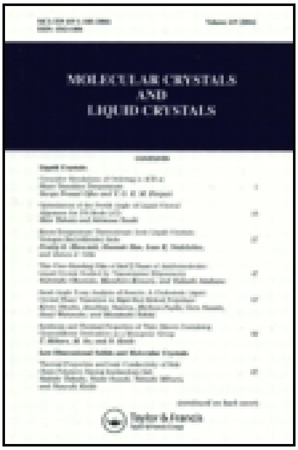

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 13 Dec 2006.

To cite this article: Ch. Bahr & G. Heppke (1987): Ferroelectric Liquid Crystals: Properties of Binary Mixtures and Pure Compounds with High Spontaneous Polarisation, Molecular Crystals and Liquid Crystals, 148:1, 29-43

To link to this article: http://dx.doi.org/10.1080/00268948708071777

Mol. Cryst. Liq. Cryst., 1987, Vol. 148, pp. 29–43
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Printed in the United States of America

Ferroelectric Liquid Crystals: Properties of Binary Mixtures and Pure Compounds with High Spontaneous Polarisation†

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(*Received September 6, 1986; in final form December 24, 1986*)

The correlation between the molecular structure and the magnitude and sign of the spontaneous polarisation of ferroelectric liquid crystals has been studied using mixtures and pure compounds. Several binary mixtures consisting of a chiral dopant and a non chiral smectic C compound have been prepared. The spontaneous polarisation with values up to 10 nC/cm^2 for mixtures containing 10% of a chiral dopant was measured. Three homologous series of new ferroelectric liquid crystals which show values of the spontaneous polarisation up to 300 nC/cm^2 have been prepared by the esterification of 4-alkyloxy-4′-hydroxybiphenyls with three α-chloro carboxylic acids obtained from the α-amino acids valine, leucine, and isoleucine. Within a homologous series the spontaneous polarisation was found to increase considerably with decreasing alkyl chain length to an extend which could not be explained by the behaviour of the tilt angle which increases only slightly.

Keywords: ferroelectric liquid crystals, spontaneous polarization, tilt-angle measurements

INTRODUCTION

It is well known that a tilted smectic phase containing chiral molecules shows ferroelectric properties e.g. a spontaneous polarisation. The direction of the spontaneous polarisation of a ferroelectric liquid

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†Paper presented at the 11th International Liquid Crystal Conference, Berkeley, CA, 30 June–4 July, 1986.

crystal is related definitely with the director by symmetry: the polarisation vector is perpendicular to both the director and the layer normal of the smectic layers. For a given tilt direction there are only two possible directions of the spontaneous polarisation which are opposite to each other and distinguished by a different sign.[1] Although the spontaneous polarisation, which is responsible for the coupling of the director with an applied dc-field, is the most important property for the use of a ferroelectric material in a display device, little is known about the dependence of the magnitude and sign of the spontaneous polarisation on the molecular structure.[2,3] Such investigations may be carried out not only on pure chiral compounds exhibiting a tilted smectic phase, but also on mixtures of a non chiral liquid crystal exhibiting the tilted smetic phase with a small amount of a chiral dopant added to it.

In this paper results on both mixtures and pure compounds are reported. Several binary mixtures containing 10 mol% of a chiral dopant have been prepared using diheptyloxyazoxybenzene (HOAB) as smectic C matrix. The sign and the value of the spontaneous polarisation were determined. For the three homologous series of new ferroelectric liquid crystals reported recently[4,5] the dependence of the spontaneous polarisation as well as the tilt angle on the alkyl chain length was investigated. Results on a binary mixture stable at room temperature showing high spontaneous polarisation and short switching times are presented.

EXPERIMENTAL

Three of the chiral dopants (see Table I) are commercially available (1: ZLI-1082, Merck; 2: CE4, BDH; 4: ZLI-811, Merck). The other chiral dopants were prepared by esterification of commercially available optically active alcohols and acids with mesogenic acids or phenols.

Optically active (S)-α-chloro carboxylic acids were obtained from the α-amino acids L-valine, L-leucine, and L-isoleucine according to a prescription of Fu *et al.*[6] and combined through their acid chlorides with homologous 4-alkyloxy-4′-hydroxybiphenyls.

The transition temperatures were determined by optical microscopy using a Leitz Lux Pol polarisation microscope and a Mettler FP 82 hot stage, the types of the more ordered smectic phases were obtained by miscibility studies.

