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Study of Isotropic-Nematic Phase Transition by Optical-Field-Induced Molecular Alignment in Binary Mixtures†

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We have used the transient optical Kerr effect and the intensity-dependent ellipse rotation to study the pretransitional behavior of the field-induced molecular alignment in the isotropic phase of binary mixtures of *p*-methoxy-benzylidene-*p*-*n*-butylaniline (MBBA) and 0–30% *n*-hexane. The results can be described very well by the Landau–de Gennes model in all cases. A number of relevant characteristic parameters of the medium are derived as functions of the *n*-hexane concentration.

I INTRODUCTION

Recently, it has been demonstrated that optical-field-induced effects in isotropic liquid crystalline materials are particularly strong because of the pretransitional behavior.[1–3] The third-order nonlinear optical coefficients due to molecular reorientation show the characteristic critical divergence of $(T - T^*)^{-1}$ as the temperature T approaches the fictitious second-order transition temperature T^*, while its response time exhibits the characteristic critical slowing down.[1,2] As an example, we find that *p*-methoxy-benzylidene-*p*-*n*-butylaniline (MBBA) at $T - T^* = 5°K$ has an optical Kerr constant 100 times larger than that of CS_2, and by varying $T - T^*$ from 0.1 to 40°K, the response time of the Kerr effect changes from 850 to 6 nsec. Thus, a liquid crystalline material can be a useful dc or optical Kerr cell medium with its response time easily adjustable over a wide range. In some applications, one

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may want to have a Kerr medium with a variable response time in the subnanosecond to nanosecond range. This can in principle be obtained by choosing an appropriate binary mixture of liquid crystal and ordinary liquid since the Kerr response time of ordinary liquids are of the order of 10 psec.

In this paper, we report some recent results of our measurements on the optical Kerr constants and the Kerr response times of a set of MBBA-*n*-hexane binary mixtures. As expected, both the response time and the optical Kerr constant of the medium at a given temperature decreases with increase of the *n*-hexane concentration. Mixing of *n*-hexane into MBBA dilutes the intermolecular interaction and suppresses T^*. This is quite analogous to a diluted magnetic system. We find that the pretransitional behavior still dominates the optical-field-induced effects in the mixtures (up to 30% of volume concentration of *n*-hexane), and that the decrease of the optical Kerr constant and the Kerr response time with increase of the *n*-hexane concentration is mainly due to the variation of T^* with the *n*-hexane concentration.

Using the Landau-de Gennes model to describe the experimental results, we are able to derive a number of material parameters as functions of the *n*-hexane concentration, e.g., T^*, the anisotropy in the optical susceptibility $\Delta\chi$, the Landau parameter a, and the viscosity coefficient ν. We have also measured the isotropic-nematic transition temperature T_K as a function of the *n*-hexane concentration. All of these quantities can be understood at least qualitatively from some simple physical reasoning.

In the following section, a quick review on the theory and experimental procedures is first given. Then, in Sections III and IV, the experimental results and discussion of the results are presented.

II THEORETICAL BACKGROUND AND EXPERIMENTAL PROCEDURES

Let us first briefly review the theoretical background and the experimental procedures. The details have already been described elsewhere,[1,2] It can be shown from the Landau–de Gennes model[4] that the dynamic equation for the tensor orientation order parameter Q_{ij} driven by an optical field $\mathbf{E}(\omega, t)$ has the form

$$\nu \frac{\partial Q_{ij}}{\partial t} + a(T - T^*)Q_{ij} = f_{ij}(t)$$

$$f_{ij} = \tfrac{1}{12}\Delta\chi(E_i^* E_j - \tfrac{1}{3}|E(\omega, t)|^2 \delta_{ij}) + \text{complex conjugate} \qquad (1)$$

where ν is the viscosity coefficient, a is the Landau parameter, and $\Delta\chi$ is the anisotropy in the optical susceptibility when all molecules are perfectly aligned. From Eq. (1), we can solve for $Q_{ij}(t)$. Then, if the optical field is linearly polarized, $\mathbf{E} = \hat{x}E$, the field-induced linear birefringence is found to be

