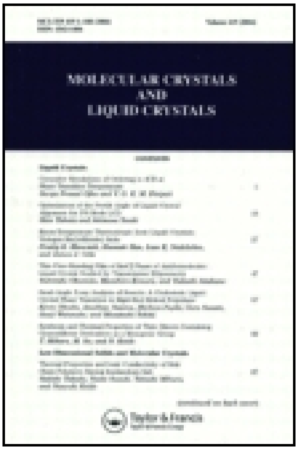

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Kerr Effect Studies on Mixtures of the Two Tolane Base Liquid Crystals

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Kerr Effect Studies on Mixtures of the Two Tolane Base Liquid Crystals

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The static Kerr effect and third order non-linearity were investigated for mixtures of the tolane-base liquid crystals within the isotropic phase in the neighborhood of the nematic phase. The nematic mixtures are characterized by components having similar molecular structure, i.e., the mixtures comprised by 4′-pentyl-3-fluoro-4-isothiocyanatotolane (5TOLF) and 4′-heptyl-3 fluoro-4-isothiocyanatotolane (7TOLF) which have a positive and large Kerr constant. The nematic to isotropic transition temperatures and nematic to crystalline temperatures for these mixtures were measured using DSC and polarizing microscopy methods. The nematic mixture of M_3 (%50 5TOLF + %50 7TOLF) shows the largest nematic range. The linear dependence of $(T - T^*)^{-1}$ on the Kerr constant is found to be in good agreement with the predications of the Landau-De Gennes model. The hypothetical second order phase transition temperatures and susceptibility values were determined for these compounds.

Keywords: electro-optic Kerr effect; liquid crystals; nematic mixture; pre-transition behavior

1. INTRODUCTION

The induction of double refraction or birefringence in a fluid by application of an external electric field is known as the electro-optical Kerr effect (EOKE) [1]. The extent of the Kerr effect depends both on polarity and polarizability of molecules. The electro-optical Kerr effect has been demonstrated to be an effective technique for studying molecular anisotropy, intermolecular ordering and pre-transional behavior

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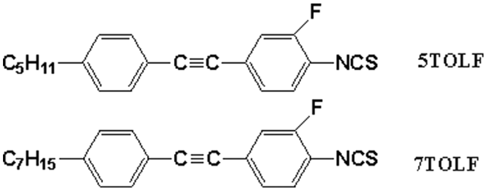

FIGURE 1 Chemical structures of the compounds.

in liquid crystals [2–5]. Measurements of the temperature dependence of electric Kerr effect and third order nonlinear susceptibility in the isotropic phase and pre-transitional behavior, related to order parameter fluctuations, of many nematic liquid crystals have been studied [6–13]. In the majority of publications, a good agreement between experimental and mean-field theory for nematic compounds was reported and discussed.

The physical properties of nematic mixture liquid crystals have received much attention. This interest is due to their desirable liquid crystalline range, optical and electro-optical properties. The physical properties of a nematic mixture depend on those of the components used and their relative concentrations. It is highly desirable to design a nematic mixture with high birefringence and low clearing temperature which are the two most critical parameters. Measurements of the temperature dependence of electric Kerr effect and pre-transional phenomena in the isotropic phase of a lot of nematic mixture liquid crystals has been studied by a number of groups [14–16].

The investigation reported here is concerned with the determination of the Kerr constant and the third order non-linearity of mixtures of 5TOLF and 7TOLF in the isotropic state. The effect of temperature on these systems has also been studied. The temperature dependences of the Kerr effect data of the pure compounds 4-pentyl-3-fluoro-4-isothiocyanatotolane (5TOLF) and 4-heptyl-3-fluoro-4-isothiocyanatotolane (7TOLF) have been reported in one of our earlier publications [17]. Both the pure compounds have an additional fluorine atom located in the neighborhood of the NCS group (Fig. 1). However, the phase is monotropic for 5TOLF.