The spontaneous polarisation of mixtures and pure compounds was measured by a Diamant bridge.[7] The layer thickness of the planar oriented samples was 9 μm. Generally the spontaneous polarisation was determined at a frequency of 50 Hz with a voltage of 20–40 V. The sign of the spontaneous polarisation was determined by observing conoscopically the moving of the tilt direction when applying a dc electric field.

The tilt angle was obtained by x-ray measurements comparing the layer spacing of the S_C-phase with the layer spacing of the S_A-phase.

RESULTS

I. Binary mixtures

Diheptyloxyazoxybenzene (HOAB) was used as matrix for the mixtures. The compound shows the transition temperatures K 74°C S_C 95°C N 124°C I. The mixtures contained 10 mol% of a chiral dopant and 90 mol% of HOAB. All mixtures show a cholesteric–smectic C* transition (Table I). The value of the spontaneous polarisation was measured 10 K below this transition.

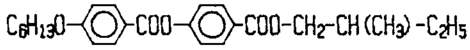
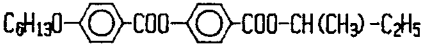
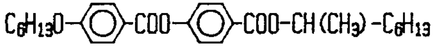
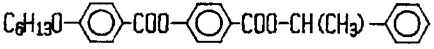
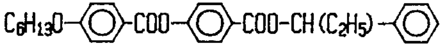
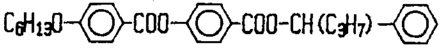
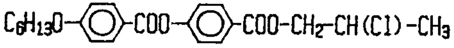
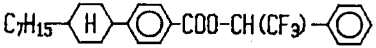
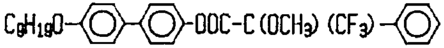
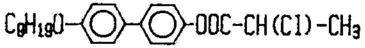
The mixtures show a spontaneous polarisation the values varying from nearly 0 to about 10 nC/cm^2. By simply extrapolating to 100% amount of the chiral dopant one gets values of the spontaneous polarisation of the order of 100 nC/cm^2. Hence, it could be concluded that ferroelectric systems with such high values could be possible.

No simple correlation seems to exist between the spontaneous polarisation of the investigated mixtures and the molecular structure of the chiral dopants (Table I). As known for pure compounds a strong dipole directly attached at the chiral center seems to favour higher values of the spontaneous polarisation. Comparing the compounds 3, 4, and 5 it also seems favourable to attach a bulky substituent at the chiral center which was observed for pure compounds too.[2] On the other hand the fixing of a second bulky substituent at the chiral center decreases the polarisation again (see compounds 5, 6, and 7). A similar effect is to be observed by attaching a second strong dipol at the chiral center: compound 10 carries a CF_3-group while compound 9 contains a CH_3-group but it shows the smaller spontaneous polarisation.

The mesogenic part of the dopant, i.e. the mesogenic acid or phenol which has been used to esterify the optically active alcohol resp. acid,

TABLE I

Binary mixtures (90% HOAB/10% chiral dopant) under investigation. The spontaneous polarisation of the mixtures was measured 10 K below the S_{C^*}-Ch transition; *n* designates the number of bonds between the aromatic core and the chiral center of the dopant

	Chiral dopant	$t(S_{C^*}\text{-Ch})/^\circ C$	$P_s/nC/cm^2$	Sign of P_s	Configuration	n
1		86	<0.5	+	S	4
2		79	0.8	+	S	2
3		86	1.0	−	R	3
4		86	4.5	+	S	3
5		82	9.7	−	R	3
6		82	6.2	−	R	3
7		82	2.1	+	S	3
8		86.5	0.6	+	S	4
9		72.5	10.5	−	R	3
10		77	7.3	−	R	3
11		80.5	6.6	−	R	3
12		86.5	9.1	−	R	3
13		92.5	3.2	−	S	3

also has some influence on the spontaneous polarisation: comparing the compounds 11 and 12 a more rigid mesogenic part seems to favour a higher spontaneous polarisation.