$$\begin{aligned}\delta n_l(t) &= (2\pi/n)\Delta\chi Q_{xx}(t)\\ &= \frac{\pi c B}{\omega t}\int_{-\infty}^{t} |E|^2(t')e^{-(t-t')/\tau}\,dt' \qquad (2)\end{aligned}$$

where B and τ are the optical Kerr constant and the Kerr response time respectively given by

$$\begin{aligned}B &= (\omega/nc)2(\Delta\chi)^2/9a(T - T^*)\\ \tau &= \nu/a(T - T^*)\\ &= \nu_0 \exp(W/T)/a(T - T^*) \qquad (3)\end{aligned}$$

If the optical field is elliptically polarized, then its two circularly polarized components experience a circular birefringence

$$\delta n_c(t) = \frac{\pi c B}{\omega t}\int_{-\infty}^{t} (|\hat{e}_+ \cdot \mathbf{E}|^2 - |\hat{e}_- \cdot \mathbf{E}|^2)e^{-(t-t')/\tau}\,dt' \qquad (4)$$

As a result, the polarization ellipse rotates as the beam traverses the medium.

In our experiment, we measured the time-dependent field-induced linear birefringence (transient optical Kerr effect) to deduce the response time τ. We used a 20-KW, 1-nsec ruby laser pulse to induce the linear birefringence in the medium and a 10-mW CW He–Ne laser beam to probe the linear birefringence. As seen in Eq. (2), $\partial n_l(t)$ should be essentially proportional to $\exp(-t/\tau)$ at t much larger than the pump laser pulsewidth. Therefore, τ can be readily obtained by measuring the long exponential tail of $\partial n_l(t)$. Knowing τ, we then measured the rotation of the polarization ellipse to find the optical Kerr constant B. We used for the measurements a single-mode, Q-switched ruby laser with a peak power of 100 KW and a pulsewidth of 12 nsec. Since the ellipse rotation is directly proportional to δn_c and $|E|^2(t)$ was known, we could readily deduce B from the measured δn_c following Eq. (4). The measurements were calibrated against CS_2 as a reference medium. Beam attenuation due to absorption and scattering loss in the medium was also properly taken into account in the data analysis.

In the present experiment, samples of binary mixtures of MBBA and 0–30 % n-hexane in volume concentration were placed in a sample cell of 4 cm long. The cell was always sealed under helium or argon atmosphere to prevent the sample from deterioration. The mixtures were prepared in the isotropic phase. They were homogeneous and remained so for many months. As the mixtures were gradually cooled down, each of them became translucent at a certain temperature T_K. We define T_K as the isotropic-nematic transition temperature.

III EXPERIMENTAL RESULTS

Variation of T_K as a function of n-hexane concentration η_l is shown in Figure 1. For n-hexane concentration larger than 15 %, the solid-nematic transition temperature T_{SN} actually lay above T_K. However, because of the broad supercooling region in the cooling process, the isotropic phase of the sample could persist far below T_{SN}. For higher n-hexane concentration, T_K became more difficult to define as the region for the coexistence of isotropic and nematic phase grew wider. In all our measurements, a thermal feedback-control system was used to set the sample temperature to within an accuracy of 0.1°K.

In Figures 2 and 3, we show some examples of the measured response times τ and optical Kerr constants B as functions of temperature for a number of mixtures. Each data point in the figures was obtained from the average of 4 independent measurements. The accuracy for measurements of τ was about 5 % while that for B was 15 %. The results are described very well by Eq. (3). In particular, extrapolation of the experimental data points for τ^{-1} versus T and B^{-1} versus T to $\tau^{-1} = 0$ and $B^{-1} = 0$ respectively yields a value for T^*. In all cases where T_K is sufficiently well defined, $T_K - T^*$ appears to be

