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DETERMINATION OF THE DYNAMIC CHARACTERISTICS OF LIQUID-CRYSTALLINE POLYMERIC SYSTEMS

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A theoretical description of the dynamic phenomena in liquid-crystalline polymeric systems in periodic mechanical disturbances in terms of the shear modulus and the loss modulus has been given. The rheological characteristics (dynamic viscosity, accumulation modulus, loss modulus, and others) of a synthesized sample of a liquid-crystalline polymeric system — aromatic polyamide — and the critical concentration of its transition from the isotropic state to a liquid-crystalline phase have been determined experimentally.

Most of the existing polymer substances change to the isotropic state in melting. This is attributed to the high flexibility of polymer chains having comparatively low melting temperatures. Because of this, the probability that a completely extended macromolecular chain can be formed is very low, even if such chains incorporate mesogenic groups with a rather high polarizability anisotropy. The total anisotropy of polarizability of a macromolecule will be insignificant because of the random orientation of mesogenic groups in the coil. Consequently, one of the most important conditions contributing to the manifestation of the mesomorphism of polymers is macromolecular rigidity. However, although rigid-chain polymers can in principle be involved in the formation of thermotropic liquid crystals, their melting temperature is very high, as a rule, and it exceeds the temperature of their thermal destruction. The problems of correlation between the structure of rigid-chain polymers and the possibility of formation of a thermotropic mesophase have been considered in detail in [1].

Production of lyotropic liquid crystals based on rigid-chain polymers is more probable. Let us consider the basic indices of the behavior of such liquid-crystalline polymers under shear actions.

One method of investigation of the elastic properties of liquid-crystalline polymers is study of their reaction to periodic loading (deformation). The corresponding deformation is small and the reaction of the medium is analyzed within the framework of the linear theory. First we consider the contribution of relaxation processes related to the macroscopic stress tensor and thereafter allow for an additional contribution (characteristic of liquid crystals) of the relaxation of the tensor ordering parameter. In this case the stress tensor is written in the form

$$\tau_{ij}(t) = K^0_{ijmn}\,\varepsilon_{mn}(t) + \int\limits_0^\infty d\tau\,\eta_{ijmn}(\tau)\,\dot{\varepsilon}_{mn}(t-\tau)\,. \tag{1}$$

Let the components of the deformation tensor vary harmonically with a material frequency ω:

$$\varepsilon_{mn} = \varepsilon^0_{mn}\exp(i\omega t)\,. \tag{2}$$

The deformation-rate tensor varies as

$$\dot{\varepsilon}_{mn} = i\omega\varepsilon^0_{mn}\exp(i\omega t)\,. \tag{3}$$

Substituting (3) into (1), we establish the expression for the stress tensor

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$$\tau_{ij}^0 = \left(K_{ijmn}^0 + i\omega \int_0^\infty d\tau \eta_{ijmn}(\tau) \exp(-i\omega t) \right) \varepsilon_{mn}^0 ; \tag{4}$$

or

$$\tau_{ij}^0 = K_{ijmn}(\omega) \, \varepsilon_{mn}^0 , \tag{5}$$

in so doing,

$$K_{ijmn}(\omega) = K_{ijmn}^0 + i\omega \int_0^\infty d\tau \eta_{ijmn}(\tau) \exp(-i\omega t) \tag{6}$$

is the tensor of complex elastic moduli.

We consider the simplest model of the relaxation function:

$$\eta_{ijmn}(\tau) = \eta_{ijmn}(0) \exp(-\tau\lambda) . \tag{7}$$

The tensor of complex elastic moduli for it is written in the form

$$K_{ijmn}(\omega) = K_{ijmn}^0 + \frac{i\omega \eta_{ijmn}(0)}{\lambda + i\omega} . \tag{8}$$

We have $K_{ijmn}(0) = K_{ijmn}^0$ when $\omega \to 0$ and $K_{ijmn}^\infty = K_{ijmn}^0 + \eta_{ijmn}(0)$ when $\omega \to \infty$. If certain components of the tensor K_{ijmn}^0 are equal to 0, the corresponding components of the tensor of high-frequency elastic moduli are totally determined by the equilibrium correlator $\eta_{ijmn}(0)$.

We find the material and imaginary parts of the component of the complex elastic modulus, i.e., represent (8) in the form

$$K_{ijmn}(\omega) = K'_{ijmn} + iK''_{ijmn} , \tag{9}$$

where

$$K'_{ijmn}(\omega) = K_{ijmn}^0 + \frac{\omega^2 \eta_{ijmn}(0)}{\lambda^2 + \omega^2} , \tag{10}$$

$$K''_{ijmn}(\omega) = \frac{\omega\lambda \eta_{ijmn}(0)}{\lambda^2 + \omega^2} , \tag{11}$$

$\dfrac{K''_{ijmn}(\omega)}{\omega} = \dfrac{\lambda \eta_{ijmn}(0)}{\lambda^2 + \omega^2}$ is the dynamic (relaxing) viscosity.