2. THEORY

The birefringence or double refraction of a medium is defined as the difference between the refractive indices for light polarized parallel ($n_{||}$) and perpendicular ($n_{\perp}$) to the orienting field direction, and is related to optical retardation or optical phase difference, δ,

$$\delta = 2\pi lBE^2 = \frac{2\pi l(n_{\|} - n_{\perp})}{\lambda} \tag{1}$$

where λ is the wavelength of the light, l is the optical path length, and B is called the "Kerr constant" of the substance, and is used to denote the magnitude of the Kerr effect [1]. The electrically induced birefringence, Δn, may also be conveniently defined by (Kerr law):

$$\Delta n = \lambda BE^2 \tag{2}$$

For the nulled intensity method of measuring Kerr effect, which involves the nulling of an optical response resulting from the application external electric field across the Kerr cell, the rotation of the plane of polarization, α, is related to the phase difference, δ, by

$$\alpha = \frac{\delta}{4} \tag{3}$$

Eliminating δ from Eqs. (3) and (4) and rearranging gives:

$$\alpha = \frac{\pi LBE^2}{2} \tag{4}$$

If the Kerr law is observed, a plot of α versus the square of applied electric field (E^2) also should give a straight line graph passing through the origin with a gradient of $(\frac{\pi LB}{2})$, from which the Kerr constant B may be determined.

The Kerr constant can be related to the third order non-linear susceptibility tensor, $\chi^{(3)}$, in an isotropic media, which is an important material parameter, using the following formula [18]:

$$B = \frac{24\pi}{n\lambda}\chi^{(3)} \tag{5}$$

The theory of Landau-De Gennes [19], has been used to describe the pre-transitional behavior in the isotropic phase of liquid crystals. According to this model the Kerr constant in the isotropic phase is given by

$$B = \frac{\varepsilon_o \Delta n_o \Delta\varepsilon_o}{4a\lambda\sqrt{\varepsilon}(T - T^*)} \tag{6}$$

where a is the temperature independent coefficient, T^* is the second-order pre-transitional temperature, which is an extrapolated temperature just below the isotropic-nematic phase transition, $\Delta\varepsilon_o$ is the low frequency dielectric anisotropy in the completely ordered phase. From the above equation, there is a reciprocal relationship between the Kerr constant, B, and temperature, i.e., $\Delta n \propto (T - T^{*})^{-1}$.

3. EXPERIMENTAL PROCEDURE

All measurements of the Kerr constant were made using the nulled intensity method [20], which involves the nulling of an optical response resulting from the application of a short duration rectangular shaped electric field across the Kerr cell.

3.1. Materials

The two pure nematic liquid crystals 5TOF (4-pentyl-3-fluoro-4-isothiocyanatotolane) and 7TOLF (4-heptyl-3-fluoro-4-isothiocyanatotolane) were synthesized by Dabrowski *et al.* in the Institute of Chemistry of the Military Technical Academy, Warsaw, Poland. The chemical structure of these compounds is shown in Figure 1. Five nematic mixtures were prepared for this study. These mixtures are M_1 (%30 5TOLF + %70 7TOLF), M_2 (%40 5TOLF + %60 7TOLF), M_3 (%50 5TOLF + %50 7TOLF), M_4 (%60 5TOLF + %40 7TOLF) and M_5 (%70 5TOLF + %30 7TOLF). The melting and clearing points for these compounds were measured using DSC and polarizing microscopy methods.

3.2. Kerr Effect Apparatus

A diagram of the apparatus used to measure the electrically induced phase difference, δ, is shown in Figure 2. A Spectra physics He-Ne laser emitting at a wavelength of 632.8 nm with a power of 5 mW was used as a probe beam. For the electro-optical investigation in the isotropic phase, a sample holder similar to that described by O'Konski and Haltner [21] was constructed. The sample holder was a quartz spectrophotometer cell with a path length of 10 mm. The stainless steel electrodes were inserted into the Kerr cell, leaving an active column of liquid $2 \times 2 \times 10$ mm. A Teflon spacer was used to provide insulation between the electrodes and to maintain an electrode gap of 2 mm. The lower part of the Kerr cell fitted into a thermostatted metal jacket, which was cut away to allow passage of the light beam. The temperatures were determined with a copper constantan thermocouple.

