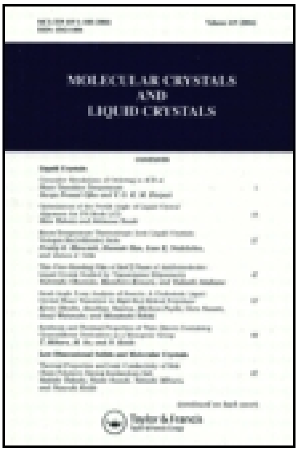

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The Influence of Cyanoterminated Compounds on the Stability of Antiferroelectric Phase

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Three bicomponent mixtures coming from the system in which antiferroelectric phase is obtained by induction as well as compound having antiferroelectric phase by itself were dopped with different cyanoterminated compounds. The influence of dopants structure on the stabilization of antiferroelectric and induced antiferroelectric phase have been tested by miscibility method in the range up to 0.2 molar fraction of dopants. Very small destabilization of antiferroelectric phase for several cyanoterminated dopants in this range is observed. Longer rigid core and longer terminal chain favour stabilization of antiferroelectric phase.

Keywords Antiferroelectric; cyanoterminated compounds; induction; liquid crystals

1. Introduction

Liquid crystals with chiral anticlinic phase (antiferroelectric – $\mathrm{SmC}^*_{\mathrm{anti}}$) are very attractive materials for display applications because of grey scale capability, high switching speed and large viewing angle. The antiferroelectric phase was discovered in 1989 [1] and the induction and enhancement of this phase was observed for the first time in 2000 [2]. The induction appears in mixtures of chiral smectic C* esters with alkyl and perfluoroalkyl terminal chain [3] or with alkyl and cyanoterminated chain [4] or with both cyanoterminated terminal chain [5]. Antiferroelectric phase in pure compound as well as obtained by the induction has application meaning only in multicomponent mixtures because then it has useful properties in a broad temperature range. Cyanoterminated compounds which do not strongly destabilize the antiferroelectric phase could be good dopants for modification of mixture properties (for example they decrease viscosity of mixtures).

The aims of this work is to compare the influence of structure of cyanoterminated dopants on the stability of antiferroelectric phase.

2. Experimental

Molecular structures with acronyms and phase sequences of components of three mixtures (I, II, III) as well as pure compound 5 used for the research are shown

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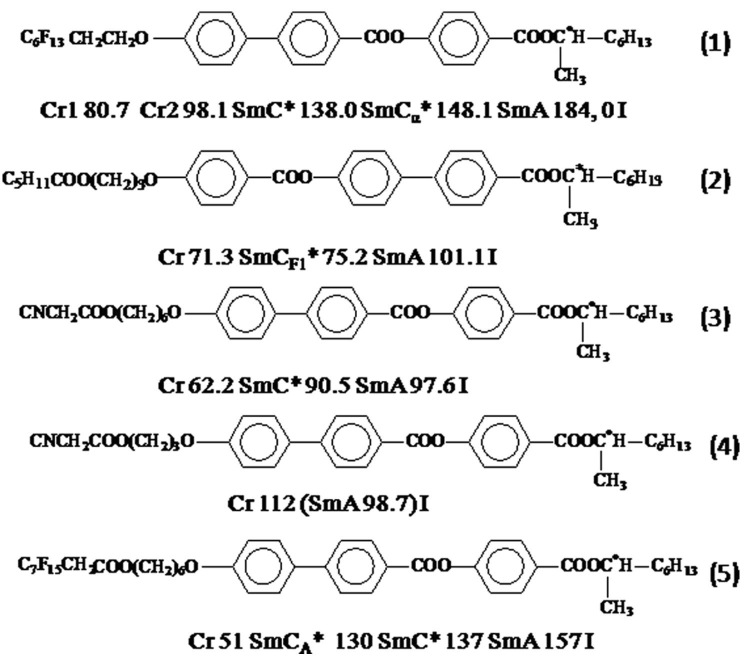
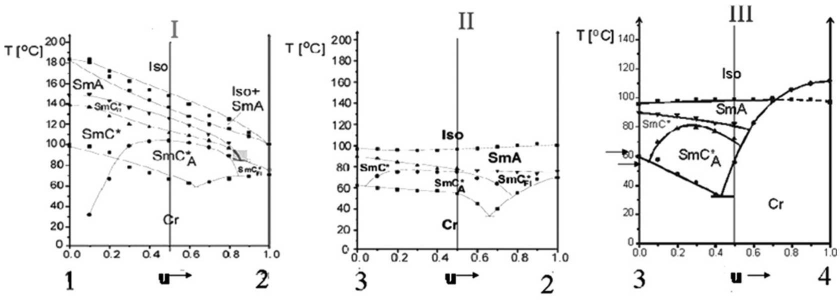


