Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Witold Drzewiński [a], Roman Dabrowski [a], Zbigniew Raszewski [a], Jolanta Rutkowska [a], Mary E. Neubert [a b] & Sandra S. East [a b]

[a] Military University of Technology, 01489, Warsaw, Poland

[b] Institute of Liquid Crystal, Kent, Ohio, USA

Version of record first published: 04 Oct 2006

To cite this article: Witold Drzewiński, Roman Dabrowski, Zbigniew Raszewski, Jolanta Rutkowska, Mary E. Neubert & Sandra S. East (1997): Infulence of Dopant Structure on the Ability of Enhancing S_c Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 195-201

To link to this article: http://dx.doi.org/10.1080/10587259708041767

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 195–201
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INFLUENCE OF DOPANT STRUCTURE ON THE ABILITY OF ENHANCING S_C PHASE

WITOLD DRZEWIŃSKI+, ROMAN DĄBROWSKI, ZBIGNIEW RASZEWSKI, JOLANTA RUTKOWSKA, MARY E. NEUBERT*, SANDRA S. KEAST*

Military University of Technology, 01-489 Warsaw, Poland

* Institute of Liquid Crystal, Kent, Ohio, USA

Abstract Seven two ring chiral benzoates with different terminal substituents being isotropic liquids or low temperature monotropic compounds were tested as dopants inducing ferroelectricity in non-chiral S_C mixtures composed from esters. It was found that some of them strongly enhance the stability of smectic C in four component ester mixture up to the concentration of 30 wt.%. The spontaneous polarization Ps, the tilt angle θ, and both parts of complex dielectric permitivity of the doped mixtures upon dopant concentration and temperature were investigated.

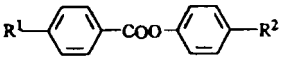
INTRODUCTION

Compounds with a smectic C phase often reveal a tendency for the destabilization of the smectic C phase, when mixed together.[1] So it is not easy to obtain a mixture with a wide range smectic C phase starting from accidentally chosen smectic C compounds. We wanted to know what it would take to counteract the destabilization of the smectic C phase in mixtures. Previously we showed that smectic C compounds may be classified into two different groups according to miscibility.[1] Formulation of mixture with a broad range of smectic C phase requires the use of component from the same miscibility group.

+ Author for correspondence

We also showed that the compounds which do not have a smectic C phase may also be used as components in smectic C mixtures in meaningful quantities. No destabilization of the smectic C phase occurs and in the case of some structures, enhancement of the smectic C phase was observed.[2,3,4] Such properties were found for the following chiral or nonchiral dopants: terphenyl diesters, hydrocarbons, dioxanes or biphenyls; especially when they contained long alkyl chains or the carbonyl group.[3,4] This gives a new method for changing the properties of ferroelectric mixtures. We would like to know which structural features of these molecules play an important role in S_C phase enhancement. Results obtained in this mater will be shown and discussed in this paper.

Lately, Neubert and coworkers synthesized the esters **1**



1

with terminal chain $C^*H(CH_3)C_6H_{13}$, attached to the benzene ring through an oxygen atom or CO, CO_2, OCO group. These two ring compounds could be useful for determining this structure - property relationship since they show either no mesophases or only monotropic smectic phases.[5] As a base, we have chosen to study four-component mixture A.[6] Its composition is as follow: 23.35 wt.% $C_8H_{17}O$-C_6H_4-COO-C_6H_4-OC_6H_{13}, 18.80 wt% $C_{10}H_{21}O$-C_6H_4-COO-C_6H_4-OC_6H_{13}, 25.41 wt.% $C_8H_{17}O$-C_6H_4-COS-C_6H_4-C_5H_{11}, 32.44 wt.% C_6H_{13}-C_8H_{12}-CH_2CH_2-C_6H_4-OOC-C_6H_4-OC_8H_{17}

RESULTS

Phase transition studies of single compounds

Temperatures of the phase transitions, as determined thermomicroscopically[5] and by DSC are compared in Table I. Compounds **1a**, **1b**, **1c**, **1e**, **1g** showed only Cr-I transition whereas compounds **1d** and **1f** showed a monotropic A phase. Phase diagrams with two standard compounds: 4-hexyloxyphenyl octyloxybenzoate and (S)-4-(2-methylbutyloxy-carbonyl)phenyl octyloxybenzoate were also determined.[1] These produced virtual transition temperatures for compounds **1a**, **1b**, **1c**, **1e** and **1g**.

