

Mixtures of 4-pentyl-4'-cyanobiphenyl and photosensitive azoxy nematics as hosts for liquid crystal dispersions of carbon nanotubes

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Received December 15, 2016

In mixtures of nematic liquid crystals with opposite signs of dielectric anisotropy (4-*n*-pentyl-4'-cyanobiphenyl (5CB), $\Delta\epsilon > 0$, and azoxy nematic ZhK440, $\Delta\epsilon < 0$), anomalous behavior of optical transmission and electrophysical properties was observed at concentrations close to the compensation point. The observed features, which could be ascribed to enhancement of the director fluctuations, were suppressed by addition of small amounts (~0.04 %) of dispersed carbon nanotubes. In such systems, it is possible to realize the Fredericks transition at relatively small (~15 %) concentration of 5CB, preserving the possibility of UV-induced effects due to *trans-cis* isomerization of azoxy nematics.

Keywords: nematic liquid crystals, dielectric anisotropy, electrophysical properties.

В смесях нематических жидких кристаллов с противоположными знаками диэлектрической анизотропии (4-*n*-амил-4'-цианобифенил (5CB), $\Delta\epsilon > 0$, и азокси-нематик ЖК440, $\Delta\epsilon < 0$), отмечено аномальное поведение оптического пропускания и электрофизических характеристик при концентрациях, близких к точке компенсации. Наблюдаемые особенности, которые могут быть вызваны усилением флуктуаций директора, исчезали при введении небольших количеств (~0,04 %) диспергированных углеродных нанотрубок. В таких системах возможна реализация перехода Фредерикса при относительно малых (~15 %) концентрациях 5CB, с сохранением возможности реализации УФ-индуцированных эффектов вследствие *транс-цис*-изомеризации азокси-нематиков.

Суміші 4-пентил-4'-ціанобіфенілу (5CB) та фоточутливих азокси-нематиків як матриці для рідкокристалічних дисперсій вуглецевих нанотрубок. О.М.Самойлов, С.С.Міненко, О.П.Федоряко, Л.М.Лисецький, Т.В.Бідна.

У сумішах нематичних рідких кристалів з протилежними знаками діелектричної анизотропії (4-*n*-пентил-4'-ціанобіфеніл (5CB), $\Delta\epsilon > 0$, та азокси-нематик ЖК440, $\Delta\epsilon < 0$), відзначено аномальну поведінку оптичного пропускання та електрофізичних властивостей при концентраціях, близьких до точки компенсації. Спостережувані особливості, які можуть бути спричинені посиленням флуктуацій директора, зникали при додаванні невеликих кількостей (~0,04 %) диспергованих вуглецевих нанотрубок. У таких системах можлива реалізація переходу Фредерікса при відносно малих (~15 %) концентраціях 5CB, зі збереженням можливості УФ-індукованих ефектів внаслідок *транс-цис*-ізомеризації азокси-нематиків.

1. Introduction

Liquid crystal (LC) dispersions of carbon nanotubes (CNT) are known as a promising material for electrooptics and optoelectronics [1–3]. In most works, standard nematic like 5CB were used as LC hosts [3–5]. The use of other types of nematics was also reported (e.g., [6–8]), but no specific properties or effects related to different chemical structure of the LC host were noted. However, in a recent paper [9] it was shown that the use of LC mixtures based on azoxy nematics could lead to some peculiar features related to the possibility of UV-induced *trans-cis* isomerization of the host molecules. In particular, when chiral components were added to induce helical twisting, the dependence of optical transmission on the CNT concentration became essentially non-linear due to formation of stacking type aggregates. Also, in induced cholesteric systems containing photosensitive components, various light-induced effects of texture transformations have been reported [10–12]. One may assume that upon introduction of CNT to such systems other effects could be expected under application of electric field. However, to achieve high sensitivity to both UV irradiation and electric field, the nematic host should exhibit sufficiently large positive dielectric anisotropy $\Delta\epsilon$, retaining the possibility of well-controlled *trans-cis-trans* isomerization of the photosensitive component. To avoid tedious synthetic work, at the first step it was natural to use, as a model system, a mixture of azoxy nematics with a standard nematic 5CB.

