Orientational relaxation of molecules in liquid crystals

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A study was made of the kinetics of the polarized luminescence of impurity molecules in liquid crystal and isotropic phases of 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) and of hexyloxyphenyl ester of decylhydroxybenzoic acid (HOPEDHB). The correlation functions, the orientational relaxation times, and the orientational order parameters were determined. An anisotropy of the orientational relaxation times was observed. It was found that the kinetics of the orientational processes depended on the short-range molecular order, which made it possible to determine the orientational local order parameter. The experimental results were compared with various models of molecular reorientations in liquid crystals.

I. INTRODUCTION

Macrodynamics and structure of liquid crystals have been investigated successfully by various physical methods. However, up to now "very little is known and even less is understood on the dynamics of liquid crystals on the molecular scale."[1] This applies equally to the microstructure (short-range molecular order). Among the spectral methods used in the investigations of the structure of nematic and smectic liquid crystals the most informative at present are the steady-state polarized luminescence and the Raman scattering of light. The orientational order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ representing the orientational distribution function of the molecules $f(\theta)$ have been determined for nematic and smectic phases and a comparison has been made with various statistical theories of the ordering of liquid crystals.

Studies of the kinetics of pulse-excited polarized luminescence make it possible to extend significantly the range of the investigated phenomena. The information which can then be obtained depends strongly on the ratio of the lifetime τ of an excited electronic state and the effective reorientation time τ_R of liquid crystals.[2–4] If $\tau \gg \tau_R$, the relative intensities of the polarized luminescence components are governed by the equilibrium orientational distribution function. In this case, as in the measurements of the dichroism of the absorption spectra, we can determine only the static order parameter $\langle P_2\rangle$. If $\tau \ll \tau_R$, then effective luminescence is obtained from molecules with a nonequilibrium distribution function, which depends both on the equilibrium distribution function and on the geometry of the polarized excitation. In this case the relative intensity of the polarized luminescence components carries information not only on the nature of the orientational order parameter $\langle P_2\rangle$, but also on $\langle P_4\rangle$. If $\tau \sim \tau_R$, the decay of the intensities of the polarized luminescence components characterizes the orientational transformation of the distribution function of excited molecules with time. In contrast to the majority of other methods, an investigation of the polarized luminescence makes it possible to determine in principle the correlation functions corresponding to different types of reorientations in liquid crystals. Since the molecular dynamics is largely determined by the packing of the adjacent molecules, kinetic measurements can give information on the microstructure of liquid crystals.

The effectiveness of the luminescence methods in the study of the dynamics of liquid crystals was pointed out a long time ago.[3,5] The majority of the reported investigations[2,4,6–11] have dealt with the theory of reorientational processes and their manifestation in the polarized luminescence. Manifestations of relaxation processes in the time dependences of the polarized luminescence were recently observed experimentally.[12,13]

A thorough investigation of the molecular dynamics of liquid crystals is possible if measurements are characterized by a high time resolution of the recording system (< 1 nsec), short excitation pulses (< 1 nsec), and use of different orientations of liquid crystals and of different polarizations of the exciting and luminescence radiations. The results of such investigations on liquid crystals (including isotropic states of mesogenic substances) are reported below.

II. SAMPLES AND MEASUREMENT METHOD

Our measurements were carried out on liquid crystals of 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) and hexyloxyphenyl ester of decylhydroxybenzoic acid (HOPEDHB). The luminescence-emitting impurity was 4-diethylamino-4-nitrostilbene (DEANS, 0.03 wt.%) whose molecules are shaped similarly to the liquid crystal molecules. In the investigated samples the temperature of the transition from an isotropic liquid to a nematic liquid crystal was 42 and 90 °C, respectively. The dipole moment of the electronic transition in DEANS was parallel to the long axis of the molecule both in the absorption and luminescence processes. The measurements were carried out on single-domain samples of thickness $\sim 100\,\mu$ with homogeneous and homeotropic orientations of the molecules. The homogeneous orientation of liquid crystals was achieved by depositing a film of polyvinyl alcohol on the surface of a quartz cell followed by directional rubbing with a paper; in the homeotropic orientation case the surfaces of the cells were treated in a solution of chromolon in isopropyl alcohol.