BLE I The phase transition temperatures (°C) and *phase transition enthalpies (kcal/mol)* of compounds 1.

Compound		Phase and enthalpy transitions[a]																	
		Heating						Cooling											
R_1	R_2	Cr_1		Cr			I	Cr_1		Cr			S_C		S_A		N*		I
$H_{13}C_6$—CH(CH$_3$)—O	OC_7H_{15}			•	34.3		*			*	3.7[b]		-		-		-		•
				*	33.0		•			*	3.8[b]		-		-		-	(-5)	*
					8.98						*6.80*								
$H_{13}C_6$—CH(CH$_3$)—O	O—C(=O)—C_9H_{19}			*	44.0		•			*	35.2		-		-		-		*
				*	43.9		*			*	35.7		*	(9)	-		•	(16.5)	*
					10.4						*8.3*								
$H_{13}C_6$—CH(CH$_3$)—O	C(=O)—C_9H_{19}			*	65.0		•			*	53.3		-		-		-		*
		*	57.2	*	62.3		•			*	59.3		*	(17)	*	(29)	-		•
			6.42		*5.1*						*10.2*								
$H_{21}C_{10}O$	COO—CH(CH$_3$)—C_6H_{13}			*	33.5		*			*	8.7		-		*	22.7	-		*
		*	0.5	•	32.7		*	*	13.1	*	15.3		-		*	21.9	-		*
			0.27		*8.28*				*4.22*		*1.29*					*1.29*			
$H_{19}C_9CO$	COO—CH(CH$_3$)—C_6H_{13}	*	(-2)	•	71.7		*	•		*	62.8[c]		-		*	(51)	-		•
			0.7		*11.2*						*11.2*								
$H_{21}C_{10}O$	O—CH(CH$_3$)—C_6H_{13}	*		•	36.8		*			*	-1.8		-		*	27.0	-		*
				*	36.4		*			*	11.3		-		*	26.0	-		*
					9.2						*6.1*					*1.3*			
$H_{19}C_9CO$	O—CH(CH$_3$)—C_6H_{13}	*		*	68.7		**			*	64.3		-		-		-		•
				*	66.4					*	64.6		-		*	(55)	-		*
					9.2						9.3								

nicroscope transition temperatures from Ref. 5, line 2 - DSC transition temperatures, values in parenthesis were estimated fr
es, and line 3- enthalpy values from DSC studies; b - metastable form; c - compoud prepared in this work

Phase diagram studies of mixture A and esters 1

The changes of the phase transition temperatures of the mixture A upon the dopant concentration **1a-1g** are shown in succession in Figure 1. All diagrams were prepared using the single concentration method.

Ester **1a**, having only the virtual nematic phase, strongly depresses the stability of the base mixture A, (Figure 1a), the same but in a moderate way is observed for the compounds **1b** and **1c** having the virtual S_C-N or S_C-S_A phase transitions. The enhancement of the S_C phase accompanied with injection of a S_A was observed, for all the