Figure 1. Molecular structures with acronyms and phase sequences of mixture components (1, 2, 3, 4) and pure antiferroelectric compound 5.

in Figure 1. The first mixture (I) consists of chiral esters: one with a phenyl biphenylate core and a perfluoroalkyl terminal chain (1) and another one with biphenyl benzoate a core and an alkyl terminal chain (2). The second mixture (II) consist of chiral esters: one with a biphenyl benzoate core and alkyl terminal chain (2) and another one with a phenyl biphenylate core and a cyanoterminated terminal chain (3). Whereas a system III is a mixture of two compounds with phenyl biphenylate cores and cyanoterminated in terminal chain (3 and 4) but differing in a methylene spacer length respectively 6 and 3. A compound 5 is a liquid crystal with a phenyl biphenylate core and seven carbon atoms fluorinated in a terminal chain.

Phase situation of three tested systems is shown on phase diagrams presented in Figure 2. In all cases the induction phenomena was observed. The bicomponent mixtures I, II, III chosen for investigation were composed in the ratio 1:1. The used of three different mixtures and pure compound 5 with antiferroelectric phase gave us possibility to compare these systems ability for stabilizing of antiferroelectric phase.

Structures, acronyms and phase sequences of cyanoterminated compounds which were used as dopants for three basic mixtures (I, II, III) and one pure compound 5 are presented in Figure 3. They differ in the alkyl chain length, the number of benzene rings, the presence of fluorine atoms in the chain or in the core and the presence of chiral carbon atom. Dopants have also different mesophases. All of compounds (except AmOCB and 8*OCB which doesn't have liquid crystal phase) have nematic phase and some of them have also smectic A phase (7CBB, 8CB, 8OCB, 7FOCBF). These differences give possibility to check dopant structure influence on the stability of antiferroelectric phase. Dopants were added to the basic mixture and to compound 5 in amount up to the 0.2 molar fraction.



I

Cr 74.0 SmC$_A$* 103.2 SmCγ* 112.0 SmC* 118.0 SmCα* 125.0 SmA 138.0 I

II

Cr 45.2 SmC$_A$* 78.0 SmC* 80.1 SmA 97.0 I

III

Cr 70.0 SmC$_A$* 75.0 SmC* 84.2 SmA 98.0 I

Figure 2. Phase diagrams and phase sequences of mixture I, II, III with induced antiferroelectric phase.

The kind of phases and phase transition temperatures were determined by polarizing optical microscope (Biolar-PZO) equipped with heating stage (Linkam THMS-600) and temperature controller (Linkam CI95). Measurements were made

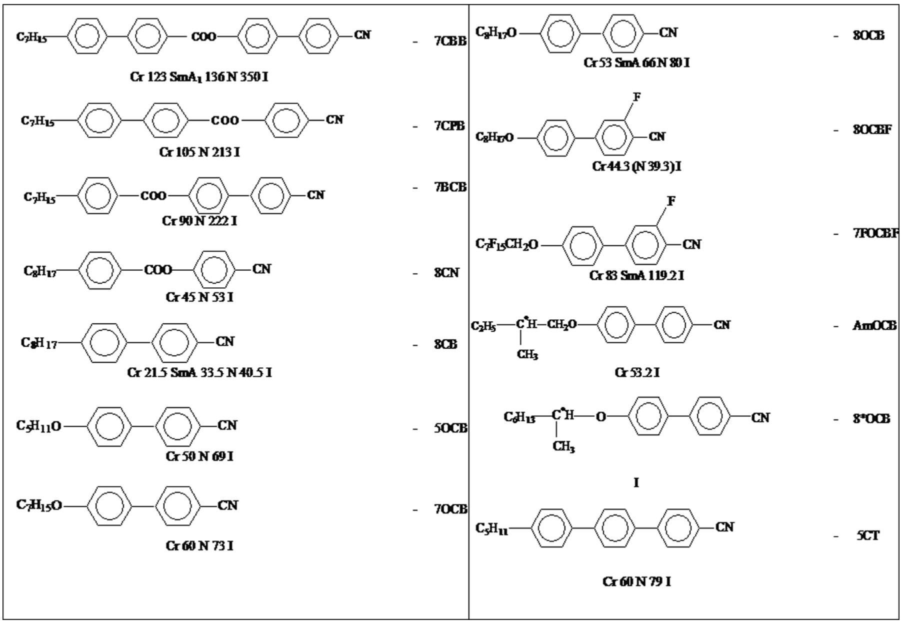


Figure 3. Structures, acronyms and phase sequences of cyanoterminated compounds which were added to mixtures I, II and III as well as to compound 5.

in a heating cycle with the rate of temperature change 1deg/min at the phase transition region. All of determined phases were easy to recognize based on the microscopic textures so we did not have to used other methods to identify them.

