 12]. In our opinion the member PMB-9 of the series is the most interesting because it has a comparatively wide temperature interval of the hyperelastic state ($T_c \approx 134^{\circ}$, $T_T \approx 167^{\circ}$), and the mesophase-isotropic melt phase transition ($\Delta H = 3.1 \text{ kJ/mole}$) occurs at relatively low temperature ($T = 209^{\circ}$) in the region of the viscous fluid state. A transition nearest to the glass β -transition is observed at $\sim 70^{\circ}$. Also according to the x-ray data of [10], there is no interpenetration of aliphatic substituents between successive layers in PMB-9 and this significantly affects the mobility of the chains.

On the other hand, liquid crystal systems in which the lateral mesogenic groups are joined with the principal chain through a polymethylene sequence are similar to low-molecular liquid-crystal compounds in their properties.

We consider the rheological characteristics of poly-*n*-methacryloiloxyphenyl ether *n*-H-nonyloxybenzoic acid (PMB-9) with the following structure for the monomeric unit



and poly-*n*-methacryloiloxy-II-undecanoiloxy-(*n*-H-butyloxyphenyl) benzoate (PM-10) with the monomeric unit structure



The samples had the following characteristics: PMB-9: $\bar{M}_w = 5.36 \cdot 10^5$ and $\bar{M}_w/\bar{M}_n = 4.6$; PM-10: $\bar{M}_w = 3.84 \cdot 10^5$ and $\bar{M}_w/\bar{M}_n = 4.1$.

The dynamical rheological method based on small-amplitude periodic shear deformations was chosen as the method of study. The method is practically nondestructive when the deformations and stresses are kept very small. This is quite significant when one takes into account the structure of the macromolecules and their layered packing.

The method yields the most important parameters characterizing the viscoelastic behavior of the system, and in particular, the components of the complex dynamical modulus: the modulus of elasticity G' and the loss modulus G'' , which characterizes dissipative losses, and also

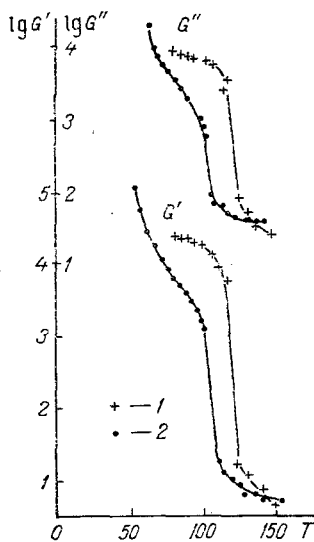


Fig. 3

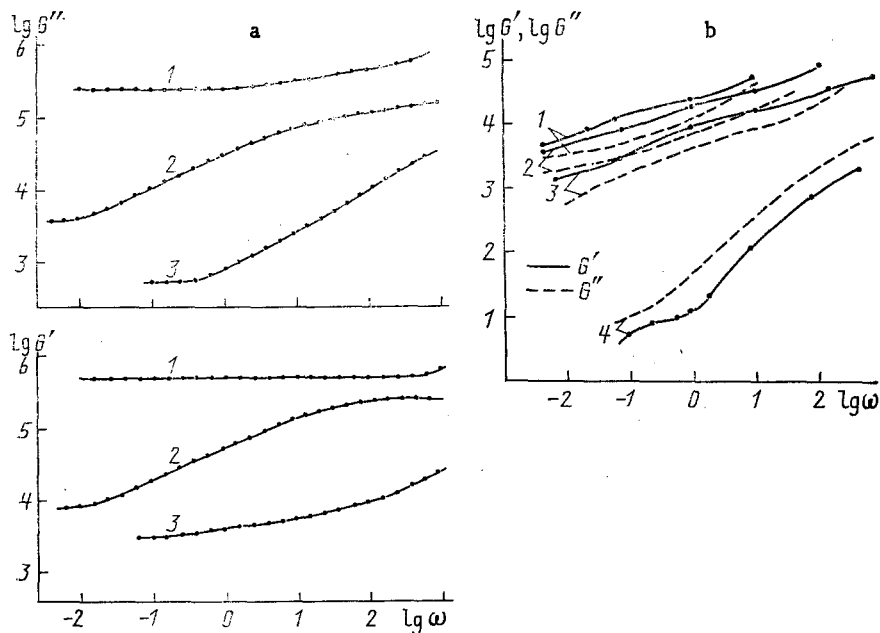


Fig. 4

Fig. 3. Temperature dependence of the dynamical elastic G' and loss G'' moduli for PM-10: 1) heating, 2) cooling. $\log G'$, Pa.

