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TERNARY PHASE DIAGRAM 60CB+80CB WITH AN OPTICALLY ACTIVE NON-MESOGENIC DOPANT

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Abstract Ternary phase diagram for reentrant nematic mixture 60CB+80CB with a non-mesogenic optically active dopant is reported.

The binary mixture of alkyloxycyanobiphenyls with alkyl chain length n=6,8 is known to be a classic system exhibiting reentrant nematic phenomenon in a molecular system with end polar groups[1]. The nematic phase (N) differs from the reentrant nematic phase (N_R) by the values of orientational order parameter[2], viscosity[3], dielectric properties[4], correlation lengths of smectic fluctuations[5] near N--S_A and N_R--S_A phase transitions. Analysis of these differences allows to assume different packing of molecular dimers, namely, that reentrant nematic phase could be considered as a mixture of two uncommensurate smectic structures formed by 80CB and 60CB molecules. Appearance of such uncommensurate structures leads to smectic density wave distortion and the reentrant nematic transition. Though distinctions between N and N_R phases are not directly reflected in the shape of the transitions line (parabola) boundaring smectic A phase in the binary mixture 60CB+80CB[5], nevertheless they would be manifested in asymmetrical changes of transition lines N--S_A and N_R--S_A in the

system disturbed, for example, by chiral dopants.

The purporse of present work was to study smectic transition phase line of the matrix mixture 60CB+80CB doped by small amounts of a highly effective non-mesogenic optically active dopant (OAD) — 2-(4'-phenylbenzylidene)-p-menthane-3-one.

Mixtures with different 60CB to 80CB ratio possessing N_R phase were used, doped with different amounts of the OAD. Isotropic transition temperatures of the initial compounds 60CB and 80CB were equal to 76.3°C and 79.8 °C, respectively. The identification of phase transitions has been made by texture observations using a polarizing microscope equipped with a thermostatic cell under cooling. Phase transition points were determined using samples of 200 μm thickness with planar boundary conditions obtained by rubbing glass surfaces with diamond paste.

The three-dimensional phase diagram obtained is shown in fig. 1, where the first axis is temperature T,

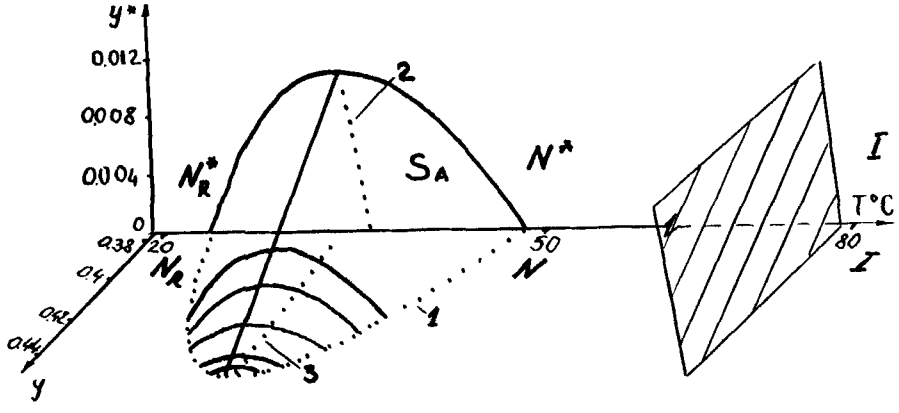

Fig. 1 Ternary phase diagram of 60CB+80CB+OAD mixture. Solid lines are boundaries of S_A phase under constant 60CB:80CB mole ratio y. Dotted lines are: S_A phase for the matrix 60CB+80CB

mixture (1), projections of the reentrant line L_R on the (y^*,T) plane (2) and the (y,T) plane (3).

second axis is mole ratio $y=x_{s\,OCB}$,mol % / $x_{s\,OCB}$,mol % and the third is mole ratio $y^*=$ x_{OAD},mol % / $x_{s\,OCB+s\,OCB}$,mol %. As a result of fitting of experimental data for initial 60CB+80CB mixtures by the least squares method the smectic phase transitions line can be described as a parabola with a vertex corresponding to the reentrant point (y_o,T_o) (see Table).