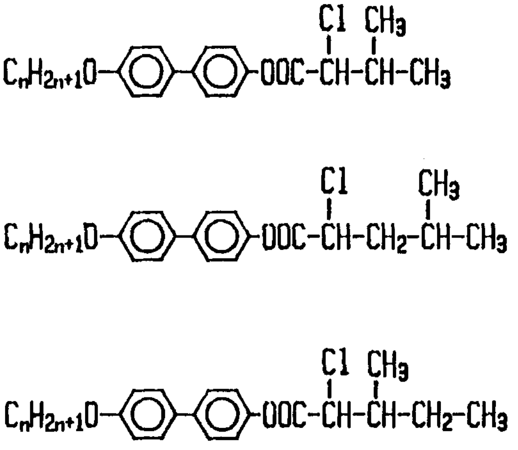
The correlation between the sign of the spontaneous polarisation and the molecular structure was described by an odd-even-rule given by Goodby *et al.*[3,8] taking into account the position and configuration of the chiral center and distinguishing between methyl branched and chloro branched chiral centers. The compounds 3, 4, 5, 6, 7, and 9 (methyl branched) fit into this rule, as also the compounds 8 and 13 (chloro branched).

The compounds 1 and 2 do not fit into this rule, however one has to consider that the rule was developed for pure compounds and may not be necessarily valid for mixtures. Since a change of sign in the spontaneous polarisation with temperature was found in a pure compound,[9] a change of sign may also occur with concentration in mixtures. Another difficulty arises out of the comparison of compounds 9 and 10. For the same steric situation the exchange of CH_3 by CF_3 should lead to the opposite direction of the lateral dipole moment and therefore also to the opposite sign of the spontaneous polarisation, whereas the same sign is found for both compounds experimentally. However, one has to take into account that the introduction of the CF_3-group in this case alters the absolute configuration according to the convention of Cahn, Ingold, and Prelog,[10] so that the same configuration (R) in the compounds 9 and 10 designates opposite steric situations. Thus, Goodby's rule as applied to other substituents at chiral centers cannot be easily generalized. This is even more obvious with the new chiral centers of the compounds 11 and 12 not investigated previously.

II. Pure compounds

For none of the investigated chiral dopants a smectic C phase was observed. The compounds 1, 2, 3, and 8 exhibit a S_A-phase, only compound 13 shows a monotropic transition to a tilted smectic phase (S_G). All other compounds are not liquid crystalline. As a comparison of the mixtures with compounds 3 and 4 shows, the spontaneous polarisation is enlarged by the elongation of the alkyl substituents at the chiral center. Thus, starting from the promising behaviour of compound 13, which is an ester of α-chloro propionic acid, it was attempted to modify it's structure in a similar way.

Other α-chloro carboxylic acids are accesible from the correspond-



series A_n

series B_n

series C_n

FIGURE 1 Molecular structures of the three homologous series of ferroelectric liquid crystals under investigation.

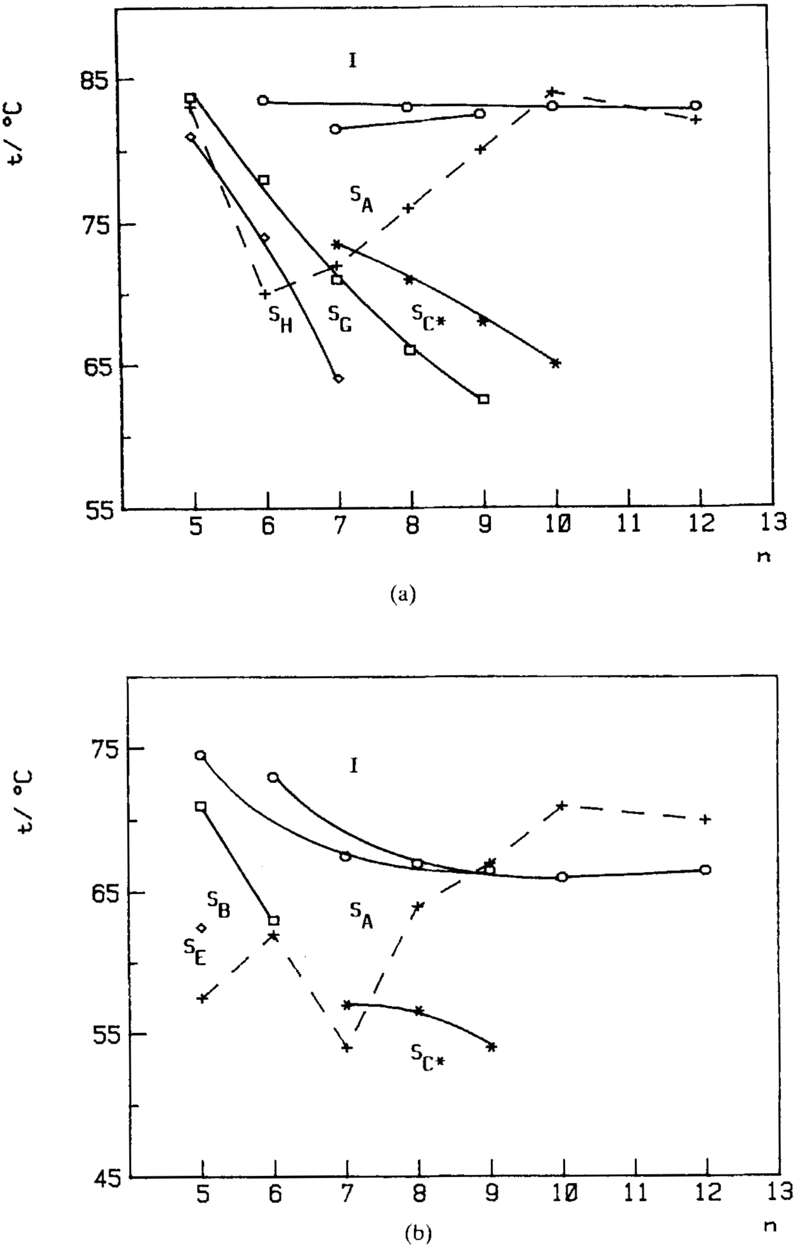
ing α-amino acids. Starting from valine, leucine, and isoleucine three new series of chiral alkyloxybiphenyl derivatives have been prepared (Figure 1), which unexpectedly are not only liquid crystalline, but exhibit mostly a S_{C*}-phase also.[4] This allowed to study the ferroelectric properties of the pure compounds.