The detection of the Kerr signal was achieved using a photomultiplier tube, type E.M.I. 9816B. The optical signal from the photomultiplier was displayed using a digital storage oscilloscope and a pc

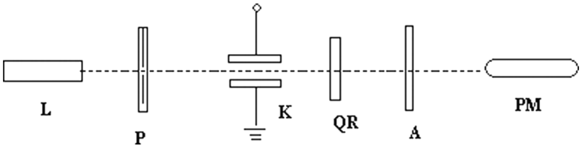

FIGURE 2 Diagram of apparatus used to measure the electro-optical Kerr effect. Principle components are: L, laser; P, Polarizer; K, Kerr cell; QR, quarter-wave retarder; A, analyzer; PM, photomultiplier.

computer. The polarizer and analyzer were Glan-Thompson double refraction type prisms of commercial origin and adjusted such that they crossed each other, making an angle 45 with respect to the applied ac field (1 kHz). The quarter wave plate used in these experiments was mica cut specifically for use at 632.8 nm and mounted between glass discs. The electric field is generated by means of a high-voltage power supply that was applied, as a short duration rectangular shaped pulse from a pulse generator, to the electrodes of the Kerr cell.

4. RESULTS AND DISCUSSION

4.1. Phase Diagrams of the Mixtures

The compounds which were selected for this study are two high birefringence laterally substituted isothiocyanatotolanes with similar molecular structure. The temperatures of phase transitions for the pure compounds and their binary mixtures measured using DSC method during the cooling runs and are given in Table 1. Figure 3 demonstrates the experimental phase diagram of the 5TOLF/7TOLF system. By changing the ratio of the pure compounds, we prepared five high birefringence and low clearing temperature LC mixtures, designated as M_1, M_2, M_3, M_4, and M_5. As it can be seen from Figure 3, the eutectic nematic mixture of M_3 (%50 5TOLF + %50 7TOLF) shows the largest nematic range ($\Delta T = 46.3^oC$).

4.2. Kerr Effect in Mixtures of 5TOLF and 7TOLF

The values of the Kerr constants, B, of the nematic mixtures at above transition temperatures were obtained from the gradient of graph of induced birefringence, Δn, plotted against the square of applied electric field (i.e., $\Delta n = \lambda BE^2$). In the samples examined the electrically induced birefringence was found to be directly proportional to the square of the

TABLE 1 The Clearing Temperature, T_C, and Pre-Transitional Temperature, T^*, of the Mixtures

Compound	$T_C(^0C)$	$T^*_C(^0C)$
4′-heptyl-3 fluoro-4-isothiocyanatotolane (7TOLF)	43.7	42.5
M1: 5TOLF/7TOLF (30/70)	43.0	41.9
M2: 5TOLF/7TOLF (40/60)	42.7	41.5
M3: 5TOLF/7TOLF (50/50)	42.5	41.3
M4: 5TOLF/7TOLF (60/40)	42.3	41.1
M5: 5TOLF/7TOLF (70/30)	41.9	40.8
4′-pentyl-3-fluoro-4-isothiocyanatotolane (5TOLF)	40.7	39.4

applied electric field (E^2), and is positive in the all cases ($\Delta n > 0$). For a comparison, the Kerr constants of the mixtures measured at different temperatures in the isotropic phase are summarized in Table 2. The strong temperature dependence of the Kerr constant for the pure compounds and for the mixtures M_1, M_3 and M_5 are shown in Figure 4. As it expected, this data show that the birefringence depends strongly on temperature and those of the components used and their relative concentrations. The Kerr constants of these liquid crystalline mixtures are found to be very high in the isotropic phase. This may be due to presence of high polarizable tolane core and polar –NSC group, which are conductive to high optical anisotropy.

The pre-transitional Kerr effect is exhibited by liquid crystal materials that are in their isotropic phase at a temperature that is close to the nematic-isotropic transition temperature. The theory of Landau-de Gennes [19] has been used to describe the pre-transitional

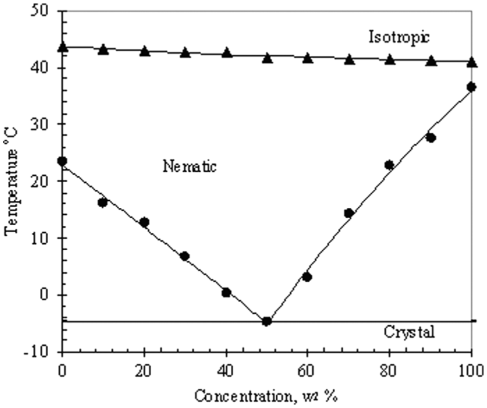

FIGURE 3 Phase diagram of the mixture 5TOLF/7TOLF.