In the general case, for liquid-crystalline polymers we must allow for an additional contribution of the relaxation of the tensor ordering parameter [2], which leads us to the following expression for the tensor of complex elastic moduli:

$$K_{ijmn} = K_{ijmn}^0 + i\omega \int_0^\infty d\tau \eta_{ijmn}(\tau) \exp(-i\omega\tau) + i\omega a_{ijmn}(\omega) . \tag{12}$$

Let us consider the case of simple-shear deformation. The corresponding components of the tensor K_{ijmn}^0 are equal to zero. Then the dynamic shear modulus acquires the form

$$G'(\omega) = \frac{\omega^2 G_\infty}{\lambda^2 + \omega^2} + \frac{\omega^2 \nu_2(0)\,\tau_1}{1 + \omega^2 \tau_1^2}\,. \tag{13}$$

If we introduce the correlation time τ corresponding to the parameter λ according to the formula $\lambda = r^{-1}$, $G'(w)$ is determined by the dependence

$$G'(\omega) = \frac{\omega^2 \tau^2 G_\infty}{1 + \omega^2 \tau^2} + \frac{\omega^2 \nu_2(0)\,\tau_1}{1 + \omega^2 \tau_1^2}\,. \tag{14}$$

Taking the logarithm of relation (14), we obtain

$$\log G'(\omega) = 2\log\omega + \log\left(\frac{\tau^2 G_\infty}{1 + \omega^2\tau^2} + \frac{\nu_2(0)\,\tau_1}{1 + \omega^2\tau_1^2}\right). \tag{15}$$

The existing experimental data on the frequency dependence of the dynamic shear modulus for liquid-crystalline polymers of hydroxypropyl cellulose (HPC-P(1)) [3] show that, at frequencies of 10 to 10^4 rad/sec, there is a linear dependence of log G' on log ω; its slope angle is determined by temperature, while the slope changes from 0.84 to 1.04.

If we disregard the second term (which holds true for $\omega\tau \ll 1$) in (15), the dependence of log G' on log ω has a slope equal to two, which differs from the above-mentioned experimental data [3]. Therefore, we attempt to interpret the experimental data by a generalized model of relaxation described by fractional derivatives and integrals.

As is well known, the exponential model of the relaxation function (memory function) is equal to the model of the time derivative of the viscous-stress tensor. In turn, differentiation with respect to time in the Fourier representation in frequency is equal to multiplication by $i\omega$.

Following [4], we generalize the relations obtained earlier by changing to derivatives of fractional order. Formally, the above transformation implies the replacement of $i\omega$ by $(i\omega)^\nu$ $(0 < \nu \le 1)$ in the expression for the complex shear modulus:

$$G(i\omega) = \frac{G_\infty (i\omega\tau)^\nu}{1 + (i\omega\tau)^\nu}\,. \tag{16}$$

Taking into account that $i = \exp\left[\frac{i\pi}{2}\right] = \cos\frac{\pi}{2} + i\sin\frac{\pi}{2}$, we compute the material part of the complex shear modulus:

$$\log G'(\omega) = \log\frac{(\omega\tau)^\nu\left(\cos\frac{\pi}{2}\nu + (\omega\tau)^\nu\right)G_\infty}{1 + (\omega\tau)^{2\nu} + 2\,(\omega\tau)^\nu\cos\frac{\pi}{2}\nu}\,. \tag{17}$$

Analogously we can obtain the formula for the imaginary part of the complex shear modulus, i.e., for the loss modulus. We note that for the frequency range in question $(0 < \omega \le 10^3\ \mathrm{sec}^{-1})$ the relaxation contribution of the orientational order is a small quantity since the corresponding relaxation time is $\tau_1 \sim 10^{-8}$ sec [2]. It can be of considerable importance only at rather high frequencies of the order of $10^{-8}\ \mathrm{sec}^{-1}$.

To compare to experimental data we separate the contribution (linear in log ω) to log $G'(\omega)$ in expression (17), taking into account that $\omega\tau$ is sufficiently high. In this case we obtain the expression

$$\log G'(\omega) = \nu \log \omega + \log \frac{\tau^{\nu}\left(\cos\frac{\pi}{2}\nu + (\omega\tau)^{\nu}\right)G_{\infty}}{1+(\omega\tau)^{2\nu}+2\,(\omega\tau)^{\nu}\cos\frac{\pi}{2}\nu}\,. \qquad (18)$$

To interpret the data of [3], where the frequency changes from 1 to 10^4 rad/sec, we will employ formula (18).