Of each series the members with the chain length from 5 to 12 (except 11) were studied. The homologs of all three series show a direct S_A-I transition except the compound A_5 which shows a S_G-I transition. As in Figure 2 shown either a more ordered smectic phase (homologs with shorter chain length) or a S_{C*}-phase (homologs with longer chain length) appears on cooling the S_A-phase.

A comparison of the results obtained with the three series shows that the compounds C_n exhibit the highest values of the spontaneous polarisation. For C_7 a value of 290 nC/cm^2 near the transition to the S_G-phase was obtained. For the compound A_7 values up to 140 nC/cm^2 and for the compound B_7 up to 80 nC/cm^2 are observed.

All the three compounds show a negative sign of the spontaneous polarisation. For series A and B this is in agreement with Goodby's rule for chloro branched systems since the chiral centers of the optically active acids are (S)-configurated. In series C both chiral centers are (S)-configurated and should produce a negative sign of the polarisation which might add and this may account for the high values of these compounds.

In series B the spontaneous polarisation only of the homolog B_7



(a)

(b)

FIGURE 2 Plot of the transition temperatures against the alkyl chain lengths (the dashed lines belong to the melting points); a) series A_n. b) series B_n. c) series C_n.

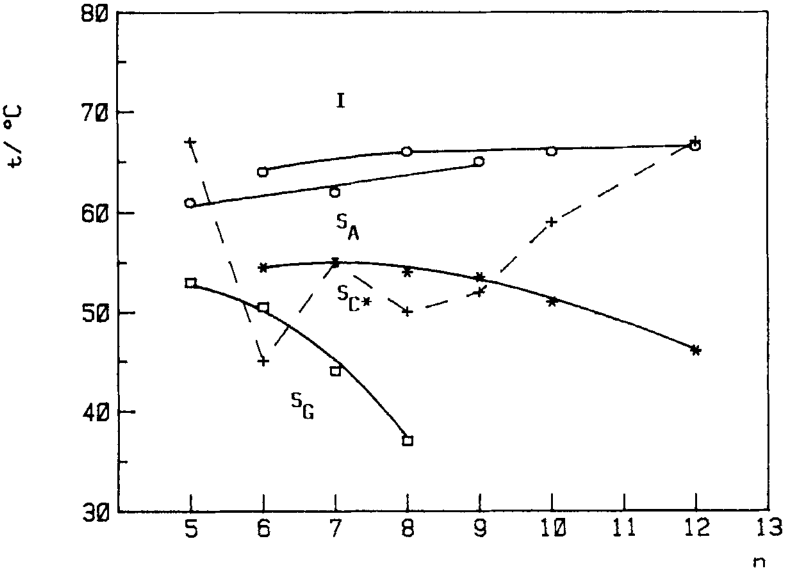


FIGURE 2 (*continued*)

was measurable because the S_{C*}-S_A transitions of the other homologs are too far below the melting point. Therefore it was only possible to study the influence of the alkyl chain length on the spontaneous polarisation for some homologs of series A (n = 7–9) and C (n = 6–9). Surprisingly a strong dependency of the spontaneous polarisation was found: The homologs A_7 and C_7 exhibit more than twice the values of the A_9 and C_9 homologs (Figures 3 and 4).