The apparatus is shown schematically in Fig. 1. The luminescence of the impurity was excited with wide-band radiation of a single-pass dye laser ($\lambda \approx 480$ nm). The dye laser was pumped by an atmospheric-pressure nitrogen laser operating at a pulse repetition frequency of 100 Hz and characterized by a $\lesssim 2\%$ instability of the pulse amplitude.[14] The duration of the dye laser pulses did not exceed 0.3 nsec. A liquid crystal sample was placed in a thermostatted quartz cell where temperature was maintained to within ± 0.2 °C.

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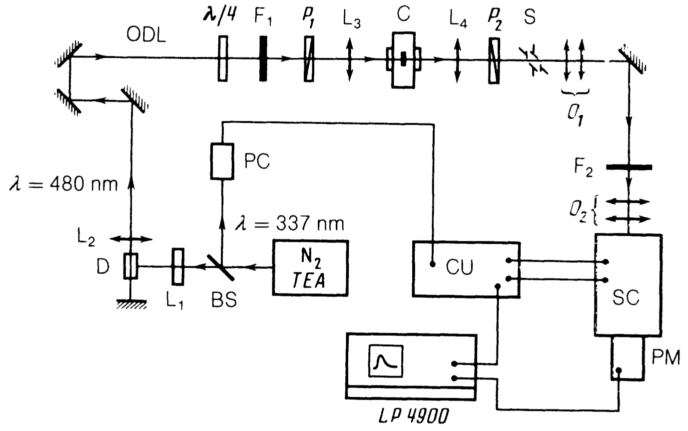

FIG. 1. TEA is a pulsed transversely excited atmospheric-pressure nitrogen laser; D is a cell with coumarin-47 dye; ODL is an optical delay line; C is a cell containing the sample; P_1 and P_2 are polarizers;, O_1 and O_2 are objectives; L_1, L_2, L_3, and L_4 are lenses; SC is a streak camera; PM is a photomultiplier LP4900 is a multichannel analyzer; CU is a control unit of the streak camera; PC is a photocell; BS is a beam splitter.

A lens L_4 projected the image of the sample in the plane of a stop S consisting of two crossed slits. The luminescence was recorded using a system comprising streak camera (SC) with a photoelectric read system and a multichannel analyzer (MCA). The image of the stop S was projected by two objectives in the "focus-into-focus" geometry on the streak camera cathode and scanned in time. The time resolution of the apparatus was largely determined by the transverse size of the stop S, so that this was selected to be sufficiently small (of the order of the spatial resolution of the streak camera). A filter F_1 transmitted dye laser radiation at the fundamental frequency, cutting off the "red" component of the superradiance. A filter F_2 prevented laser radiation from reaching the streak camera cathode ($\lambda_{\text{lum}} \approx 630$ nm). The image of the time scan was analyzed photometrically using a fixed photomultiplier operating in the photon-counting regime. The image was scanned as follows. A stop of size which was the same as the image of the stop S on the streak camera screen was placed in front of the photomultiplier (PM). The deflection system in the streak camera was subjected to a sweep voltage as well as a stepped scanning voltage formed by a specially constructed unit controlled by the MCA. Therefore, each MCA channel corresponded to a certain moment of time relative to the beginning of the sweep. The time resolution of the system was determined by the streak camera and the sensitivity mainly by the read system. In our experiments the time resolution was ~0.3 nsec. The precision of locking to a laser pulse (<0.05 nsec) and the high stability of the exciting pulses made it possible to accumulate average results representing large numbers of light pulses. The results of the measurements were analyzed employing a microprocessor built into the MCA and allowance was made for the reduction in the intensity of the laser beam transmitted by the liquid crystal layer because of the absorption and scattering,[4,15,16] and also for the errors associated with the nonlinearity of streak camera sweep.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the decay curves of the components of the luminescence polarized at right angles (I_{zx}) and parallel (I_{zz}) to the director $\mathbf{n}(\mathbf{n}\|\mathbf{z})$ obtained for the homogeneous orientation of liquid crystals when the polarization of the exciting light was parallel to the director. The decay of the sum of the components of the polarized luminescence $I(t) = I_{zz}(t) + 2I_{zx}(t)$ (curves 3 and 4 in Fig. 2) was determined by the total number of the excited molecules and was independent of the molecular reorientation processes. After the excitation pulse (Fig. 2) the dependence $I(t)$ was exponential with the decay time $\tau \approx 1.8$ nsec for MBBA and $\tau \approx 2.2$ nsec for HOPEDHB. The decay of the individual components was determined by the number of excited molecules and by the time-dependent distribution function of these molecules. In our case (uniaxial mesophase, dipole moment parallel to the long axis of the molecule) the general expression for the intensities of the components of the polarized luminescence is of the form[2]