The results are presented as the maximum temperature of appearance of antiferroelectric phase (T) versus molar fraction of dopants (u) in all Figures. Lines which are bend and suddenly go towards zero in some Figures represent cases in which we did not observe antiferroelectric phase for 0.2 molar fraction.

3. Results and Discussion

3.1. *The Comparison of Stability of Antiferroelectric Phase of Mixtures I, II, III and Pure Compound 5 after Dopping with Cyanoterminated Compounds*

Parts of phase diagrams with marked four curves determining the upper boundary of appearance of antiferroelectric phase in four systems dopped with cyanoterminated compounds used in this work are presented in Figure 4.

Three basic mixtures and compound 5 differ in maximum temperature of antiferroelectric phase existence (for mixture I it is about 103°C, for mixture II 78°C, for mixture III 75°C and for compound 5 130°C). Dopants with higher lengths (7CBB, 7CPB, 8CB, 8OCB) as well as 5CT do not destabilize antiferroelectric phase in big grade in studied systems. The antiferroelectric phase in pure compound 5 is the most stable because some special intermolecular forces must be present to induction antiferroelectric phase. So the anticlinic phase in mixture is more sensitive to dopping. The mixture III is the least sensitive to the dilution among basic mixtures with the induced antiferroelectric phase because of the similarities in structure (existence of −CN group) of all mixture components.

3.2. *The Comparison of Cyanoterminated Dopants on the Stability of Antiferroelectric Phase in Basic Mixtures and the Compound 5*

In order to compare the dopants structure on the stability of antiferroelectric phase several parts of phase diagrams have been prepared. The influence of the alkyl chain length, the number of benzene rings, presence of fluorine atoms in the chain or the core and presence of chiral carbon atom is presented.

3.2.1. *The Influence of the Core Structure.* The stability of antiferroelectric phase increases with the increase of the number of benzene rings in the rigid core of dopants in all studied systems, Figure 5. Although the 8CB dopant has the shortest core, it destabilizes antiferroelectric phase less than 8CN because the length of the terminal chain is enough to formed smectic phase and thanks to that it better fits to smectic layers in bicomponent systems with induced antiferroelectric phase and in pure compound 5. The influence of the terphenyl 5CT is comparable to four ring compound 7CBB. The phenyl biphenylate structure of dopants less destroys anticlinic order than the biphenyl benzoate. The benzoate structure destabilizes the antiferroelectric phase the most. The antiferroelectric phase of pure compound 5 is the least sensitive to the dilution with cyanoterminated compounds, Figure 5d.

3.2.2. *The Influence of Presence of a Fluorine Atom in the Core and the Chain.* We have used a octanoxycyanobiphenyl (8OCB), its derivative with a fluorine atom in orto-position to a cyanoterminated chain and a compound with fluorine atom in