Generally the spontaneous polarisation is assumed to be proportional to the tilt angle. Hence, the tilt angles of the compounds were determined by x-ray measurements of the layer spacing. Figures 5 and 6 show that the tilt angle increases only slightly with decreasing chain length. Thus, the differences of the tilt angles of different homologs are too small to account for the behaviour of the spontaneous polarisation.

Remarkably, for some compounds a clear jump of the layer spacing occurs at the S_{C*}-S_A transition. This may indicate that the tilt angle does not go continously to zero at the transition which is in agreement with DSC measurements of the same compounds showing that the S_{C*}-S_A transition seems to be first order in contrast to the general behaviour of S_C-S_A transitions being second order. Further investigations on this point are in progress.

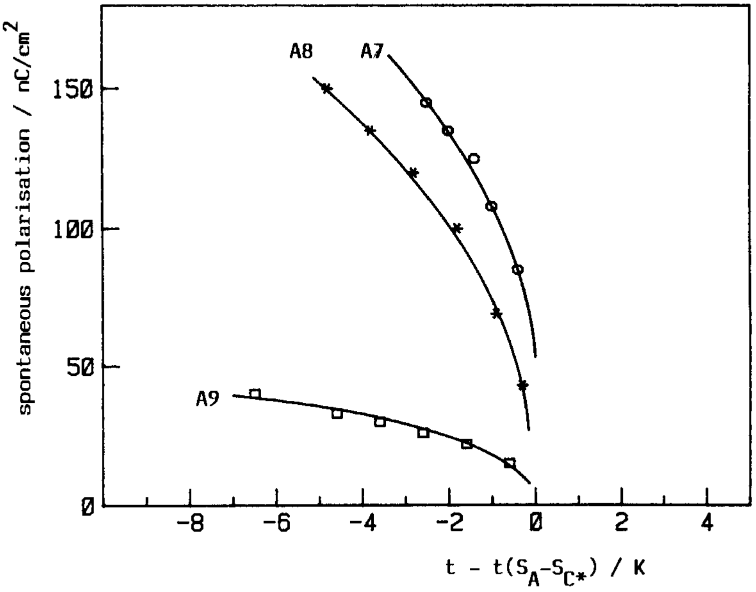


FIGURE 3 Temperature dependence of the spontaneous polarisation of the compounds A_7, A_8, and A_9.

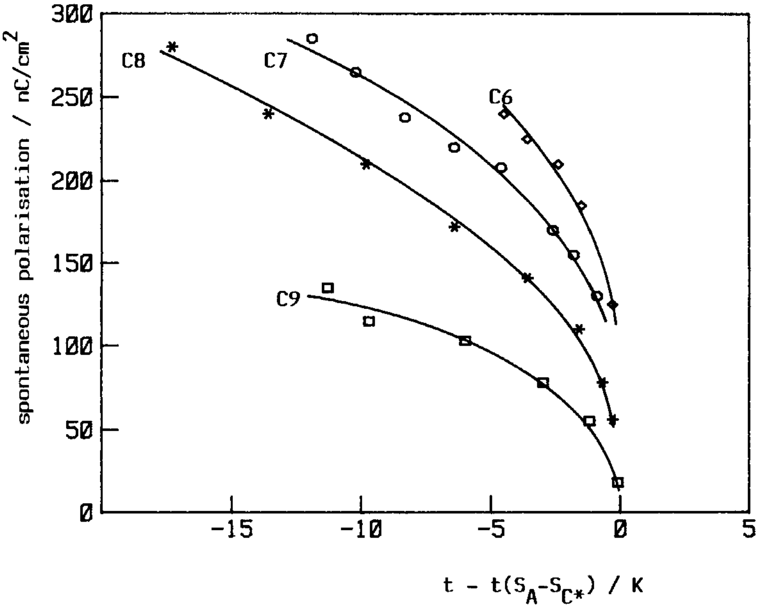


FIGURE 4 Temperature dependence of the spontaneous polarisation of the compounds C_6, C_7, C_8, and C_9.