$$\begin{aligned} I_{zz}(t) &\propto [1+4\langle P_2\rangle+4\Phi_{00}(t)]F(t), \\ I_{zx}(t) \propto I_{xz}(t) &\propto [1+\langle P_2\rangle-2\Phi_{00}(t)]F(t). \end{aligned} \qquad (1)$$

$$I_{xx}(t) \propto I_{yy}(t) \propto [1-2\langle P_2\rangle+\Phi_{00}(t)+3\Phi_{20}(t)]F(t),$$
$$I_{xy}(t) \propto I_{yx}(t) \propto [1-2\langle P_2\rangle+\Phi_{00}(t)-3\Phi_{20}(t)]F(t).$$

Information on the molecular dynamics is carried by the correlation functions $\Phi_{00}(t)$ and $\Phi_{20}(t)$ corresponding to reorientation of the excited liquid crystal molecules in the plane of the director and relative to the rotation axis perpendicular to the director; $F(t)$ is the number of the excited molecules $[F(t) \propto \exp(-t/\tau)]$.

The relaxation processes (Figs. 3a, 3b, and 4) were separated from the experimental dependences $I_{ij}(t)$ by calculating the following ratios for the homogeneous and homeotropic orientations of liquid crystals:

$$P_2'(t) = \frac{I_{zz}(t)-I_{zx}(t)}{I_{zz}(t)+2I_{zx}(t)} = \frac{\langle P_2\rangle+2\Phi_{00}(t)}{1+2\langle P_2\rangle}, \qquad (2)$$

$$r(t) = \frac{I_{xx}(t)-I_{xy}(t)}{I_{zz}(t)+2I_{zx}(t)} = \frac{2\Phi_{20}(t)}{1+2\langle P_2\rangle}, \qquad (3)$$

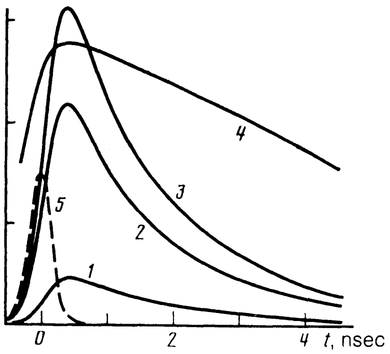

FIG. 2. Experimental decay curves of the polarized luminescence components emitted from MBBA (34 °C) 1) $I_{xx}(t)$; 2) $I_{zz}(t)$; 3) $I(t) = I_{zz}(t) + 2I_{zx}(t)$; 4) $\ln I(t)$; 5) excitation pulse.

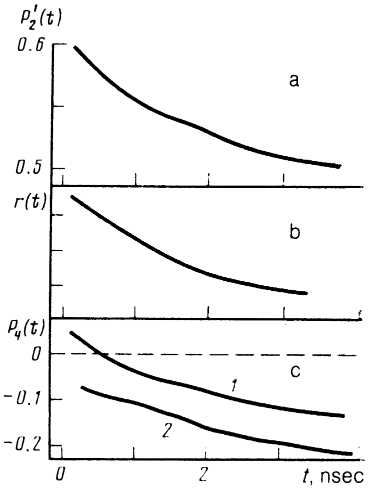

FIG. 3. polarization characteristics of orientational relaxation of MBBA (34 °C): a) homogeneous orientation $P_2'(t)$; b) homeotropic orientation $r(t)$ (rel. units); c) homogeneous orientation $P_4(t)$ at 34 and 40 °C (curves 1 and 2, respectively).

$$h(t)=\frac{I_{xz}(t)-I_{xx}(t)}{I_{zz}(t)+2I_{zx}(t)}=\frac{\langle P_2\rangle-\Phi_{00}(t)-\Phi_{20}(t)}{1+2\langle P_2\rangle}. \tag{4}$$

The expressions for $r(t)$ and $h(t)$ in the form of Eqs. (3) and (4) are more convenient in the analysis of the experimental results than those proposed in Ref. 2, because they do not contain the correlation functions in the denominator. In the case of the isotropic distribution function we have $P_2'(t) = r(t) = h(t)$. It is clear from Figs. 3a, 3b, and 4 that in the investigated range of times the relaxation processes are important for both substances.