Fig. 4. Dependence of the dynamical elastic G' and loss G'' moduli on the frequency ω : (a) PMB-9 at 170 (curve 1), 200 (curve 2), and 220°C (curve 3); (b) PM-10 at 80 (curve 1), 100 (curve 2), 115 (curve 3), and 140°C (curve 4). $\log \omega$, sec^{-1} ; $\log G''$, Pa.

the mechanical loss tangent $\tan \delta = G''/G'$, which is an important characteristic in the analysis of relaxational transitions in the system. By performing the experiments at various frequencies and determining the dependences $(G'; G''; \tan \delta) = f(\omega)$, it is possible to characterize the viscoelastic properties of the polymer not only for periodic deformations, but also for continuous deformations of solutions and melts in the case of steady flow [13]. In addition, when the temperature is scanned at constant frequency, one can characterize the boundaries of the relaxational states of the system in the series glasslike, hyperelastic, and fluid, and one can identify different relaxational transitions in the system due to the structural features.

The measurements were done on the automated mechanical spectrometer DKhP-2 [14] operating in the circular frequency range from 10^{-3} to 10^3 sec^{-1} and over a wide temperature range.

It follows from the temperature dependence of the elastic G' and loss G'' moduli and $\tan \delta$ that the PMB-9 mesophase can exist in three physical states characteristic of amorphous polymers. Several relaxational maxima are found on the curve of $\tan \delta(T)$ in the temperature region 70-170°.

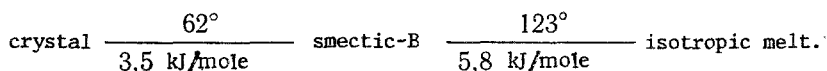
We consider first the behavior of PMB-9 in the temperature interval 170-220°. The maximum of $\tan \delta(T)$ at 170° is due to a transition of the system into the fluid state. This transition is accompanied by a decrease in the values of G' and G'' . It is noted that at the phase transition point only a change in the slopes of the curves $G'(T)$, $G''(T)$, and $\tan \delta(T)$ is observed, whereas for crystalline polymers it is known [15] that a transition through the melting point is accompanied by a maximum in the $\tan \delta(T)$ curve and a sharp decrease in the values of G' and G'' (Fig. 1).

According to Fig. 1, below 170° the sample is found in the hyperelastic state and the modulus G' varies only weakly with temperature. The growth of the $G'(T)$ and $\tan \delta(T)$ curves for $T < 70^\circ$ can be explained by the transition of the system into a state which for ordinary polymers corresponds to the filmlike state. The bumps on the $\tan \delta(T)$ curve at 90, 140, and 170° are due to relaxation. Indeed, according to the linear dilatometry data [12] changes in the linear dimension of the sample occur at approximately the same temperatures and this reflects the mobility of the mesogenic groups and the principal chain and a transition into the fluid state, respectively.

Hence, it follows from these results that the polymer studied here, which has a thermodynamically stable liquid-crystal structure, shows all of the relaxational features characteristic of amorphous polymers up to the phase transition point.

The thermogram of PM-10 (Fig. 2) clearly shows two endopeaks, corresponding to the transition from the crystalline phase into the mesophase and from the mesophase into the isotropic melt, at the temperatures 62 and 123°, respectively. It should be pointed out that upon repeated heating of the sample the temperature and enthalpy of both phase transitions increase somewhat and then remain unchanged upon further heating and cooling cycles.