In fact, mixtures of cyanobiphenyls and azoxy nematics have been long known as systems where induced smectic phase could be observed, probably due to formation of charge transfer complexes between cyanobiphenyls and azoxy molecules [13, 14]. Since the stoichiometry of these complexes was established as 1:1, manifestations of induced smectic ordering would be the most strongly expressed at concentrations close to 50:50 %. However, practically no studies of such mixtures were carried out in the region of low 5CB concentrations, where small negative $\Delta\epsilon$ of azoxy nematics would be already compensated for, but eventual effects of intermolecular complexing would be still negligible. Only some isolated data could be noted on mixtures of azoxy nematics with alkoxy cyanobiphenyls [15, 16], where effects of induced smectic formation

were much stronger, and only a very narrow nematic region was observed. No attention was paid to possible effects of dielectric compensation. This lack of interest for such systems is rather natural, because most electrooptical applications require nematics with high dielectric anisotropy (positive or negative). However, dielectrically compensated nematics with $\Delta\epsilon$ close to zero could be interesting because of their potential flexoelectric properties [17–19].

According to various experimental data, for 5CB at room temperature $\Delta\epsilon \approx +11$, and for ZhK440 $\Delta\epsilon \approx -0.4$, so, the relevant range of 5CB concentration c range would be around ≈ 5 –10 % (taking into account possible deviations of $\Delta\epsilon$ vs. concentration plots from linearity due to the charge transfer complex formation). In our work, we used a mixture of 5CB with a well-known azoxy nematic ZhK440, measuring optical transmittance, dielectric permittivity, electric conductivity in a broad concentration range, determining the response of these characteristics to UV irradiation, and studying the effects of carbon nanotubes on these properties and on the electric field-induced Fredericks-type transition.

2. Materials and methods

The photoactive nematic ZhK440 (a mixture of 4-*n*-butyl-4'-methoxyazoxybenzene + 4-*n*-butyl-4'-heptanoylazoxybenzene in 2:1 ratio) was obtained from NIOPIK, Russia, and additionally purified by column chromatography on silica gel using a mixture of petroleum ether and benzene as the eluent. After evaporation of the solvent, the material was recrystallized from hexane at -20°C . Nematic 5CB (4-*n*-pentyl-4'-cyanobiphenyl) of 99.5 % purity was obtained from Chemical Reagents Plant, Ukraine. The single-walled carbon nanotubes (SWCNT) of $d \sim 1.5$ nm and $l \sim 5$ –10 μm were obtained from Arry, Germany. The LC + CNT dispersions within 0.01–0.15 % CNT concentration range were obtained by adding the appropriate weights of the nanotubes to the LC solvent in the isotropic state with subsequent 2–3 min sonication of the mixture using a UZD-22/44 ultrasonic disperser (Ukrrospribor, Sumy, Ukraine).

UV irradiation was carried out using a DRT-240 Hg lamp emitter in geometry with known spectral distribution of illuminance [20]. A typical UV radiation dose was 1.9 J/cm^2 , which, according to [21], resulted in a photostationary state with about