The analysis of [3] enables us to infer that in the frequency range in question the second term in (18) is small, and this allows evaluation of the parameter ν by the slope of experimental straight lines describing the dependence of $\log G'$ on $\log \omega$. For HPC-P(1) liquid-crystalline polymers we have $\nu = 0.85$, $\tau = 10^4$ sec and $G_{\infty} = 6.35 \cdot 10^{-4}$ Pa at $t = 80^{\circ}$C and $\nu = 0.85$, $\tau = 10^4$ sec, and $G_{\infty} = 2.1 \cdot 10^{-4}$ Pa at $t = 100^{\circ}$C.

It is significant that fractional derivatives and associated fractional integrals modeling the memory functions are closely related to the Cantor fractional set [5], and the index ν is the fractal dimension of the latter. According to [5], ν corresponds to the fraction of states preserved in the process of nonequilibrium evolution of a physical system and hence is the characteristic of the system's memory.

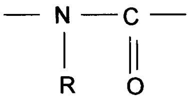
Thus, the value $\nu = 1$ corresponds to exponential memory while $\nu = 0$ describes the Markovian system with a total absence of memory.

To obtain experimental confirmation of the above dependences of the mechanical indices of liquid-crystalline polymers on the deformation we synthesized a sample belonging to the aromatic polyamide class.

Systematic investigations of the solutions of rigid-chain polymers have been carried out in [6, 7] using poly-γ-benzyl-L-glutamate (PBG) as an example. They showed that PBG solutions are isotropic at low concentrations; when the boundary values determined by the molecular mass of the polymer are attained, the solutions break down into a polymer-enriched anisotropic phase and the isotropic phase with a low concentration of PBG, which are in equilibrium. When the second boundary concentration of PBG is attained, the entire system becomes the anisotropic phase.

Aromatic polyamides, for example, poly-*p*-benzamide and poly-*p*-phenyleneterephthalamide, are an interesting class of rigid-chain polymers forming the mesophase [8]. In the region of isotropic solutions of the second substance, one observes a rapid growth in the viscosity of the system with increase in the concentration of the polymer. At the instant anisotropic macromolecular aggregates appear, at $C \cong 8.5$ wt.% the solution viscosity sharply decreases; thereafter, as C increases further, the system's viscosity increases again, and at $C = 13$–14 wt.% the system changes to the stagnant state. The existence of the yield stress is attributed to the occurrence of transverse bonds between ordered aggregate planes in the mesomorphic systems formed.

Particularly high rigidity is exhibited by parasubstituted polymers containing benzene nuclei in the main chain, nitrogen atoms with an unshared electron pair, and carbonyl groups, which is caused by the conjugation effects in the main chain. The decisive contribution of the conjugation effect to the rigidity of polymer chains is shown by the example of polyalkylisocyanates [9] whose main chain contains the groups



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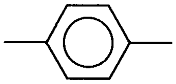
Aromatic polyesters are also characterized by high rigidity of the macromolecular chains [10].

In the case of aromatic parasubstituted polyamides, the coplanar and regular arrangements of the amide groups along the chains contribute to the stabilization of the extended shape of a molecule having the conformation of a crankshaft. With such a conformation the axes of rotation of all monomer links are in parallel to each other, although they are not lying on the same straight line. It is assumed that the trans position of the neighboring benzene rings relative to the bond —NH—C=O is predominantly realized. However the inequality of the valence angles at the C and N atoms and the deformation of the flexible amide group under the action of thermal motion lead to a somewhat broken ideal rod shape of a macromolecule and to the fact that the flexibility parameter of the macromolecule becomes less than zero. With increase in the flexibility of the chains the limiting concentrations of formation of the liquid-crystalline state shift to the region of higher concentrations of the polymer. Owing to this, the lyotropic liquid-crystalline state must manifest itself at higher concentrations of the polymer for chains characterized by higher (but lower than the critical value of 0.63) values of the flexibility coefficient.

Aromatic polyamides can be produced by different methods. The most widespread of them are the methods of interphase or low-temperature polycondensation of aromatic dicarboxylic acids and aromatic diamines in the solution of dichloroanhydrides following the scheme

$$n\,H_2NRNH_2 + ClCOR'COCl \longrightarrow \left[\ NHRNHCOR'CO\ \right]_n + 2n\,HCl$$

R, R' =



The samples of aromatic polyamide were produced by the method of low-temperature polycondensation in the solution of dimethyl acetamide according to the above scheme. The synthesis temperature was equal to (approximately) zero degrees Celsius. We employed triethylamine as the acceptor of hydrogen chloride released in polycondensation.