TABLE 2 Kerr Constants, B, and Susceptibility, $\chi^{(3)}$, of the Mixtures, for $\lambda = 632.8\,\text{nm}$

Sample	Temperature (°C)	10^{11} B/mV^{-2}	B^{-1}/10^{11}m^{-1}V^{2}	$10^{20}\chi^{(3)}$/m^{2}V^{-2}
M$_1$: 5TOLF/7TOLF (30/70) 43.0	55.0	2.07	0.48	28.43
	52.0	2.68	0.37	36.85
	49.0	3.91	0.26	53.81
	46.9	5.50	0.18	75.73
	45.0	9.12	0.11	125.7
	44.2	12.02	0.08	165.7
	43.9	13.97	0.07	192.8
	43.7	15.05	0.07	207.4
	43.5	17.79	0.06	245.2
M2: 5TOLF/7TOLF (40/60)	50	3.36	0.30	46.48
	48.5	4.29	0.23	59.36
	46.7	5.64	0.18	78.07
	44.7	9.38	0.11	129.9
	43.9	11.9	0.08	164.8
	43.7	12.7	0.08	175.9
	43.4	14.6	0.07	202.2
	43.3	16.7	0.06	231.3
M3: 5TOLF/7TOLF (50/50)	53.5	2.11	0.47	29.04
	51.4	2.63	0.38	36.24
	50.5	2.86	0.35	39.42
	47.9	4.24	0.24	58.50
	44.6	9.04	0.11	124.95
	43.7	13.1	0.08	181.36
	43.3	15.7	0.06	217.35
	43.2	16.7	0.06	234.58
	43.1	18.2	0.05	251.68
M4: 5TOLF/7TOLF (60/40)	52.5	2.45	0.41	33.95
	50.4	2.87	0.35	39.78
	48.4	3.73	0.27	51.72
	46.4	5.33	0.19	73.93
	44.4	8.59	0.12	119.2
	43.6	12.91	0.08	179.2
	43.2	14.17	0.07	196.7
	43.1	14.7	0.07	204.6
	43.0	16.49	0.06	228.8
M$_5$: 5TOLF/7TOLF (70/30)	52.0	2.83	0.35	38.95
	50.0	3.30	0.30	45.39
	48.1	4.39	0.23	60.39
	46.0	6.17	0.16	84.93
	44.1	10.1	0.10	139.56
	43.1	14.6	0.07	201.12
	42.9	17.1	0.06	236.15
	42.8	19.3	0.05	265.84

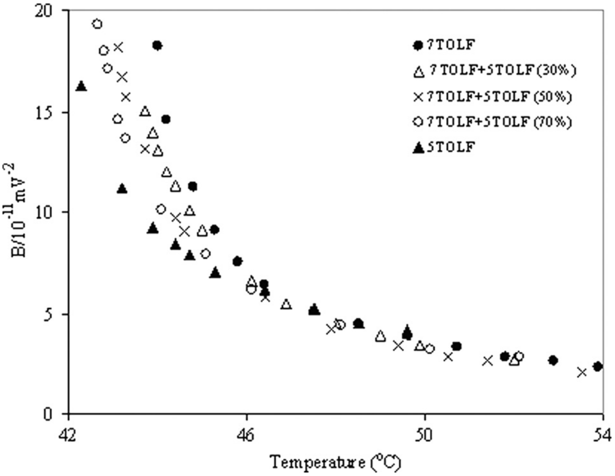

FIGURE 4 Temperature dependence of B for the nematic mixtures obtained using the pulsed a.c. field method ($f = 1\,\mathrm{kHz}$).

behavior in the isotropic phase of liquid crystals. This theory is essentially based on the assumption that short-range forces predominate in the region of the nematic-isotropic transition. According to this model the birefrengence (Δn) in the isotropic phase is given by