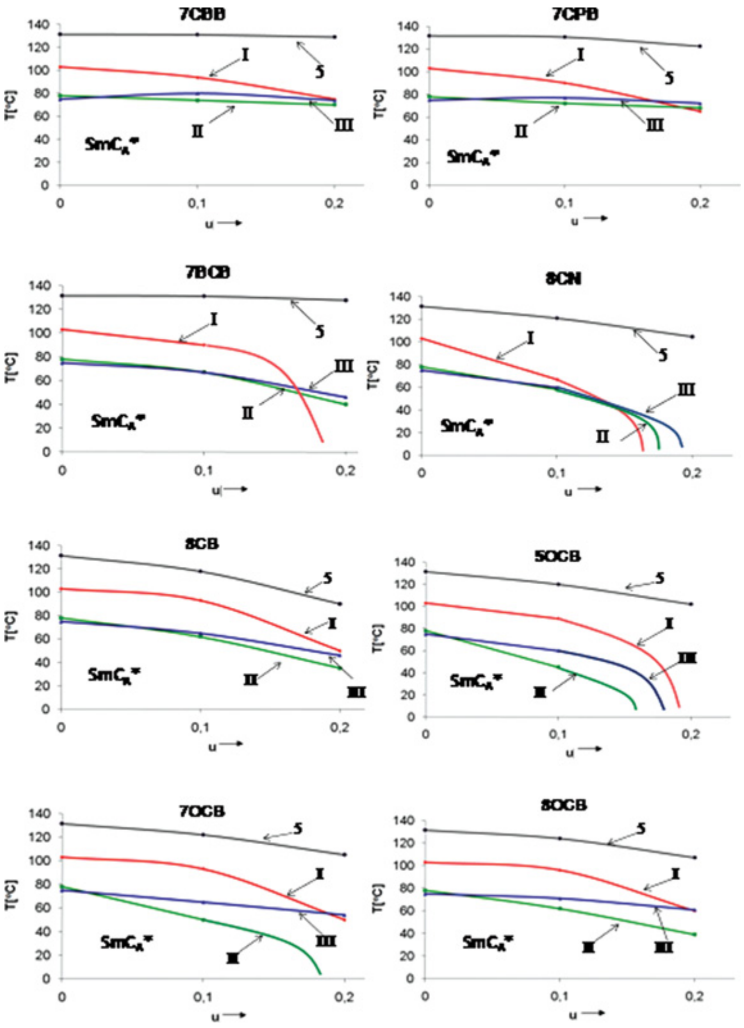


Figure 4. Part of phase diagrams showing the maximum temperature of antiferroelectric phase existence in mixture I, II, III and compound 5 dopped with different cyanoterminated compounds.

the core and the chain (7FOCBF) as dopants for comparison of their ability to stabilize antiferroelectric phase, Figure 6.

As one can see in all studied systems the dopant with a fluorine atom in the core causes bigger destabilization of antiferroelectric phase than its derivative without a fluorine atom. Only mixture with pure compounds 5 has anticlinic phase for 0.2 mole fraction for both compounds. The fluorination of seven carbon atoms in terminal chain causes less destabilization. Looking at the phase situation of dopants it can be noted that 8OCB Has SmA and N phases, so the structure is enough to stable layered arrangement. The presence of fluorine atom in the lateral position cause the disappearance of the smectic order in phase of 8OCBF. Whereas the presence of fluorine atoms in the terminal chain cause the appearance layer arrangement

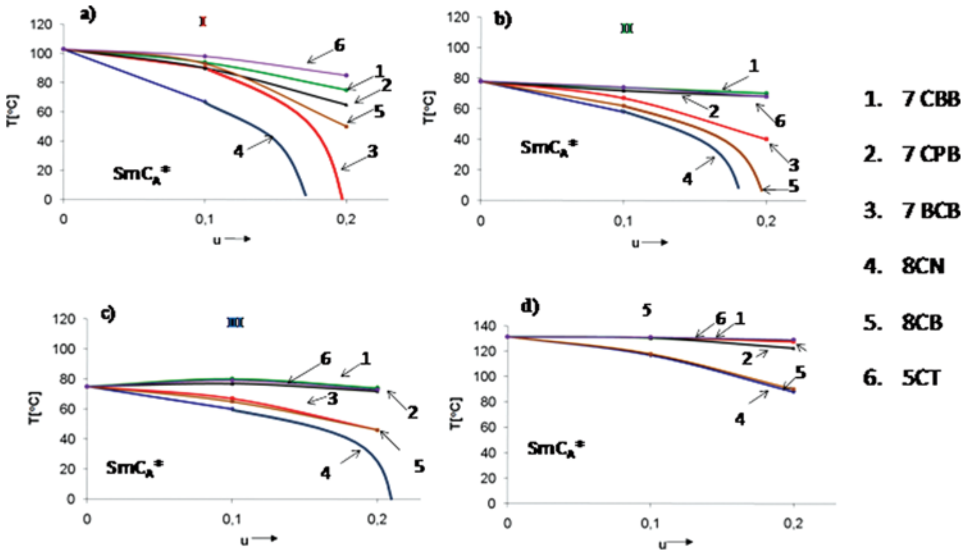


Figure 5. Part of phase diagrams showing the maximum temperature of antiferroelectric phase existence in four systems (a) mixture I, (b) mixture II, (c) mixture III, (d) compound 5 doped with cyanoterminated compounds differing in the core structure.

(7FOCBF). This is one reason of the different influence these dopants on the stability of antiferroelectric phase in mixture I, II, III and compound 5. The antiferroelectric phase of pure compound is so stable that the addition of three compounds 8OCB, 8OCBF and 7FOCBF does not influence its stability very much.