The rheological characteristics of the above-described liquid-crystalline polymer system, i.e., aromatic polyamide, were experimentally determined using a HAAKE Rheostress RS-150 device in the regime of forced harmonic oscillations. The working unit represented a cone–plane system with an angle of 2^o (this system is typical of rheological measurements of viscoelastic liquids) [11]. Its main advantages are a constant rate of shear in the gap irrespective of the radius, insignificant edge effects, and small amounts of the tested sample, which is particularly important for biological liquids and polymers synthesized, as in our case, for scientific investigations. The principle of operation of the measuring cell is based on the deformation of the sample under study between two surfaces, one of which (plate) moves under the action of forces produced by the drive of the device and the other (cone) moves as a consequence of stresses occurring in the investigated material due to shear of the first surface. The stresses were recorded by measuring the angle of twist of the calibrated torsion bar.

In the general case, irrespective of the form of stress applied to the sample (shear, tension, torsion, etc.) and varying as

$$\sigma = \sigma_0 \exp(i\omega t) \tag{19}$$

in the sample which is homogeneous, there occurs the deformation ε also varying periodically with a frequency ω but lagging behind the stress by an angle δ in phase:

$$\varepsilon = \varepsilon_0 \exp(i\omega t + \delta)\ . \tag{20}$$

In the case of shear deformation the measured quantity is the complex shear modulus G^*:

$$G^* = \frac{\sigma}{\varepsilon} = \frac{\sigma_0}{\varepsilon_0} \exp(i\delta)\ , \tag{21}$$

where

$$G^* = G' + iG''\ ;\quad G' = \frac{\sigma_0}{\varepsilon_0} \cos(\delta)\ ;\quad G'' = \frac{\sigma_0}{\varepsilon_0} \sin(\delta)\ . \tag{22}$$

If the quantity G^* that is the characteristic of a material is independent of the magnitude of the deformation amplitude, we are dealing with a linear viscoelastic body. When G^* turns out to be dependent on the deformation amplitude under the influence of a given action, this indicates the nonlinear behavior of the sample. In this case, the problem of determination of the characteristic constants of the material becomes unambiguous. The measurements have been carried out so that the results obtained are independent of the amplitude, i.e., under small deformations.

Figure 1 gives results of the experiments on determination of the rheological properties of the dimethylacetamide solution of aromatic polyamide. We employed the concentrations of the polymer C = 15, 25, 35, 40, and 45%. The measurements were carried out at room temperature. The data have been obtained at a frequency of f = 0.1 Hz.