According to the x-ray data of [16], this polymer has a single-layer structure formed by the mesogenic groups. The mesogenic groups make up the crystalline part, and the polymethylene series make up the amorphous regions. These results are in good agreement with the data for thin polymer layers using the method of IR-dichroism [17]. In the crystalline phase the mesogenic groups are packed in a hexagonal arrangement, and this arrangement is preserved upon transition into the liquid-crystal phase, but it becomes more defective. The parameters of the x-ray diffraction reflections identify the liquid-crystal phase of PM-10 as a smectic-B phase. Therefore the phase transition diagram for PM-10 has the form [16]:



In contrast to linear thermotropic polymers (see [18], for example) the mesophase in PM-10 can be formed from the supercooled isotropic phase ($\sim 119^\circ$), as is evident from the thermogram in Fig. 2.

From the temperature dependence of the dynamical characteristics of PM-10 (Fig. 3), obtained by heating the sample at a rate of 2° per minute and then cooling in air, it is evident that the transition into the isotropic melt is accompanied by a change in the viscoelastic parameters. Also when the isotropic melt is cooled the transition into the mesophase occurs at lower temperature, and this leads to the phenomenon of hysteresis in the dependence of G' and G'' on temperature. Obviously, the magnitude of the hysteresis must depend on the cooling regime of the system. The existence of hysteresis in the temperature dependence of the viscoelastic dynamical characteristics of several linear high-crystalline polyolefins at the melting and crystallization transitions and its connection with the heating and cooling regimes employed were first described in [15]; however for liquid-crystal polymers the rheological parameters vary over much wider intervals. Comparison of the dynamical characteristics of PMB-9 and PM-10 as functions of temperature shows that the transition into the isotropic melt for PM-10 is accompanied by a sharper change of the viscoelastic parameters (G' changes by more than three orders of magnitude). In addition, this transition occurs over a narrow temperature interval (5°). This behavior is typical of polymers with a high degree of crystallinity [15].

Important information can be obtained from the frequency dependence of the dynamical characteristics of PMB-9 at different temperatures (170, 200, 220°) (Fig. 4a). At 170° the material is found in a "quasi-cross-linked" state, since its elastic and loss moduli are practically independent of ω . This indirectly demonstrates the existence of a structural skeleton in the system, i.e., a quasicrystalline lattice formed by interchain contacts of mesogenic groups with a relatively high value of the elastic modulus G' . On the other hand, noting the large values of the quantity G'' and hence also $\tan\delta \approx (0.7-0.8)$, one concludes that this lattice is significantly defective. It is well-known [15] that for crystalline polymers with a sufficiently uniform crystalline lattice (polyethylene, polypropylene) the value of $\tan\delta$ is significantly lower (0.2-0.3) in the region of the hyperelastic state.

At 200° the $G'(\omega)$ and $G''(\omega)$ curves display a hyperelastic plateau in the region $\log\omega > 1$, and the decreasing branches of these curves indicate that the fluid state is reached for $\log\omega < 1$. From the slopes of the curves $G'(\omega)$ and $G''(\omega)$, it follows that the flow cannot be Newtonian (where we must have the conditions $G' \sim \omega^2$ and $G'' \sim \omega$). In addition it is evident that when $\log\omega < -2$, the moduli G' and G'' are practically independent of frequency, and this indicates the existence of a secondary long-time plateau, analogous to that for systems with the capacity of flow. These results can be explained by assuming that at 200° (i.e., the transition of the polymer into the isotropic state) the interchain contacts break up and the structural skeleton is fluctuational in nature.

The flow capacity observed in $G'(\omega)$ and $G''(\omega)$ at $\log\omega < -2$ (obtained at 220°) indicates the presence of definite structural order in the isotropic melt of the polymer as well. The

weak growth of $G'(\omega)$ for $\log\omega > -2$ and the sharp change of G'' at this value is typical of two-phase systems, where one of the phases has a cross-linked structure, and the second is similar to a Newtonian fluid in its properties [19].