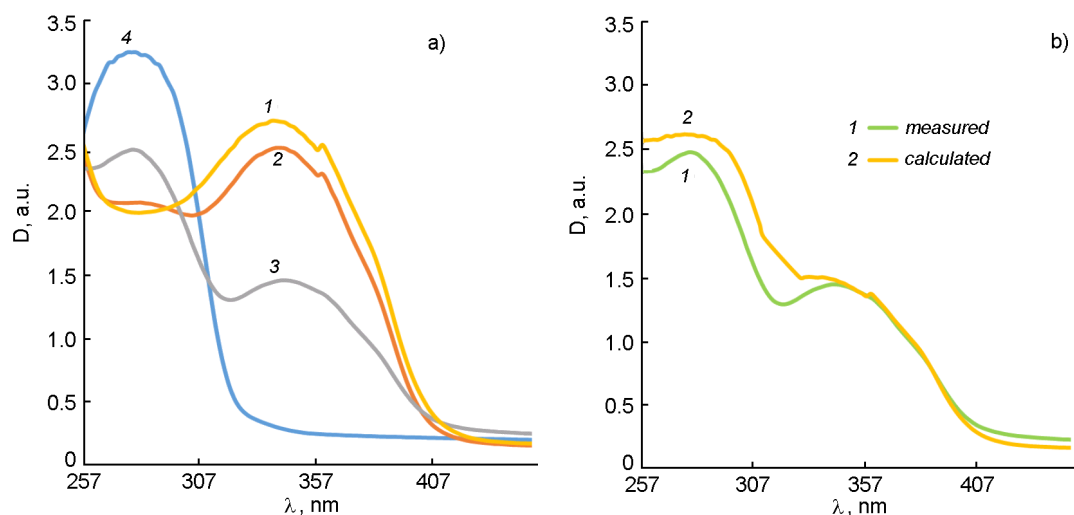


Fig. 1. UV absorption spectra in the nematic system ZhK440 + 5CB (room temperature, cell thickness — 50 μm): (a) actually measured spectra: 1 — ZhK440, 2 — 10 % 5CB + 90 % ZhK440, 3 — 50 % 5CB + 50 % ZhK440, 4 — 5CB; (b) difference between the actually measured spectrum for 50 % ZhK440 + 50 % 5CB mixture and the calculated additive spectrum.

50 % of azoxy molecules in the *cis* form. The reverse *cis-trans* transition was realized by irradiation under the same conditions using a ZhS-10 filter cutting off the wavelengths below ~ 400 nm, in the same way as in our previous works [22, 23]. Optical transmission was measured using a Shimadzu UV-2450 (Japan) spectrophotometer within 190–1100 nm spectral range. Sandwich-type LC cells (50 μm thickness) were used. The sample was introduced between the cell walls using the capillary forces at temperatures above the transition to the isotropic phase. The measurements were carried out at 20°C, with temperature stabilization by a flowing-water thermostat (± 0.1 K). The values of optical transmission were determined at 800 nm, considered to be sufficiently far from any bands of selective reflection or absorption of the liquid crystalline host. The optical transmission data were re-calculated to optical density values in the same way as in our previous paper [24].

Phase transition temperatures were determined using differential scanning calorimetry (Mettler DSC 1, Switzerland) from position of the maximums of the DSC peaks. The measurements were done at the heating rate of 2 K/min with the sample mass of 20 mg.

For measurement of electrophysical characteristics we used a home-made cell, which included a grounded guard ring to reduce the edge effects. The cell was a capacitor with metal plates, covered by a polyvinyl alcohol film rubbed in one direction for ensuring the planar texture. The cell thick-

ness (50 μm) was set by a Teflon spacer. Before the measurements, the cell parts were washed in hexane and dried at 390 K. After assembling, the cell was connected to E7-12 L,C,R-meter (KALIBR, Belarus), making sure that tangent of dielectric loss angle $\tan\delta$ of the empty cell did not exceed 0.0001. The procedure was essentially similar to that described in [7, 25]. The real ϵ' and imaginary ϵ'' components of dielectric permittivity in the region below 30 MHz were measured by the oscillographic method. By measuring the voltage and current through the sample studied, the cell capacitance C_c and tangent of dielectric loss angle $\tan\delta$ were determined. The values of ϵ' and ϵ'' were evaluated as $\epsilon' = C_s/C_0$ and $\epsilon'' = \epsilon \tan\delta$, where $C_s = C_c/(1 + \tan\delta)^{0.5}$ and C_0 are the sample and empty cell capacitance, respectively.

For electrical conductivity σ measurements, the ac voltage of 0.25 V and 1 MHz was used, which should not affect the LC director field.

The experimental set-up provided application of dc bias voltage up to 40 V to the cell. The external DC voltage could align the molecules, thus leading to re-orientation of the nematic director and corresponding changes in electrical conductivity.

3. Results and discussion

The first step in our studies was measurement of transmission spectra of ZhK440 + 5CB mixtures with the aim of tracing the