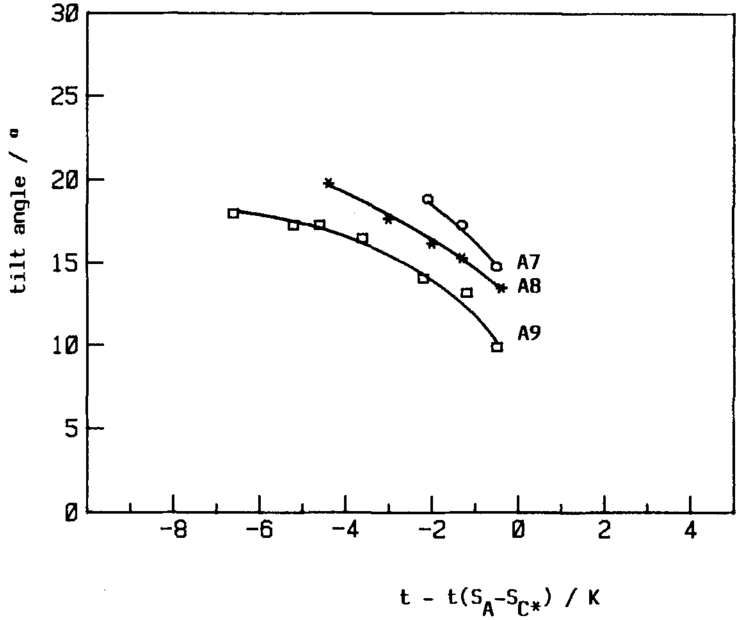


FIGURE 5 Temperature dependence of the tilt angle of the compounds A_7, A_8, and A_9.

For the three ferroelectric liquid crystals A_7, B_7, and C_7 mixtures consisting of 90% HOAB and 10% chiral compound were prepared analogous to part I. As Table II shows the values of the spontaneous polarisation of the mixtures are indeed higher than that obtained for compound 13 (Table I). A comparison with the values of the pure compounds is difficult because of the different phase sequences (S_{C^*}-S_A and S_{C^*}-Ch respectively) and the different temperature dependence of the spontaneous polarisation in mixtures and pure compounds. Nevertheless, the values of the 10% mixtures reflect the same order of magnitude as the values of the pure compounds.

In order to study the concentration dependence of the spontaneous polarisation in binary mixtures a non chiral compound exhibiting both smectic A and C phases in the same temperature range as the new compounds was chosen. The binary system of C_7 with 4-butyloxyphenyl-4′-octyloxybenzoate (8.0.4) is given in Figure 7. The S_A- and $S_{C(*)}$-phases of both compounds are found to be completely miscible. In the S_{C^*}-phase the spontaneous polarisation of mixtures of different compositions was measured 10 K below the S_A-S_C transition. The results (Figure 8) show a nonlinear dependence of the spontaneous

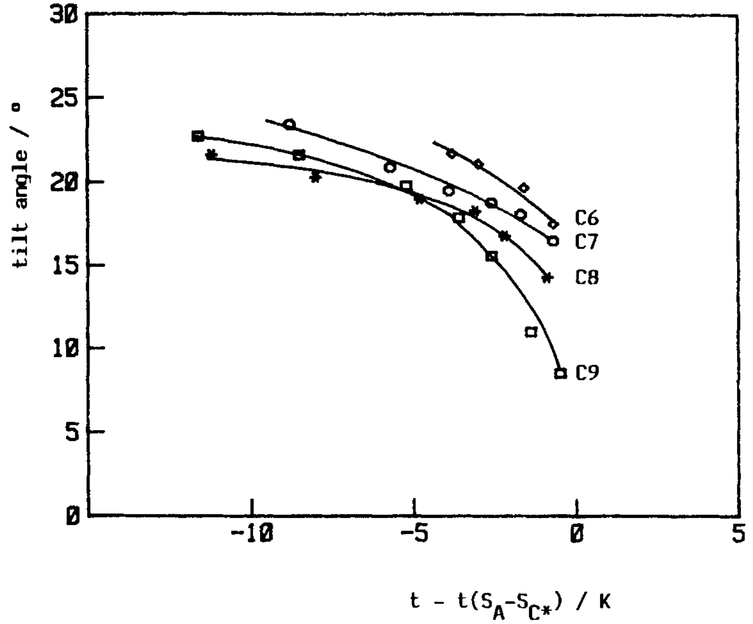


FIGURE 6 Temperature dependence of the tilt angle of the compounds C_6, C_7, C_8, and C_9.

polarisation on the concentration: the 50% mixture exhibits only 25% of the polarisation of the pure C_7.