The form of the frequency dependence of the dynamical characteristics for PM-10 in the temperature interval 80–140° (Fig. 4b) implies the existence of the hyperelastic state. The hyperelastic state exists over a very small range of ω , which is typical for low-molecular systems. For low ω the existence of liquid-crystal order shows up in the relatively weak variations (G' and G'') = $f(\omega)$. In the isotropic melt the dependence of G' and G'' on ω is typical of elastic low-molecular fluids or dilute solutions of polymers. The data obtained here agrees closely with the results of [2], in which it was noted that liquid crystal systems in which the lateral mesogenic groups are joined with the principal chain through a polymethylene sequence are similar to low-molecular liquid-crystal compounds in their properties. Nevertheless we note that in the frequency region $\log\omega < 0$ a plateau can be clearly identified in $G'(\omega)$. The existence of the plateau can be explained by the restricted mobility of the mesogenic groups bound to the principal chain. The data for PM-10 at different temperatures in the mesophase and in the isotropic melt can be used to calculate the dynamical viscosity of the system $\eta' = G''/\omega$ for low-frequency deformation rates, where the fluid state is realized. From the values of η' obtained at different temperatures in the mesophase and in the isotropic melt, the activation energy of viscous flow was calculated for the liquid-crystal polymer PM-10 in the mesophase and in the isotropic melt. The values are 108.8 and 64 kJ/mole, respectively. The relatively high value of the activation energy in the isotropic melt and also the presence of a secondary long-time relaxational plateau (Fig. 4b) are undoubtedly a consequence of the short-range structural order in PM-10.

NOTATION

G' , G'' , elastic and loss moduli — the real and imaginary parts of the complex modulus, Pa; $\tan\delta$, mechanical loss tangent; η' , dynamical viscosity, Pa·sec; ω , circular frequency, sec^{-1} .

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METHOD FOR CALCULATING THE RELAXATION ERRORS FOR MARKER NUCLEAR-MAGNETIC FLOWMETERS OF THE NUTATION-PHASE TYPE FOR LAMINAR FLOW

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A marker nuclear-magnetic flowmeter for proton-containing liquids is developed and a method for calculating its relaxation errors is proposed.

Methods and apparatus for measuring the flow rate of liquids are very important for modern production operations. Currently used flowmeters are becoming ineffective for low fluid flow rates owing to the significant effect of the contributed hydraulic resistance to the flow and the low accuracy, so that there is a general trend toward the use of non-contract methods, of which the most promising are methods based on nuclear magnetic resonance (NMR) [1, 2].

Amongst the well-known modifications of NMR flowmeters (amplitude, nutation, marker, etc.) the best parameters are obtained with marker flowmeters [1-3] which are the most accurate, informative, and easy to build.

In the design and construction of flowmeters it is necessary to evaluate the possible errors associated with the spread in the values of the relaxation times for different liquids. We shall examine a method for determining the relaxation errors for the example of a marker flowmeter of the nutation-phase type (Fig. 1).

This type of flowmeter operates on the principle of magnetic marking of the liquid and detection, with the help of the NMR effect, of the moment at which the marked liquid passes through the measuring section.

After flowing through the strong field of the polarizer B_p the liquid is polarized, i.e., the magnetic moments of the nuclei in it are oriented predominantly at an acute angle to the induction vector of the magnetic field B_p , as a result of which a nuclear magnetization vector M parallel to B_p is created. Then the liquid flows into the magnetic field B_n along the transport section of the tube L_T , where part of the liquid is marked by dynamic reorientation (nutation) of the nuclear magnetization vector [4, 5]. The marking is recorded in the analyzer, located at some distance $L_1 + L_a$ from the location of marking. At the same time the marked volumes of the liquid are demagnetized in the sections L_T and L_1 and completely magnetized in the field of the analyzer on the section L_a (to simplify the analysis we assume that there are no leakage fields from the magnet systems).

As the liquid flows along the measurement section $L_1 + L_a$ from the nutation section to the recording coil, owing to the distribution of velocities, each layer of liquid is demagnetized and magnetized to a different degree with a characteristic longitudinal relaxation time T_1 . As a result, the contribution of the magnetization of each layer of liquid to the resulting magnetization in the volume of the recording coil depends on the relaxation time, while the recorded propagation velocity of the nuclear-magnetic marker differs from the average velocity of the liquid.

At the inlet into the marker coil the magnetization of the liquid can be written in the form