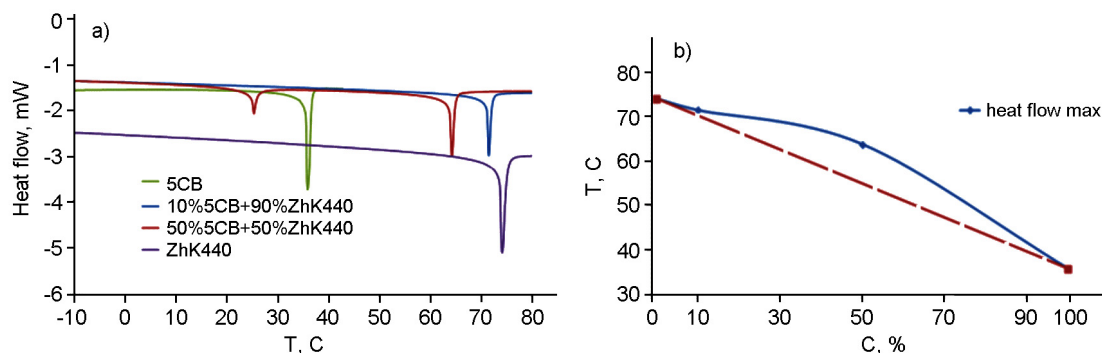


Fig. 2. (a) DSC thermograms for ZhK440, 5CB and their mixtures: 5CB (1), 10 % 5CB + 90 % ZhK440 (2), 50 % 5CB + 50 % ZhK440 (3), ZhK440 (4); (b) nematic-isotropic transition temperature T_i vs. concentration of 5CB in ZhK440 + 5CB mixtures.

signs of the eventual charge transfer (CT) complex formation. We tested two concentrations — 50:50 (wt. %), where the complex formation effects would be the strongest, and 90 % ZhK440 + 10 % 5CB, i.e., the concentration where we planned to study the effects of dielectric anisotropy compensation. The results are shown in Fig. 1. For better illustration, we also present, for the 50:50 concentration, the calculated would-be additive spectrum and the actually measured one. The noted slight differences confirm the possibility of weak CT complexes; however, no such differences have been found for the 90:10 concentration.

For the same mixtures, phase transition temperatures from the nematic liquid crystal to isotropic liquid (T_{ni}) were determined by differential scanning calorimetry. The measured DSC peaks are shown in Fig. 2a, and Fig. 2b shows T_{ni} as function of 5CB concentration in the ZhK440 + 5CB mixture. Clear deviations from linearity are noted for concentrations close to 50:50, while for small concentrations of 5CB the dependence is practically linear. This also confirms the assumption that formation of CT complexes does not affect properties of these mixtures at low 5CB concentrations where dielectric compensation is expected.

Fig. 3 shows optical transmission of ZhK440 + 5CB mixtures as function of 5CB concentration. An unexpected feature was the presence of a well-defined minimum at ~10 % 5CB. This could be related to stronger fluctuations of the nematic director in the compensated mixture ($\Delta\epsilon \approx 0$), with correspondingly stronger light scattering. The effect weakened under UV irradiation (due to formation of *cis*-isomers, the influence of factors originating from negative dielectric anisotropy of ZhK440 natu-

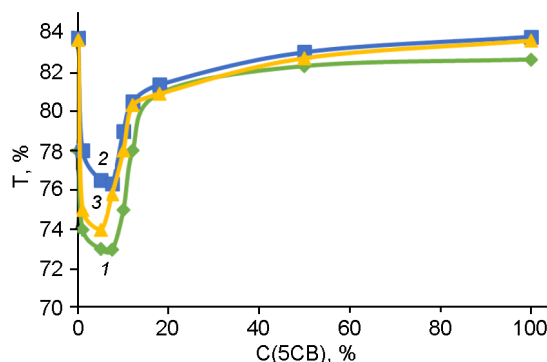


Fig. 3. Optical transmission in the nematic phase of ZhK-440 + 5CB mixture (room temperature, 800 nm) as function of 5CB concentration: 1 - before irradiation, 2 - after 15 min UV irradiation and 3 - after subsequent "reverse" irradiation through ZhS-10 filter .

rally diminished). The reverse irradiation (through a filter cutting off wavelengths below 400 nm) partially restored the situation with *trans*-isomers becoming again predominant.

After introduction of carbon nanotubes in rather small quantities (~0.04 %), the general level of optical transmission naturally lowered, and the anomalous minimum practically disappeared (Fig. 4). One can assume, as a tentative explanation, that carbon nanotubes suppress the director fluctuations, thus stabilizing the system.