TABLE Mole ratio of initial mixture 60CB+80CB, fitting parameters of parabola $Y=-aT^2+bT-c$, its slope distortion k, vertex coordinates (y_o,T_o), and the slope of isotropic transition line k_{NI}.

y	$y_o^*\cdot10^2$	T_o(°C)	$a\cdot10^{-5}$	$b\cdot10^{-3}$	$c\cdot10^{-1}$	k	k_{NI}
0.363	1.28	35.04	8.84	6.19	0.96	164.7	86.7
0.407	0.506	36.49	9.48	6.92	1.21	142.1	89.5
0.415	0.358	36.94	9.13	6.74	1.21	107.8	85.5
0.424	0.202	36.97	7.77	5.75	1.04	177.8	133.1
0.432	0.082	37.10	8.18	6.07	1.12	388.5	217.1
0.435	0.045	37.41	14.06	10.52	1.96	162.5	163.0
0.437	0	37.33	57.0	42.5	3.57	-	-

Addition of an OAD affects $N-S_A$ and N_R-S_A transition temperatures in different ways. In the former case non-mesogenic OAD destabilizes the smectic phase, destroying smectic fluctuations and lowering the temperature T_{NA}. In the latter case the change of temperature T_{NRA} is much smaller showing a stabilizing influence of the OAD on the smectic phase near the transition point. One can connect this fact with structure differences of the N and N_R phases. Asymmetry

of the phase transition lines could be explained in terms of the Landau free energy expansion accounting for the smectic order fluctuation[5]. Namely, the $M \sim (T-T^*)^{2\nu_\perp-\gamma}$ factor at the gradient term[5] $|(\nabla_\perp + iq_o n_\perp)\Psi|^2$ should be different in N^* and N_R^* phases, leading to different critical index $\nu_\perp$ values. In fact[6], in the N_R^* phase of the 60CB+80CB mixture (y=0.433, y_o^*=0.004) $\nu_\perp$=0.63, while in the corresponding N^* phase $\nu_\perp$=0.50. Thus, OAD addition suppresses smectic fluctuations in the N^* phase more strongly than in the N_R^* phase.

In general, phase diagram changes upon OAD addition depend on similarity of molecular structures of OAD and matrix. So, 4-cyano-4'-(2-methylbiphenyl) as an OAD to the 60CB+80CB mixture causes broadening of the S_A range[7]. In some cases[8] OAD addition does not lead to significant changes of smectic range.

The boundaring line of the S_A phase in the coordinates (y,T) can be approximated by a parabola subjected to a distortion along T, which is proportional to the value of y^*. Fitting parameters are listed in Table. For the distortion line one can observe correlation with the slope of the isotropic transition line, in accordance with the data for binary and pressure-induced reentrant nematic systems[9], where temperature of isotropic transition T_{NI} depends strongly upon concentration or pressure, respectively. One should note that in work[9] fitting was carried out to an ellipse in the coordinates (T,x). For determining reentrant points coordinates (y_o^*,T_o) under certain parameter ratio conditions, which are met in the present case, differences between 'elliptical' and 'parabolic' description can be neglected.

The sequence of points (y_o^*,T_o) in the three-

dimensional phase diagram (Fig.1) can be called a reentrant line L_R, (which is apparently a straight line). In particular, relationship between y_o^* and y reflects the limit of maximum S_A stability upon OAD addition. The y_o^* value can be used for calculation of critical index $\nu_\perp$ from temperature dependence of the induced helical pitch. In particular, neglecting asymmetry, the induced helical pitch temperature dependence accounting for critical behaviour of the correlation length $\xi_\perp$ could be expressed as[6]

$$P(T) = P_o + A[(T-T_M)^2 + B(y-y_o^*)^{-\nu_\perp}],$$

and the influence of the virtual smectic region on P(T) can be analyzed.

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