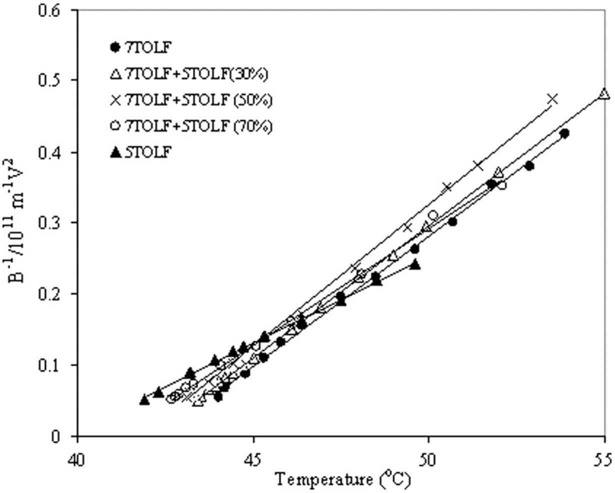

FIGURE 5 Temperature dependence of B^{-1} for the nematic mixtures obtained using the pulsed a.c. field method.

$$\Delta n \propto (T - T^{*})^{-\gamma} \tag{7}$$

where T* is the second-order pre-transitional temperature, which is an extrapolated temperature just below the isotropic-nematic phase transition, and can be obtained by a linear extrapolation of the Kerr constant (B^{-1}) vs. temperature. γ, is a numerical factor that equal unity in a Maier-Saupe theory.

In Figure 5 the reciprocal of the Kerr constant, B^{-1}, for the compounds is shown and compared as a function of temperature. For the samples studied the inverse of the Kerr constant varies linearity with temperature, i.e., $\gamma \cong 1$, as predicted by the Maier-Saupe mean-field theory for liquid crystals [22], and this aspect is clearly independent of the nature of the electric field used to measure the Kerr constant. The extrapolated temperatures T* for these liquid crystals are just below the isotropic phase transitions T_C (i.e., approx. 1.2–1.4°C). The pre-transitional temperature, T*, and the nematic to isotropic transition temperatures observed for the mixtures of different weight fractions are shown in Figure 6.

The electro-optical Kerr effect is used to determine the third order non-linear susceptibility tensor $\chi^{(3)}$. The third order non-linear

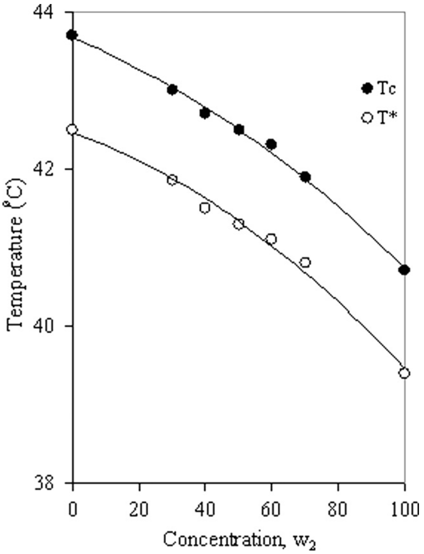

FIGURE 6 Change in nematic-isotropic transition temperature and second order pretransitional temperature with weight fraction of 5TOLF in 7TOLF.

susceptibility data of the mixtures measured at different temperatures in the isotropic phase are also summarized in Table 2.

5. CONCLUSIONS

The temperature dependence of the Kerr constant was obtained for 5TOLF, 6BOBT and their mixtures at temperatures greater than the nematic–isotropic transition temperature. All the samples had a positive Kerr constant, which increased with decreasing of temperature. The second-order phase-transition temperatures, T^*, were also determined for these compounds. In the pre-transition region the short-range order leads to pseudo-nematic domains of highly correlated molecules in the isotropic phase. The experimental results show a significant variation in the magnitude of the Kerr constant and susceptibility between these liquid crystals. For the samples studied the dependence of the Kerr constant on $(T - T^*)^{-1}$ is found to be in good agreement with the prediction of the Landau-de Gennes model.

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