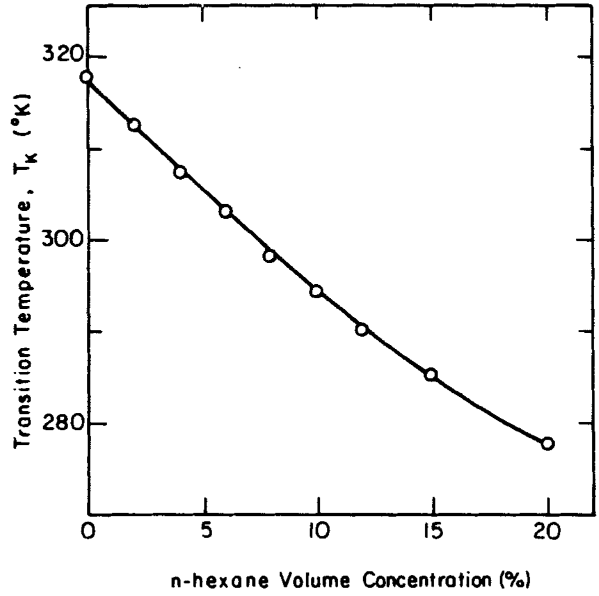

FIGURE 1 Isotropic-nematic transition temperature T_K of MBBA-n-hexane mixtures as a function of the n-hexane volume concentration. The solid curve is obtained from Eq. (5).

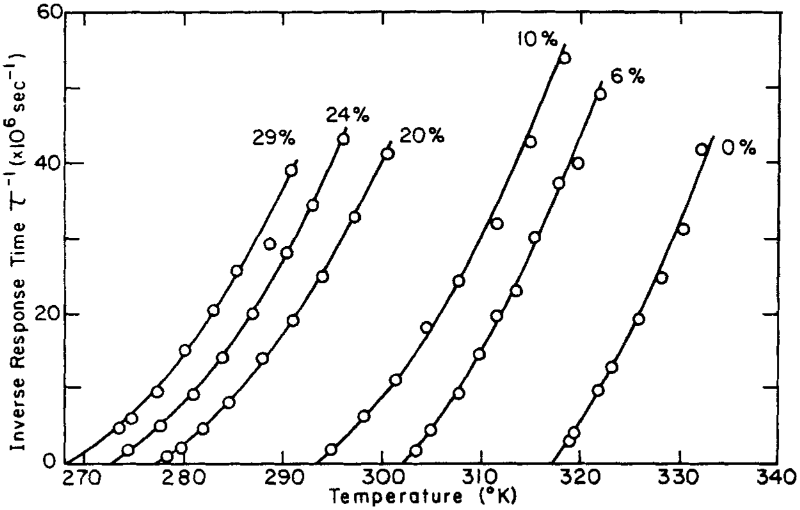

FIGURE 2 Inverse response time τ^{-1} as a function of temperature for various mixtures of MBBA and *n*-hexane with 0%, 6%, 10%, 20%, 24%, and 29% *n*-hexane volume concentrations. The solid curves are obtained from Eq. (3).