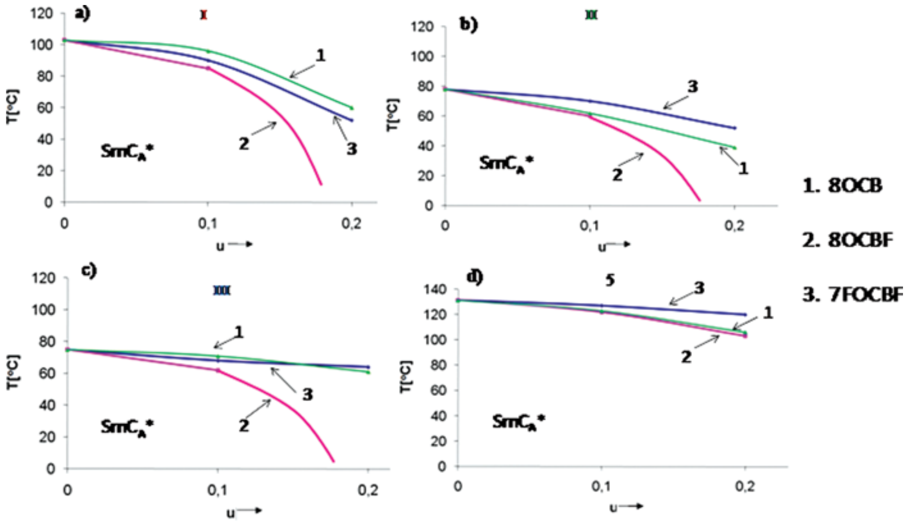


Figure 6. Part of phase diagrams showing the maximum temperature of antiferroelectric phase existence in four systems: (a) mixture I, (b) mixture II, (c) mixture III, (d) compound 5 doped with cyanoterminated compounds differing in substitution of fluorine atom in the core and in the terminal chain.

But the stability of antiferroelectric phase obtained by the induction effect is sensitive especially to the steric hindrance of lateral substitution in the core of 8OCBF.

3.2.3. *The Influence of the Alkyl Chain Length and Presence of the Oxygen Atom in the Terminal Chain on the Stability of Antiferroelectric Phase.* For cyanoterminated dopants with the identical core but differing in the terminal chain length the increase of the stability of antiferroelectric phase with increasing the number of carbon atom in the terminal chain is observed, Figure 7. It can be explain by the least difference between the length of 8OCB molecules and the thickness of smectic layers in basic systems. The dopant with the oxygen atom influences in the lesser grade on the destability antiferroelectric phase than his derivative without the oxygen atom in the terminal chain. The reason for this can be the increase of the terminal chain length and the increase of donor-acceptor (intermolecular) forces in the case of used the 8OCB dopant. The least differences in the influence of these dopants on the anticlinic phase of compound 5 is shown on phase diagram presented in Figure 7d.

3.2.4. *The Influence of the Branching of the Terminal Chain on the Stability of Antiferroelectric Phase.* Dopants with chiral carbon atoms more destabilize the antiferroelectric phase than dopant with linear structure of terminal chain, Figure 8. The compound with the chiral terminal chain similar to that in components of basic mixture and pure compound 5 destabilizes the anticlinic phase in the biggest grate. None of studied systems have antiferroelectric phase for 0.2 molar fraction of dopants with the exception of compound 5. This may result from the length of their molecules and the steric hindrance of chiral carbon atoms in AmOCB and 8*OCB especially in bicomponent systems with induced antiferroelectric phase which