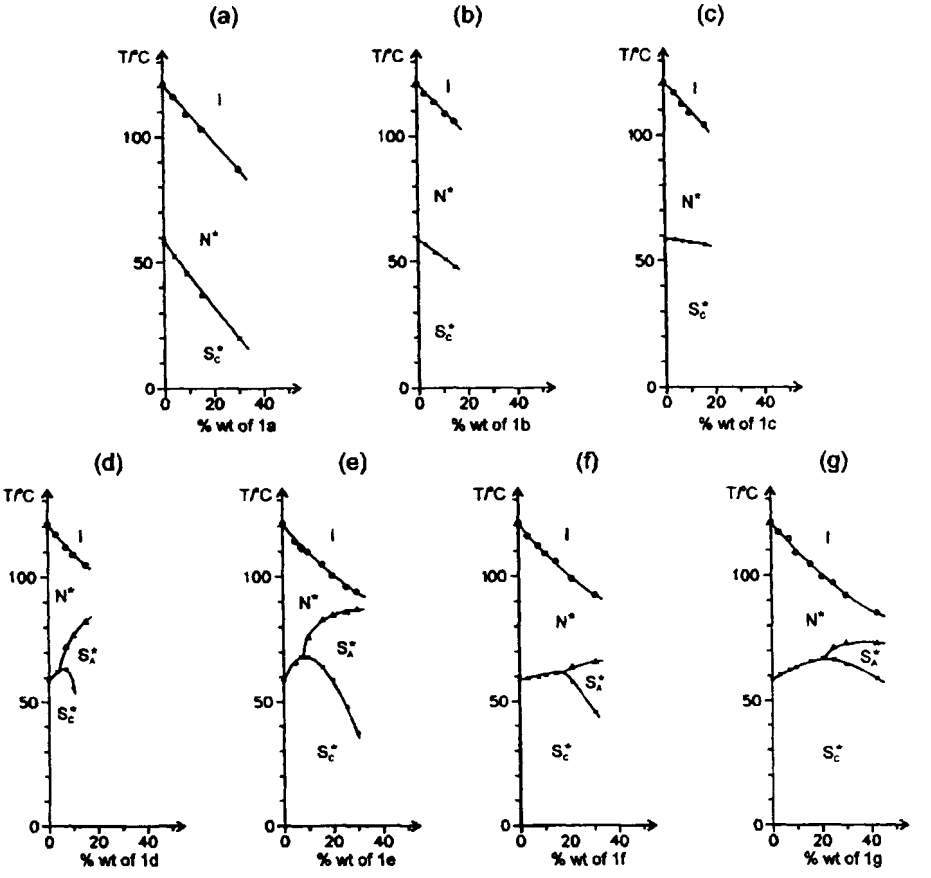


FIGURE 1 Change of phase transition temperatures of mixture A with concentration variations of dopants **1**.

esters 1d-1g having only the monotropic or virtual S_A phase, Figure 1d-1g.

The concentration range, in which the enhancement of the S_C phase is observed depends on the molecular structure of dopants. For compound 1g, enhancement of the S_C phase is observed over the largest range of concentration and the S_C-N and S_C-S_A phase transition temperatures increase by the largest amount.

Spontaneous polarization and tilt measurements

The spontaneous polarization P_s of mixture A doped with 1g was determined using the Diamont method. The tilt angle θ was derived from the optical switching angle of the sample. The sign of the polarization was determined from the relative configuration of the electric field and the switching position of the sample during the observation under a polarizing microscope.

The spontaneous polarization P_s, the tilt angle θ, and both parts of the complex dielectric permittivity of mixture A doped with 1g up to 40 wt.% were investigated as a function of temperature. From these data, we derived the concentration dependence of P_s and θ at constant temperature below the S_C* - S_A or S_C* - N* phase transitions (Figure 2a and 2b). Summarizing these data one can see that the measured spontaneous