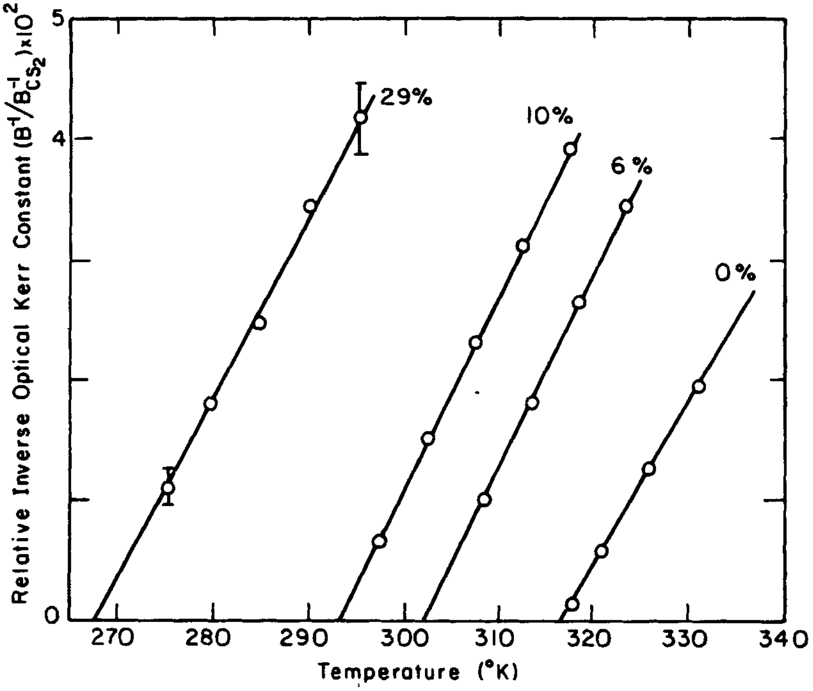

FIGURE 3 Inverse optical Kerr constant B^{-1} as a function of temperature for MBBA-*n*-hexane mixtures with 0%, 6%, 10%, and 29% *n*-hexane volume concentrations. The solid curves are obtained from Eq. (3).

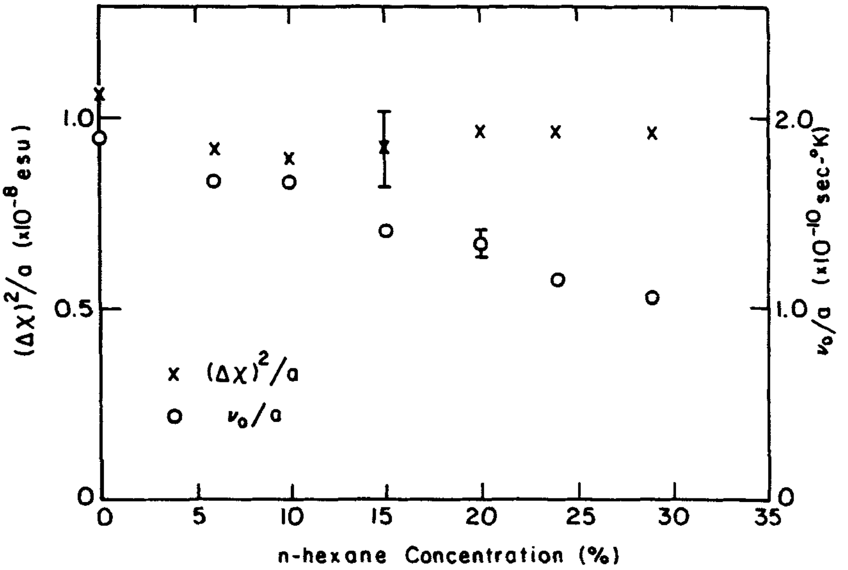

FIGURE 4 Values of $(\Delta\chi)^2/a$ and ν_0/a versus the n-hexane volume concentration derived from fitting of Eq. (3) to the experimental results of B^{-1} versus T and τ^{-1} versus T respectively.

within 0.5 to 0.9°K and does not seem to have any regular dependence on n-hexane concentration.

In fitting the experimental data of B versus T and τ versus T to Eq. (3) for the series of mixtures, we could deduce the parameters $(\Delta\chi)^2/a$, ν_0/a, and W as functions of the n-hexane concentration, η_l. Within the experimental accuracy, however, we can set $W = 2500°\text{K}$ as a constant independent of the mixtures. We then find $(\Delta\chi)^2/a$ and ν_0/a as functions of η_l. They are shown in Figure 4.

