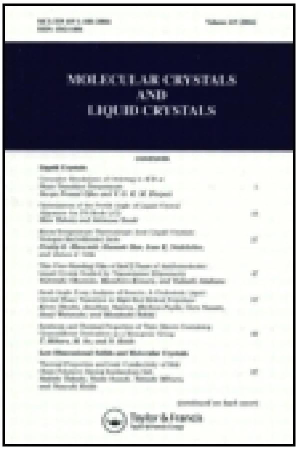

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Thermostabilized Electrooptical Liquid Crystalline Systems with Induced Chiral Structure

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Thermostabilized Electrooptical Liquid Crystalline Systems with Induced Chiral Structure

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Five ways of thermostabilization of the threshold field of cholesteric-nematic transition in systems with induced spiral structure are suggested and discussed.

It has been established both theoretically and experimentally that the cholesteric structure can be transformed into nematic structure by application of electric field.[1,2] Cholesteric-nematic transition occurs at the threshold field

$$V_{th} = \frac{\pi^2 d}{P_0}(4\pi k_{22}/\Delta\varepsilon)^{1/2},$$

where d is liquid crystal cell thickness, P_0 is pitch of undisturbed cholesteric helix, k_{22} is twist elastic constant and $\Delta\varepsilon$ is dielectric anisotropy.

The cholesteric-nematic transition can occur only when dielectric anisotropy is positive ($\Delta\varepsilon > 0$). Usually this condition is not fulfilled with most cholesterol derivatives and their mixtures, which also exhibit cholesteric behavior over a limited temperature range and are characterized with small pitch P_0 and therefore large V_{th} value. It is more promising to use mixtures of nematic matrices with optically active dopants (OAD), i.e. induced chiral systems. These systems are preferable since there is a rich choice of nematic liquid crystals with wide temperature operating range and a small quantity of OAD slightly changes the properties of initial nematic matrix.

In accordance with theoretical suggestion the threshold field varies inversely with the pitch of the helix, thus one ought to choose optically active dopant with large helical twisting power to dope OAD in a nematic matrix in a small quantity (up to 5% by weight). The value of the pitch must be large enough to decrease V_{th}. On the other hand, it must not be larger than $d/2$ to avoid the appearance of non-controlled deformations of the helix by cell walls, so called strains-texture.[3]

The main problem for investigator is the obtaining of induced chiral mixtures with cholesteric-nematic threshold field independed of temperature. For the thermostabilization of V_{th} it is necessary to obtain systems with designed pitch-temperature dependences dP/dT. It was shown,[4,5] that in systems with rather small negative values of dP/dT temperature dependences of the twist elastic constant and the dielectric anisotropy are compensated with pitch variations. Thus the temperature dependence of V_{th} becomes negligible.

Five ways of thermostabilization of the V_{th} in systems with induced spiral structure are discussed in the present paper.

The first four ways are suggested for non-smectogenic matrices:

1. It is well known[6] that in induced chiral mixtures with right-handed cholesterol esters (e.g., cholesterol cloride) as OAD near the twist compensation point the sign of dP/dT changes from positive to negative. However $dP/dT < 0$ value is too large in this case. The same phenomenon is observed in the mixtures at simultaneous doping of optically active additions of opposite chirality[4] or having various absolute configurations of molecules (R and S)[7] close to the point of twist compensation. When we used this kind of OADs separately in nematic matrix we observed $dP/dT > 0$. At simultaneous doping of these OADs $dP/dT < 0$, the value of dP/dT is small enough (Figure 1) and the thermostabilization of V_{th} is performed.
2. In our earlier report[8] we investigated in detail the features of pitch-temperature dependences in induced chiral systems containing non-mesogenic l-menthol and tigogenin derivatives as OAD. We used these compounds because they are characterized by a high helical twisting power value and good solubility in nematics. It was shown that the value and the sign of dP/dT depend dramatically on the geometric structure of the OAD molecules. In induced chiral systems steroic molecules of tigogenin derivatives provide $dP/dT < 0$, however in this case the dP/dT value is large. Non-steroic l-menthol derivatives give $dP/dT > 0$, that is in the framework of the known theory of intermolecular interaction in induced chiral mixtures. So at the simultaneous

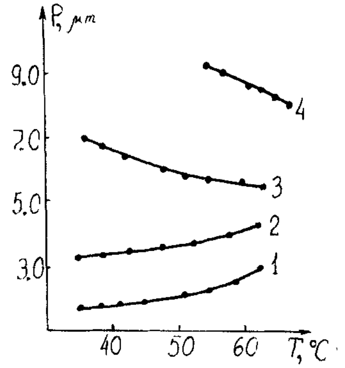

FIGURE 1 $P(T)$ dependence for mixture (85% p-butyl-p'-methoxyazoxybenzene + 15% p-cyanophenyl ester of p-hexylbenzoic acid) with methylbenzylamin amid p-cyanobenzoic acid (R and S modifications): 1, 3% S; 2, 3% R; 3, (0.5% R + 2.5% S), $V_{th} = 40$ V; 4, (0.5% S + 2.5% R), $V_{th} = 44$ V; $d = 20$ μm.

doping of these materials in nematic matrix with regard for their helical twisting power $dP/dT < 0$ is small enough (Figure 2) and V_{th} does not depend on temperature variations. This way seems to be the most attractive for obtaining thermostabilized electrooptical systems.