The correlation functions $\Phi_{00}(t)$ and $\Phi_{20}(t)$ for the liquid crystal state were calculated using the diffusion (Refs. 2 and 6–8) and strong collision (Refs. 2 and 8) models and by computer modeling of the molecular dynamics. For the values of the order parameter in the range $\langle P_2\rangle < 0.7$, typical of nematic phases of liquid crystals, the diffusion and strong collision models give the same result: the dependences $\Phi_{00}(t)$ and $\Phi_{20}(t)$ are exponential[2,4,8]:

$$\begin{gathered}\Phi_{00}(t)=[\langle(P_2)^2\rangle-\langle P_2\rangle^2]\exp(-t/\tau_0)+\langle P_2\rangle^2,\\ \Phi_{20}(t)=[{}^1/_5-{}^2/_7\langle P_2\rangle+{}^3/_{35}\langle P_4\rangle]\exp(-t/\tau_2),\end{gathered} \tag{5}$$

which are in qualitative agreement with the experimental results (Figs. 3 and 4). The bell-shaped plots of $P_2'(t)$ and $h(t)$ predicted on the basis of machine modeling of molecular motion in liquid crystals[9] are not supported by the experimental results.

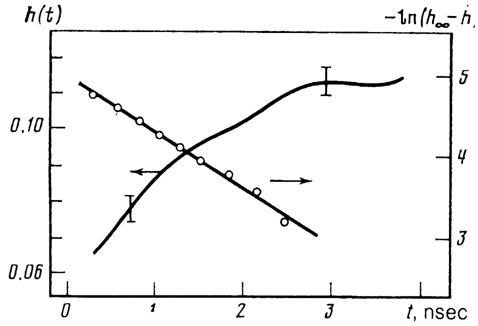

FIG. 4. Homogeneous orientation of HOPEDHB $h(t)$ (86 °C).

The limiting values of $P_2'(t)$ and $h(t)$ are independent of the choice of the model and are determined by the equilibrium values of the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$:

$$\begin{gathered}P_2'(\infty)=\langle P_2\rangle,\qquad h(\infty)=\frac{\langle P_2\rangle(1-\langle P_2\rangle)}{1+2\langle P_2\rangle},\\ P_2'(0)=\frac{2\langle(P_2)^2\rangle+\langle P_2\rangle}{1+2\langle P_2\rangle}.\qquad h(0)=\frac{5\langle P_2\rangle-3\langle P_4\rangle-2}{5(1+2\langle P_2\rangle)}.\end{gathered} \tag{6}$$

The rapid fall of the illumination intensity (Fig. 2) and the associated increase in the error in the determination of $P_2'(t)$ and $h(t)$ (when $t > 3$ nsec) prevented us from determining the plateaus of functions $h(t)$ and $P_2'(t)$ in the limit $t\to\infty$ from the time dependences. Therefore, the order parameter $\langle P_2\rangle$ was found from the relative values of the integral intensities.[4,6] In our case for impurity liquid crystal molecules of MBBA we obtained $\langle P_2\rangle \approx 0.41$ (34 °C) and 0.34 (at 40 °C), and $\langle P_2\rangle \approx 0.52$ (86 °C) for HOPEDHB. The values of $P_4(t)$ were calculated from the initial values of $P_2'(t)$ and $h(t)$ (Figs. 3a and 4) and their values were found to be ≈ 0.05 for MBBA at 34 °C and $\langle P_4\rangle \sim 0$ HOPEDHB at 86 °C. The values of $\langle P_4\rangle$ found in this way for MBBA liquid crystals were greater than those deduced in Ref. 15 from steady-state measurements of the polarized luminescence, where the experimental data were analyzed ignoring the molecular relaxation processes. Figure 3c shows the time dependences $P_4(t)$ described by

$$\begin{aligned}P_4(t)&=\frac{1}{8}\left(35\langle\cos^2\theta\cos^2\theta(t)\rangle-30\langle\cos^2\theta\rangle+3\right)\\ &=\frac{1}{8}\left(\frac{35}{3}\frac{I_{zz}(t)}{I_{zz}(t)+2I_{zx}(t)}(1+2\langle P_2\rangle)-10(1+2\langle P_2\rangle)+3\right)\end{aligned} \tag{7}$$

and we can see that $P_4(t) = \langle P_4\rangle$ is true only at $t = 0$.