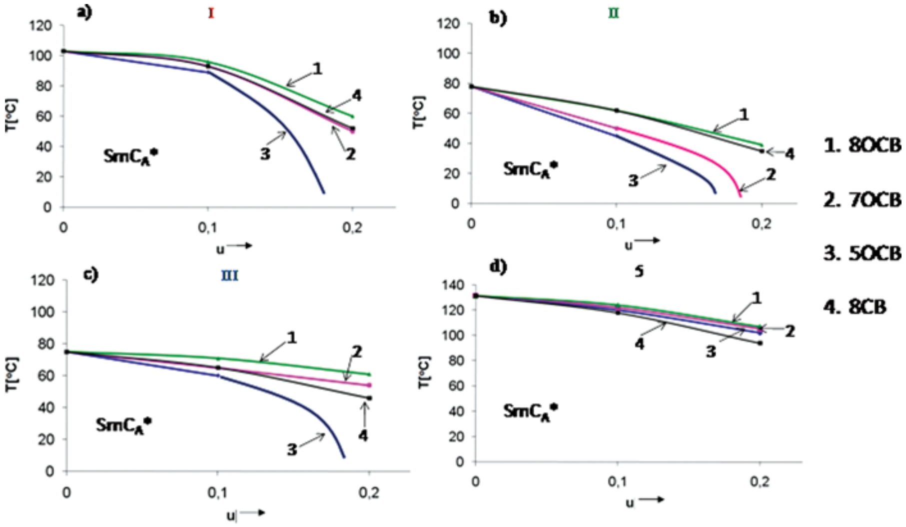


Figure 7. Part of phase diagrams showing the maximum temperature of antiferroelectric phase existence in four systems (a) mixture I, (b) mixture II, (c) mixture III, (d) compound 5 dopped with cyanoterminated compounds differing in the alkyl chain length and the presence of the oxygen atom in terminal chain.

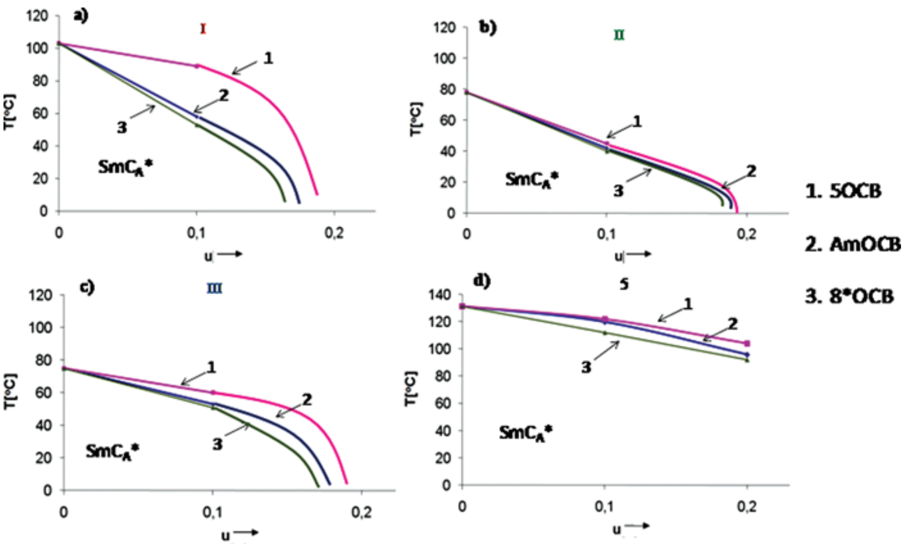


Figure 8. Part of phase diagrams showing the maximum temperature of antiferroelectric phase existence in four systems (a) mixture I, (b) mixture II, (c) mixture III, (d) compound 5 dopped with cyanoterminated compounds differing in the presence of chiral carbon atom in terminal chain.

stability depend very much on the intermolecular forces. That difference does not have such a big meaning for dopping pure compound 5.

4. Conclusion

The influence of the structure of cyanoterminated dopants for the stability of antiferroelectric phase in three bicomponent systems with induced antiferroelectric phase and one pure antiferroelectric compound was studied in the range of 0.2 molar fraction. Dopping cyanoterminated compounds to the systems with antiferroelectric phase cause the destabilization of this phase in all studied systems. The most stable is the antiferroelectric phase in of our compounds. The antiferroelectric phase obtained by the induction phenomena is more sensitive to the dilution because it is easier to destroy this phase. Some special intermolecular forces must be present to induce antiferroelectric phase. The mixture III is the least sensitive among basic mixtures with induced the antiferroelectric phase to the dilution of such dopants because of the similarity of the structure with the structure of dopants, especially the presence of –CN group for all compounds. The most important conclusions from our work are as follow.

1. The smaller destability of the antiferroelectric phase is caused by:
   - the increase of the number of benzene rings
   - no presence of the fluorine atom in the structure of dopants core
   - the increase of terminal chain length of dopants
   - the linear structure of terminal chain of dopants
   - presence of the oxygen atom in the terminal chain
   - presence of fluorine atom in the terminal chain

Dopants having smectic phase are better mixture components because they have structure favouring layer arrangement.

2. Very small destabilization of antiferroelectric phase gives possibility to use cyanoterminated compounds (especially three and four ring) as dopants for modification of the mixtures properties (the decrease viscosity and than the increase rate of electro-optical response) with anticlinic phase in a small amount.

Acknowledgment

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