3. The same intermolecular interaction mechanism works, when compounds, molecules of which contain steroic and prolongated fragments, are used as OAD. For example, tigogenin-l-mentoxyacetate was synthesized to obtain proper $dP/dT < 0$ value (Figure 3).
4. The thermostabilization of V_{th} is observed in mixtures containing salicylidenanilene derivatives both for matrices and for OADs (Figure 4).

In Reference 9 the proper $dP/dT < 0$ was obtained in mixtures with OADs, molecules of which contained p-(1-methyl-alkoxy)-phenyl fragments. In both cases the geometrical shape of intermolecular associates causes weak unwinding of the cholesteric helix.

5. In a smectogenic nematic matrix a typical picture of pre-transitional phenomena is observed for all kinds of OAD.[10] Here the $dP/dT < 0$ value is large, which is caused by the unwinding of the cholesteric helix near the cholesteric-

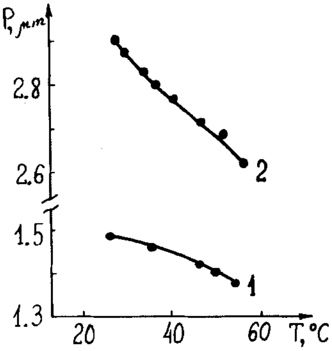

FIGURE 2 $P(T)$ dependence for mixture of cyanobiphenyls with l-menthyl-p-methoxycinamate (OAD 1) and tigogenin caprate (TC): 1, 1% TC + 1.26% OAD 1, V_{th} = 22 V; 2, 0.76% TC + 0.88% OAD 1, V_{th} = 12 V; d = 20 μm.

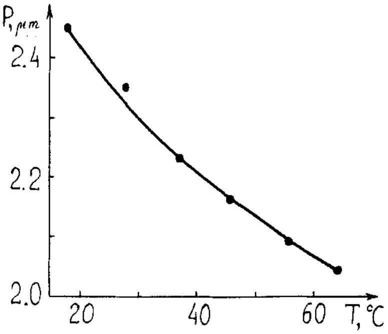

FIGURE 3 $P(T)$ dependence for mixture 97% (85% p-butyl-p′-methoxyazoxy-benzene + 15% p′-cyanophenyl ester of p-hexylbenzoic acid) + 3% tigogenin-l-menthoxyacetate, V_{th} = 58 V; d = 20 μm.

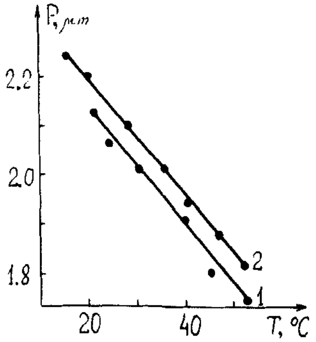

FIGURE 4 $P(T)$ dependence for mixture p-n-propiloxysalicyliden-p-n'-butylanylene with OAD: 1, 3% p-methyloxysalicyliden-p-n-(l-menthyl-benzoate) anyle; V_{th} = 24 V; 2, 3% p-ethyloxybenzilyden-p-n-(l-menthylbenzoate) anyle; V_{th} = 31 V; d = 20 μm.

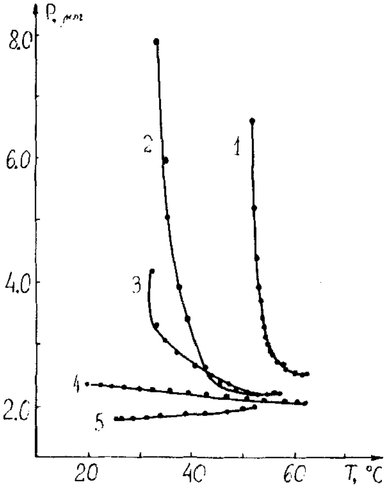

FIGURE 5 $P(T)$ dependence for mixtures 97% [(100-n)% p-oktyloxy-p'-cianobiphenyl + n% p-amiloxy-p-cyanobiphenyl] + 3% l-menthilnitrobenzoate: 1, n = 0; 2, n = 10%; 3, n = 25%; 4, n = 40%, V_{th} = 60 V; 5, n = 100%, d = 20 μm.

smectic transition point. However it is possible to choose appropriate cases $dP/dT < 0$ for matrices containing mixtures of two compounds, one of which must be smectogenic and the other—non-smectogenic or weak-smectogenic (Figure 5).

Thus, there are several different ways of thermostabilization of threshold field of cholesteric-nematic transition and the choice of appropriate systems depends on temperature operating range and on the value of V_{th} in the device being elaborated.

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