IV DISCUSSION

The isotropic-nematic transition temperature T_K should decrease as the intermolecular interaction decreases, and is presumably proportional to the pair interaction in the first order. According to the simple mean-field model of Maier and Saupe,[5] we have $T_K \propto 1/V^2 \propto N^2$ for a pure liquid crystalline medium, where V is the molar volume and N is the number of molecules per unit volume. For mixtures, we can then write

$$\begin{aligned} T_K &= A_{11}N_{LQ}^2 + A_{12}N_{LQ}N_l + A_{22}N_l^2 \\ &= T_{KO} + a\eta_l + b\eta_l^2 \end{aligned} \tag{5}$$

where N_{LQ} and N_I are the densities of MBBA liquid crystal (LQ) molecules and n-hexane impurity (I) molecules respectively, A_{11}, A_{12}, and A_{22} are coefficients proportional to the LQ-LQ, LQ-I, and I-I pair interactions respectively, T_{KO} is the isotropic-nematic transition temperature for pure MBBA, η_I is the volume concentration of n-hexane and a and b are constants.

As shown in Figure 1, the theoretical curve derived from Eq. (5) with $a = -255°\mathrm{K}$ and $b = 265°\mathrm{K}$ fits very well the experimental data.

The isotropic-nematic transition is known to be nearly second-order transition characterized by a small latent heat and a small $T_K - T^*$.[1,2,6] Addition of impurities should not change such characteristics, as we have found in the present experiment. First, the results in Figures 2 and 3 clearly indicate that the pretransitional behavior of the mixtures in the isotropic phase is well described by the Landau–de Gennes model. Then, in all cases, T^* deduced from the results is never more than 1°K below T_K.

We have seen that Eq. (3) describes very accurately the experimental data on the optical Kerr constant B and the Kerr response time τ for the mixtures. As shown in Figure 4, the parameters $(\Delta\chi)^2/a$ and v/a deduced from the fitting do not change drastically with the n-hexane concentration. Thus, variations of B and τ with the n-hexane concentration are mainly determined by the variation of T^* with the n-hexane concentration. We believe this could be true for other binary mixtures composed of nematic substance diluted with weak Kerr liquid.

In order to find the values of $\Delta\chi$, a, and v separately, we need another independent measurement. Since such measurement is not available in the present case, we resort here to a theoretical estimate of $\Delta\chi$. According to the Vuks model,[7] $\Delta\chi$ which is the anisotropy in the optical susceptibility of the mixture with perfect molecular alignment can be written as

$$\Delta\chi = (\bar{n}^2 + 2)(N_{LQ}\Delta\alpha_{LQ} + N_I\Delta\alpha_I)/3 \tag{6}$$

where $\bar{n}^2 = \bar{\varepsilon}$ is the average optical dielectric constant of the mixture, and $\Delta\alpha_{LQ}$ and $\Delta\alpha_I$ are the polarizability anisotropies of the MBBA and the n-hexane molecules respectively. Using the value of $\Delta\chi_{LQ} = 8 \times 10^{-2}$ for pure MBBA from the previous measurement,[1] we find $\Delta\alpha_{LQ} = 2.2 \times 10^{-23}$ esu. We can also find $\Delta\alpha_I$ for n-hexane from the relation[8]

$$\Delta\alpha_I = \frac{3}{(n_I^2 + 2)}\left[\frac{125\,\mathrm{kT}\,n_I\lambda}{2\pi N_{IO}}B_I\right]^{1/2}. \tag{7}$$

where $n_I = 1.38$, $N_{IO} = 4.6 \times 10^{21}\ \mathrm{cm}^{-3}$, and $B_I = 4.5 \times 10^{-9}$ esu[9] are the refractive index, the density of molecules, and the optical Kerr constant for pure n-hexane respectively. We find $\Delta\alpha_I = 1.7 \times 10^{-24}$ esu. Since n-hexane is a weak Kerr liquid whose molecules are much less anisotropic than MBBA, $\Delta\alpha_I \ll \Delta\alpha_{LQ}$ as expected. Therefore, Eq. (6) shows that $\Delta\chi$ is approximately