The mixture 25% 8.0.4/75% C_7 shows a stable S_{C^*}-phase in the temperature range from 21°C to 50°C, therefore, it was chosen to demonstrate it's electrooptic properties. At room temperature (25°C) the mixture exhibits a spontaneous polarisation $P_s > 200$ nC/cm^2 (Figure 9) and an optical rise time (10% to 90%) of 12 μs (applying a voltage step from −40V to +40V at 9 μm, Figure 10).

TABLE II

Binary mixtures of HOAB with the ferroelectric compounds A_7, B_7, and C_7. The spontaneous polarisation of the mixtures was measured 10 K below the S_{C^*}-Ch transition. The right column gives the spontaneous polarisation of the pure compounds 2 K below their S_{C^*}-S_A transition

Compound	$t(S_{C^*}$-Ch)/°C (mixture)	P_s/nC/cm^2 (mixture)	$t(S_{C^*}$-$S_A)$/°C (pure compound)	P_s/nC/cm^2 (pure compound)
A_7	88	15	73.5	140
B_7	87.5	5	57	70
C_7	87.5	16	55	160

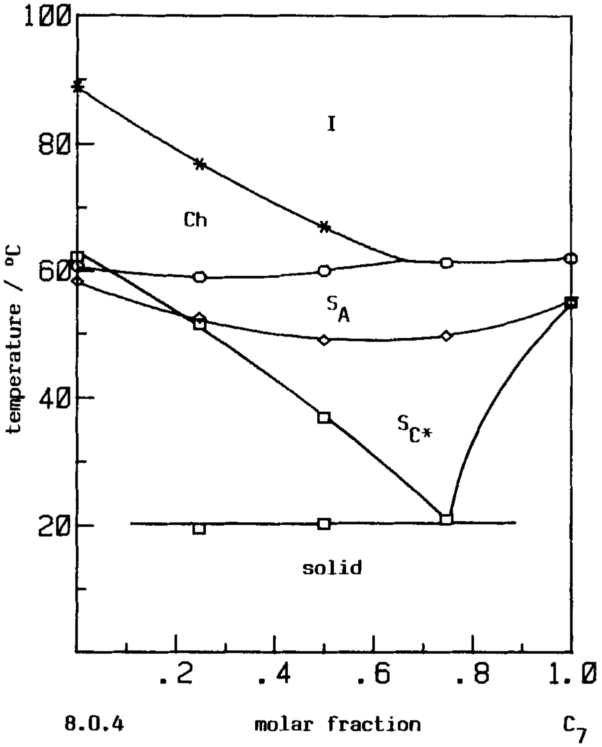


FIGURE 7 Binary phase diagram of 8.0.4 (4-butyloxyphenyl-4′-octyloxybenzoate) and C_7.

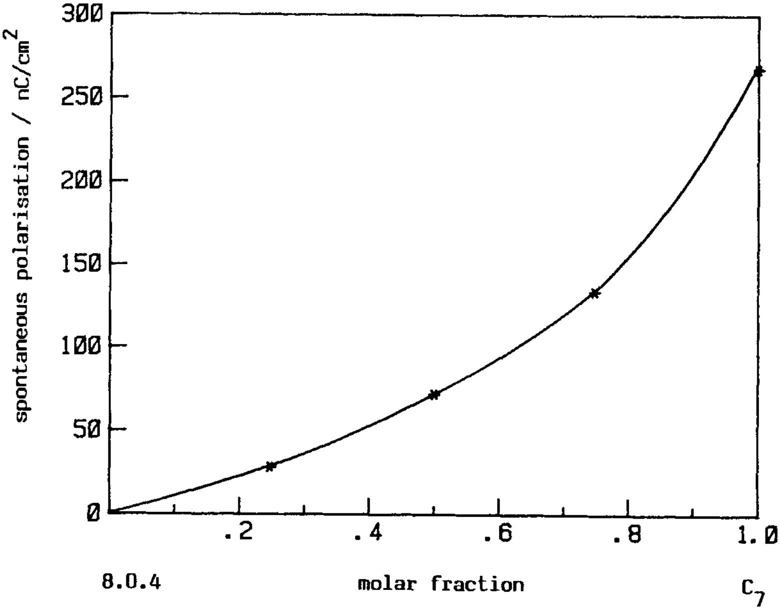


FIGURE 8 Concentration dependence of the spontaneous polarisation of the binary system 8.0.4/C$_7$. The values were measured 10 K below the S_{C^*}-S_A transition (see Figure 7).