In the investigated range of times (Fig. 3) the relaxation processes were anisotropic. The characteristic relaxation times for MBBA were $\tau_0 \approx 4$ nsec and $\tau_2 \approx 3$ nsec. The initial part of the dependence $P_2'(t)$ near $t\to 0$ corresponded to somewhat lower values of τ_0:

$$\tau_0=-\frac{2(\langle(P_2)^2\rangle-\langle P_2\rangle^2)}{1+2\langle P_2\rangle}\left[\frac{dP_2'(t)}{dt}\right]^{-1}_{t=0}\approx 3.5\text{ nsec}, \tag{8}$$

but which were nevertheless greater than τ_2. In the case of HOPEDHB the relaxation time was ≈ 1.4 nsec [this was the average time; $h(t)$ represents the relaxation processes of two types $\Phi_{00}(t)$ and $\Phi_{20}(t)$].

The solution of the diffusion equation for the anisotropic distribution function made it possible to obtain[2,6,7] analytic expressions for the orientational relaxation times, but a comparison with the experimental results has not yet been made. The expressions for τ_0 and τ_2 contain the perpendicular component of the rotational diffusion tensor $D_\perp$ and the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ (Refs. 2, 6, 7):

$$\begin{gathered}\tau_0=\frac{1}{6D_\perp}\frac{7+10\langle P_2\rangle+18\langle P_4\rangle-35\langle P_2\rangle^2}{7+5\langle P_2\rangle-12\langle P_4\rangle},\\ \tau_2=\frac{1}{6D_\perp}\frac{7-10\langle P_2\rangle+3\langle P_4\rangle}{7-5\langle P_2\rangle-2\langle P_4\rangle}.\end{gathered} \tag{9}$$

In the case of MBBA when $\langle P_2\rangle = 0.41$ and $\langle P_4\rangle = 0.05$, we find from Eq. (9) that $\tau_0 = (1/6D_\perp)0.72$ and $\tau_2 = (1/6D_\perp)0.63$. Therefore, the anisotropy of the relaxation process in the liquid crystal state with $\tau_0 > \tau_2$, predicted by the

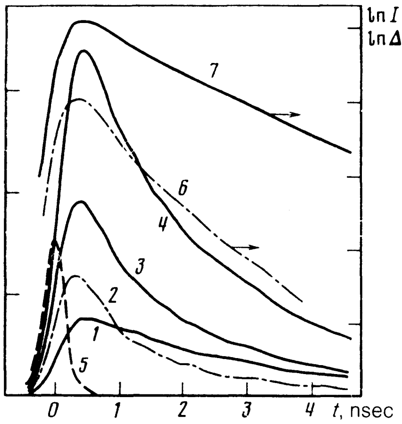

FIG. 5. Decay curves of the polarized luminescence components emitted by HOPEDHB (95 °C): 1) $I_\perp(t)$; 3) $I_\parallel(t)$; 4) $I(t) = I_\parallel(t) + 2I_\perp(t)$; 7) $\ln I(t)$; 2) $\Delta I(t) = I_\parallel(t) - I_\perp(t)$; 6) $\ln \Delta I(t)$; 5) excitation pulse.

diffusion model, is supported by the experimental results.

The luminescence decay curves for the isotropic phase of the liquid crystals are plotted in Figs. 5 and 6. The kinetics of the total luminescence $I(t) = I_\parallel(t) + 2I_\perp(t)$ (curves 4 and 7 in Figs. 5 and 6) was characterized by the same times as in the liquid crystal state: $\tau \approx 2.2$ nsec for HOPEDHB and $\tau \approx 1.8$ nsec for MBBA. The faster fall of the difference luminescence $\Delta I(t) = I_\parallel(t) - I_\perp(t)$ in the case of MBBA, and particularly for HOPEDHB, was an indication of a considerable contribution of a reorientational motion to the kinetics of the individual luminescence components. The reorientation processes were separated, as in the liquid crystal state, using the dependences shown in Fig. 6:

$$r(t) = (I_\parallel(t) - I_\perp(t))/(I_\parallel(t) + 2I_\perp(t)). \tag{10}$$

The initial slopes of the $r(t)$ curves in the range $t < 1.5$ nsec corresponded to the orientational relaxation times of $\tau_R \approx 2.3$ nsec for HOPEDHB at 95 °C and $\tau_R \approx 3$ nsec for MBBA at 55 °C. Cooling increased τ_R (at 43 °C its value was $\tau_R \approx 4$ nsec for MBBA), in agreement with the temperature dependence of the viscosity.[17] The rotational diffusion coefficient $D_\perp$ and the value of $\tau_R = 1/6D_\perp$ were estimated using the Perrin formula modified to fit our case of anisotropic molecules in the shape of an elongated ellipsoid[5]:

$$D_\perp = \frac{3kT}{16\pi\eta a^3}\left(2\ln\frac{2a}{b} - 1\right). \tag{11}$$

where a and b are the major and minor axes of the ellipsoid. The viscosity of MBBA is $\eta \approx 13$ cP at (T_c + 13 °C) and $\eta \approx 19$ cP at (T_c + 1 °C)[17] and for $2a = 20$ Å and $2b = 5$ Å, we obtain $\tau_R \approx 2.6$ nsec and $\tau_R \approx 3.9$ nsec, in good agreement with the experimental values deduced from the initial slopes of the dependences $r(t)$.