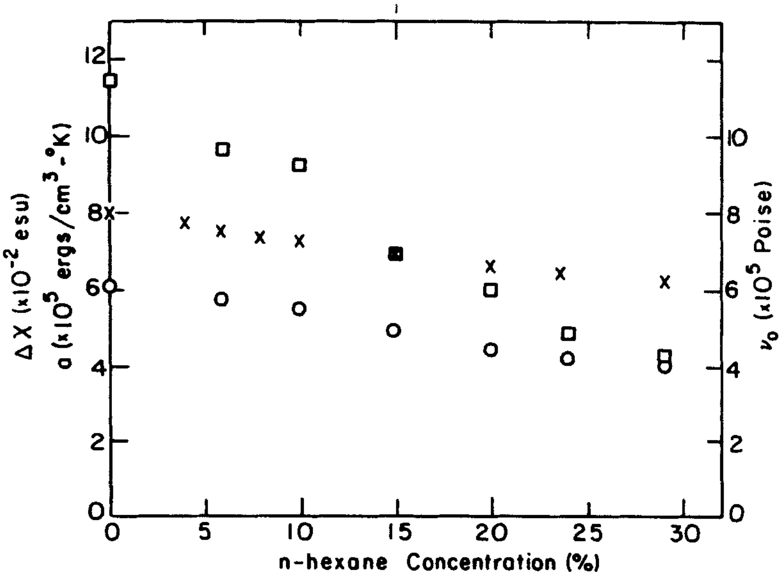

FIGURE 5 Values of $\Delta\chi$, a, and ν_0 versus the *h*-hexane concentration.
× ——$\Delta\chi$; O——a; □——ν_0

proportional to $N_{LQ}\Delta\alpha_{LQ}$. Further dependence of $\Delta\chi$ on the MBBA concentration comes in through $\bar{n}^2$ which can be calculated from the relation

$$\frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{N_{LQ}}{N_{LQO}} \frac{n_{LQ}^2 - 1}{n_{LQ}^2 + 2} + \frac{N_I}{N_{IO}} \frac{n_I^2 - 1}{n_I^2 + 2} \tag{8}$$

where n_{LQ} and N_{LQO} are the average refractive index and the density of molecules of pure MMBA respectively. Knowing $\bar{n}^2$, $\Delta\alpha_{LQ}$, and $\Delta\alpha_I$, we can now calculate $\Delta\chi$ as a function of the *n*-hexane concentration from Eq. (6). The results are shown in Figure 5. From $\Delta\chi$ and $(\Delta\chi)^2/a$ and ν_0/a in Figure 4, we can then find a and ν_0 as functions of the *n*-hexane concentration. They are also shown in Figure 5.

The value of a decreases with increase of the *n*-hexane concentration. Theoretically, the simple mean-field theory of Maier and Saupe,[5] assuming an average intermolecular potential of $A(3\cos^2\theta - 1)\langle 3\cos^2\theta - 1\rangle$ with θ being the angle between the molecular axis and the average direction of molecular alignment in the mixture, predicts a to be a constant proportional to the number of molecules per unit volume in a pure liquid crystalline material. Here, if we take a to be proportional to the number of MBBA molecules per unit volume in the mixtures, then we can explain the behavior of a in Figure 5 quite well. This may reflect the weaker alignment effect of the *n*-hexane molecules in the mixtures.

The viscosity coefficient ν_0 also decreases with increase of the *n*-hexane concentration. This is expected as *n*-hexane is less viscous than the liquid crystalline medium.

V CONCLUSION

We have measured the optical Kerr constants and the Kerr response times of a series of binary mixtures of MBBA and *n*-hexane in the isotropic phase. Both quantities show a critical pretransitional behavior proportional to $(T - T^*)^{-1}$, with T^* decreasing with increase of the *n*-hexane concentration. The results are in good agreement with the prediction of the Landau–de Gennes model. Values of the relevant material parameters, such as the anisotropy in the optical susceptibility $\Delta\chi$, the Landau parameter a, and the viscosity coefficient ν, have also been obtained for the mixtures as functions of the *n*-hexane concentration.

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