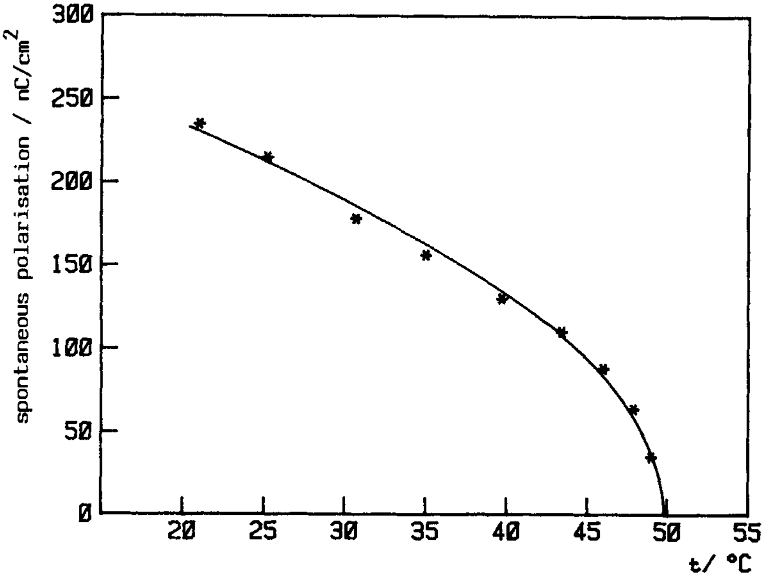


FIGURE 9 Temperature dependence of the spontaneous polarisation of the mixture 25% 8.0.4/75% C$_7$.

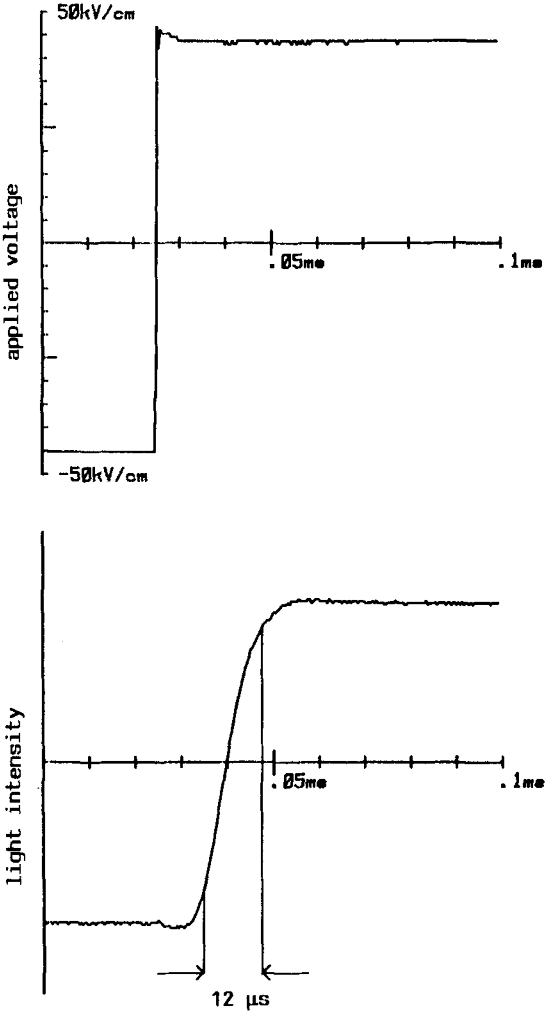


FIGURE 10 Electrooptic behaviour of the mixture 25% 8.0.4/75% C_7 at 25°C. Upper part: applied voltage, lower part: optical response.

Acknowledgments

The financial support of the Deutsche Forschungsgemeinschaft is acknowledged. The authors are very grateful to N. K. Sharma and B. Sabaschus for their help in miscibility studies and DSC measurements. Ch.B. thanks the Fonds der Chemischen Industrie for a scholarship.

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