The introduction of carbon nanotubes also stabilized the electric conductivity, with the involved mechanism generally similar to that governing the optical transmission (Fig. 5). Measurements of the perpendicular component of dielectric permittivity showed a rather unstable situation at concentrations around the compensation point, with the obtained values becoming

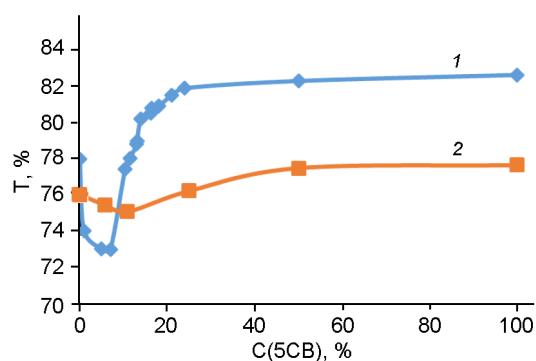


Fig. 4. Optical transmission in the nematic phase of ZhK440 + 5CB mixture (room temperature, 800 nm) as function of 5CB concentration in the presence of dispersed SWCNT: 1 — ZhK440 + 5CB, 2 — ZhK440 + 5CB + 0.04 % SWCNT.

very sensitive to uncontrolled factors of each measurement (Fig. 6), which also supports the proposed picture of enhanced director fluctuations.

To support our idea of enhanced director fluctuations in the vicinity of the compensation point of dielectric anisotropy, several arguments can be thought of. A marked decrease in optical transmission in a narrow temperature range just below the nematic-isotropic phase transition was noted in [26], where it could be naturally ascribed to a decrease in short-range orientational order parameter. The compensation of $\Delta\epsilon$ can lead to weaker short-range orienting forces between molecules of different components, with subsequent weakening of the local orientational order and enhancement of director fluctuations (see, e.g., [27]), resulting in stronger light scattering and lower measured transmission values. Incorporation of highly anisometric CNTs increases the tendency towards orientational ordering, and the concentration anomaly disappears.

An important practical implication of the results obtained can be envisaged. There is a well-known fact that nematics with negative dielectric anisotropy can hardly be oriented in a homeotropic (vertical) alignment. Really, homeotropic orientation of azoxy nematics like ZhK440 is difficult to imagine on the molecular level, taking into account the dipole moment directed nearly perpendicular to the long molecular axis. This problem was considered in [28, 29], where vertical alignment of a nematic with large negative $\Delta\epsilon$ on a silicon oxide-based aligning material was achieved by addition of 5CB. One should also recall an interesting result of [30], where the inverse problem was

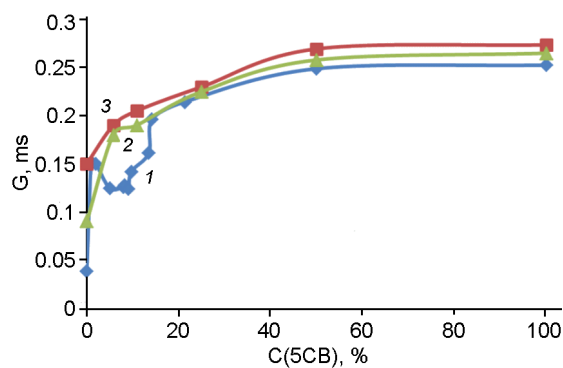


Fig. 5. Electrical conductivity in the nematic phase of ZhK440 + 5CB mixture as function of 5CB concentration in the presence of dispersed SWCNT: 1 — ZhK440 + 5CB, 2 — ZhK440 + 5CB + 0.01 % SWCNT, 3 — ZhK440 + 5CB + 0.04 % SWCNT.

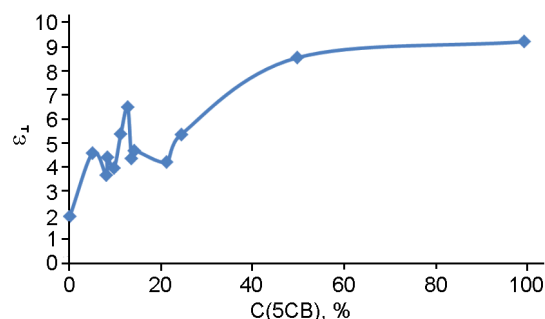


Fig. 6. Perpendicular component of dielectric permittivity in the nematic phase of ZhK440 + 5CB mixture as function of 5CB concentration.

solved — large positive $\Delta\epsilon$ of 5CB was fully compensated by addition of just 1 % (mass) of a dye SG3 with complex molecular structure (SG3). In our case, we could expect obtaining positive $\Delta\epsilon$ values by adding rather small (~10 %) quantities of 5CB to ZhK440. This would combine the possibility of Fredericks transition under standard conditions with photosensitive properties of azoxy nematics. Further studies of possible effects in such systems in the presence of dispersed nanotubes are currently under way.

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