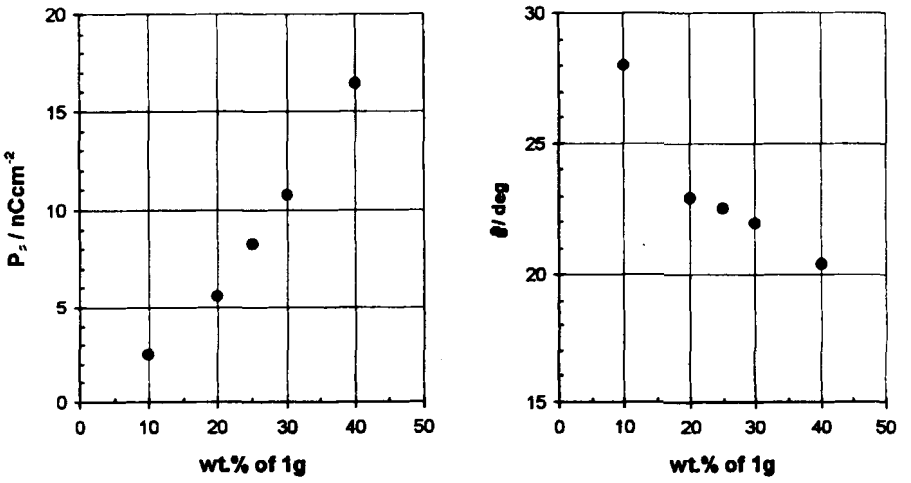


FIGURE 2 Spontaneous polarization (a) and tilt angle (b) vs. concentration of 1g.

polarization P_s as well as the tilt angle shows a non-linear dependence on the concentration of the chiral dopant. The tilt shows a drop near the concentration of the dopant, when the S_A phase is injected. To remove the tilt angle dependence of the measured spontaneous polarization, the definition of a reduced ferroelectric polarization P_o has been proposed[7] as:

$$P_0 = \frac{P_s}{\sin\theta}$$

and the polarization power δ_P as:

$$\delta_P = \frac{\partial P_0(x_{wt})}{\partial x_{wt}}$$

where δ_P describes the possibility of a given chiral dopant to induce a spontaneous polarization in a smectic C host phase at a fixed temperature below the phase transition.

The dependence of the reduced polarization P_o on the weight fraction of the chiral dopant in the smectic C phase of the host mixture A at a constant temperature $T=T_c-15°C$ is given in Figure 3. It can be seen that in our case $P_o(x_{Wt})$ is non-linear and the calculated value of the polarization power δ_P is rather moderate (+51 nC cm^{-2}). In the range of the

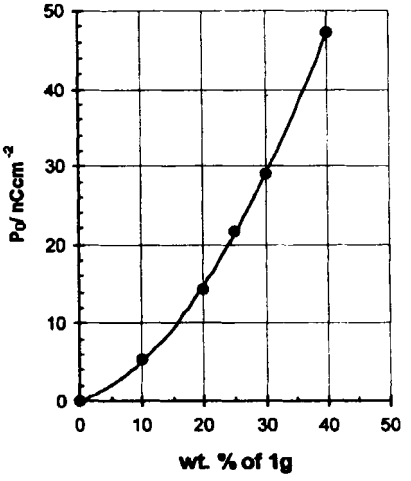


FIGURE 3 P_o as a function of chiral dopant **1g**.

concentration dopant **1g**, when the S_C phase is enhanced, the spontaneous polarization P_o is decreased. In most cases, the reduced polarization depends only on the kind of chiral dopant, not on the smectic C host phase and shows a linear dependence on a weight

fraction of the chiral dopant. It is true if the transverse dipole and the chiral centers are parts of the side chains of the dopant molecule. Recently, it was found[7-9] that P_o depends on the nature of the smectic C host phase and its concentration dependence is non-linear. Especially if the transverse dipole and the chiral centers are the parts of the central rigid core of the chiral molecule. In agreement with a model presented by Osipov[10] to explain some ferroelectric properties of the smectic phase C*, the non-linear concentration dependence of P_o is caused by the interaction between the permanent dipoles of the chiral molecules. The molecule of chiral dopant **1g** has two CO dipoles located closely to the central rigid core and it has the transverse dipole moment rather larger than the other studied dopants.

To explain the chiral dopant **1g** behavior, molecular calculations are necessary as well as further experimental investigations, especially with another smectic C host phase.

This work was supported by M.Curie-Skłodowska Found under grant No PAN/NSF-96-249.

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