Assuming an exponential form of the correlation function $r(t) = \frac{2}{5}\exp(-t/\tau_R)$, we estimated the effective molecular relaxation time from the relative values of the integral intensities of the polarized luminescence components using $\tau_R^c = 5\tau(I_\parallel - I_\perp)/3(3I_\perp - I_\parallel)$. The values obtained in this way were $\tau_R^c \approx 2.5$ nsec for HOPEDHB at 95 °C and $\tau_R^c \approx 3.2$ nsec for MBBA at 55 °C, which were slightly longer than the times deduced from the initial parts of the dependences $r(t)$ because of the nonexponential nature of $r(t)$ (Fig. 6). This can be regarded as evidence of a relationship between the short-range molecular ordering, which exists in the isotropic phase of liquid crystals, and the orientational molecular dynamics. In allowing for the short-range molecular order we have to consider several molecular relaxation mechanisms. The nonequilibrium distribution function of excited molecules relaxes initially to the distribution function characterizing the short-range orientational order. This process should give the limiting value $r(\infty) = (2/5)\langle P_2\rangle_l^2$ (Ref. 8), Where $\langle P_2\rangle_l$ is the local order parameter. The final relaxation to the equilibrium distribution [in the case of the isotropic phase to $f(\theta) = \text{const}$] should involve reorientation of a large ensemble of molecules described by longer times τ_R'. If $\tau_R' \gg \tau_R$, then assuming that the reorientation is described by one exponential function, we find that

$$r(t) = {}^2/_5(1 - \langle P_2\rangle_{\text{л}}{}^2)\exp(-t/\tau_R) + {}^2/_5\langle P_2\rangle_l^2. \tag{12}$$

In the description of the experimental $r(t)$ curves (Fig. 6) by the dependence (12) the local order parameter should be taken as $\langle P_2\rangle_l \approx 0.3$, which is close to the microscopic order parameter $\langle P_2\rangle$ in the liquid crystal state near the temperature of the transition to the isotropic liquid.

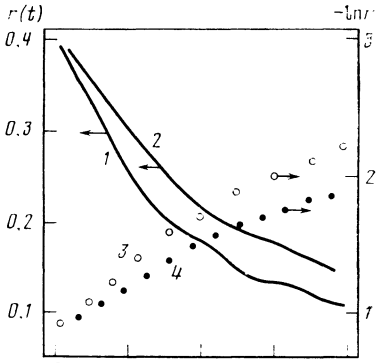

FIG. 6. Anisotropy of the luminescence emitted by HOPEDHB (95 °C, curve 1) and the dependence $\ln r(t)$ (curve 3); anisotropy of the luminescence emitted by MBBA (55 °C, curve 2) and the dependence $\ln r(t)$ (curve 4).

IV. CONCLUSIONS

Our investigation of the polarized luminescence of liquid crystals has shown that a study of the luminescence kinetics is an informative method for investigating the molecular dynamics and structure of liquid crystals. The anisotropy of the molecular relaxation times indicates that the molecular dynamics results in a more rapid establishment of an orientational equilibrium in respect of the azimuthal angle φ which occurs in the distribution function $f(\theta, \varphi)$ than in the plane of the director of the liquid crystal (angle θ). The experimental data of the luminescence kinetics are in agreement with the diffusion model of reorientational processes in liquid crystals. A topical subject in studies of liquid crystals is the short-range molecular order, which may differ quantitatively and sometimes qualitatively from the macroscopic ordering of molecules. The time dependences make it possible to determine not only the macroscopic order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ but also the local orientational order parameter of the isotropic phase. The kinetics of the polarized luminescence can be used as a method for investigating the local molecular order in cubic liquid crystals (blue phases, smectic *D* phase), when the traditional optical methods (absorption, Raman scattering, etc.) for the study of the orientational order are unsuitable.

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