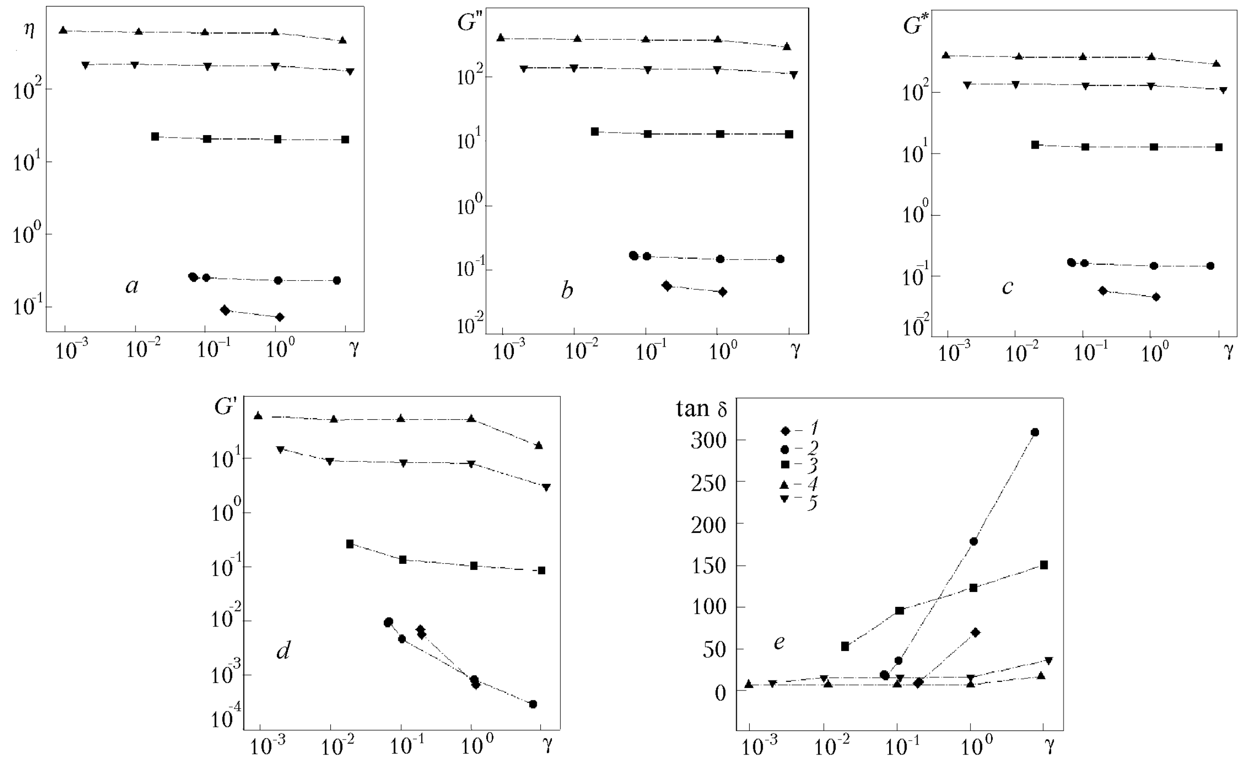


Fig. 1. Dependences of the dynamic viscosity (a), the loss modulus (b), the complex shear modulus (c), the accumulation modulus (d), and the dissipative loss (e) on the relative-deformation amplitude: 1) C = 15, 2) 25, 3) 35, 4) 40, and 5) 45%. η, Pa·sec; G', G'', and G^*, Pa.

As follows from the dependence of the dynamic viscosity η on the amplitude of relative deformation (γ) (see Fig. 1a), the sample of aromatic polyamide in question at concentrations of the polymer of 15, 25, and 35% exhibits the Newtonian behavior for all γ, while at concentrations of 40 and 45% and γ above 0.8 the descending dependence of η on γ is observed. We emphasize that at concentrations of the polymer of about 40% one observes the anomalous (resonance) behavior of the shear viscosity — it rapidly rises as this concentration is approached and thereafter drops. The analogous dependence on the relative-deformation amplitude is exhibited by the loss modulus (see Fig. 1b) and the complex shear modulus (see Fig. 1c). The dependence of the accumulation modulus (see Fig. 1d) on γ is stepwise in character, which indicates entropy structural changes: as the concentration of the polymer increases, the substance changes from the isotropic state to a more ordered — liquid-crystalline — state. In passage to the region of the critical concentration (about 40%), G' rapidly increases in magnitude. Figure 1e reflects the measure of dissipative loss as a function of γ. Thus, we have revealed the critical concentration of the aromatic polyamide (about 40%), which determines the isotropic-to-liquid-crystalline transition.

Obtaining the liquid-crystalline state of a polymer substance opens up vast possibilities of forming and fixing anisotropic structures in the polymer with the aim of imparting the desired properties to them.

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NOTATION

$K^0_{ijmn}\,\varepsilon_{mn}$, locally equilibrium stress tensor; K^0_{ijmn}, equilibrium elastic-modulus tensor; ε_{mn}, small-deformation tensor; $\dot{\varepsilon}_{mn}$, deformation-rate tensor; $\eta_{ijmn}(t)$, relaxation function; K^∞_{ijmn}, tensor of high-frequency elastic moduli; τ^0_{ij}, amplitude of the stress tensor; ε^0_{mn}, amplitude of the deformation tensor; G_∞, high-frequency shear modulus; $\nu_2(0)$, shear viscosity at zero frequency; τ, correlation time; $\tau_y(t)$, stress tensor; τ_1, one time of orientational relaxation; λ, inverse correlation time; $K'_{ijmn}(\omega)$, real part of the elastic-modulus tensor; $K''_{ijmn}(\omega)$, imaginary part of the elastic-modulus tensor; $K_{ijmn}(\omega)$, tensor of complex elastic moduli; a_{ijmn}, tensor of complex coefficients of viscosity which are determined by the relaxation of the tensor ordering parameter; i, j, m, and n, tensor indices; ν, index of the fractional derivative; σ, stress; σ_0, amplitude value of the stress; ω, frequency; t, time; ε, deformation; ε_0, amplitude value of the deformation; G^*, complex shear modulus; G', accumulation modulus; G'', loss modulus; η, dynamic (shear) viscosity; δ, angle; γ, relative-deformation amplitude; C, concentration of the polymer solution.

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