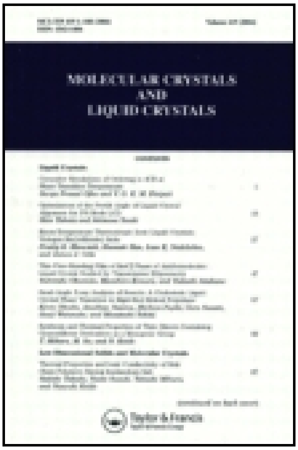

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Short Range Order in Polar S_A Phases through Dielectric Relaxation

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Short Range Order in Polar S_A Phases through Dielectric Relaxation

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Using dielectric relaxation we investigated two S_A-S_A changes in binary polar systems. First, we studied a S_{A_d}-S_{A_2} phase transition for which the short range order observed through the relaxation does not suffer drastic change. We think that the distribution of relaxation times revealed in S_{A_d} phase must be connected to the particular property of this system which exhibits two different layering modulations. Secondly, we performed dielectric measurements along the gradual passage from S_{A_d} to S_{A_1}. In this latter case we conclude that the same thermodynamic S_A phase with only one layering modulation can possess two short range local orders.

1. INTRODUCTION

Since the discovery of the S_A polymorphism in thermotropic polar systems, the question of phase transitions between different smectic A phases is a problem which is not completely solved.[1] It is clear that sometimes the transition from one type to another takes place through a regular thermodynamic transition (S_{A_1}-S_{A_2}, S_{A_d}-S_{A_2}, S_{A_1}-S_{A_d}), in some other cases this passage appears without a phase transition ($S_{A_d} \to S_{A_1}$). The different aspects of this problem was previously discussed;[1] certainly all the possibilities have not been observed (eg.: S_{A_d}-S_{A_2} continuous change).

In this paper we want to bring new information using dielectric relaxation. Since this phenomenon is sensible to the local order of the molecules, we can by this mean probe the short range order and compare the results with other investigations on the long range order.

We chose to investigate two different situations: first, we studied a S_{A_d}-S_{A_2} transition and secondly a gradual passage from the S_{A_d} to the S_{A_1} phase. It is interesting that precisely in the case of the gradual passage we observed a drastic change of the short range order and not in the case of the S_{A_d}-S_{A_2} transition.

2. EXPERIMENTAL

2.1. The systems investigated (Table I)

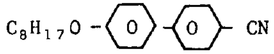
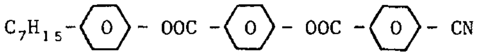
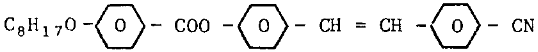
The materials we used are mixtures of two different compounds. In the serie "DB$_n$" some compounds exhibit the S_{A_d}-S_{A_2} phase change[1] but their transition temperatures are relatively high (above 150° C) and this makes the dielectric measurement very difficult. We performed measurements on a mixture of 8OCB and DB$_7$ (8OCB–0.79DB$_7$ with the following sequence:

$$N \xrightarrow{152^\circ\mathrm{C}} S_{A_d} \xrightarrow{133^\circ\mathrm{C}} S_{A_2}$$

In the second case we studied mixtures of the compounds "T$_8$" and "T$_5$NO$_2$". The pure compound "T$_8$" exhibits the sequence [2]I-N-S_A-N-S_A. The high temperature S_A phase is a S_{A_d} and the low temperature S_A phase is a S_{A_2}. By addition of T$_5$NO$_2$ the reentrant nematic disappears.[3] The two S_A domains coalesce into one S_A phase. However, near the N-S_A transition, the phase is still a S_{A_d} phase and by decreasing the temperature it becomes gradually a S_{A_1} phase: in a previous study[4] we showed that the parallel relaxation ($E \| n$) is different in the two S_A phases and there is a coexistence of two relaxations in the reentrant nematic phase. This is in agreement with the different arrangements of the S_A phases.[5] However the disappearance of the reentrant nematic phase without appearance of a S_{A_d}-S_{A_1} transition indicates that we have the same thermodynamic phase. The question is whether the coexistence of the two relaxations is an intrinsic property of the reentrant nematic phase or not.

TABLE I

Materials used in the experiments

Acronym	Name	Structure and transition temperature (°C)
8OCB	4-cyano-4′-octyloxybiphenyl	 $\mathrm{N} \overset{67}{\text{—}} \mathrm{S_A}$
DB_7	4-cyanobenzoyloxybenzoate-4′-heptylphenyl	 $\mathrm{N} \overset{172}{\text{—}} \mathrm{S_{A_d}} \overset{168}{\text{—}} \mathrm{S_{A_2}}$
T_8	4-octyloxybenzoyloxy-4′-cyanostilbene	 $\mathrm{N} \overset{247}{\text{—}} \mathrm{S_A} \overset{139}{\text{—}} \mathrm{N} \overset{96}{\text{—}} \mathrm{S_A}$
T_5NO_2	4-pentyloxybenzoyloxy-4′-nitrostilbene	 $\mathrm{N} \overset{200}{\text{—}} \mathrm{S_A}$

2.2. Dielectric experiments

a. 8OCB-DB$_7$ system. In figure 1 we present the variation of $\epsilon_{\parallel}(T)$ and $\epsilon_{\perp}(T)$ at 20 kHz, below all the relaxation frequencies. In the nematic phase, the DC conduction begins to be important and the low frequency values of the quasi-static permittivity may be modified. Therefore we have verified that the values of $\epsilon_{\parallel}$ at 20 kHz are very near to the values we obtained by extrapolation of the Cole-Cole diagram (see below). As expected from a material with antiferroelectric order (at short range in the S_{A_d} phase, at long range in the S_{A_2} phase), $\epsilon_{\parallel}(T)$ decreases with T. $\epsilon_{\perp}(T)$ has small variations with T but it slightly increases when reaching the S_{A_2} phase. Such a behavior seems characteristic of the S_{A_2} phase since it was observed in other materials[6,10] in their S_{A_2} phase and it implies probably ferroelectric correlations of the perpendicular dipoles.

In figure 2, we show the Cole–Cole diagram at different temperatures: 110°C (S_{A_2}), 130°C (S_{A_2} near the S_{A_d}-S_{A_2} transition) and 150°C (S_{A_d}) corresponding to the $E \parallel n$ geometry. This diagram is not a semi-circle as it is frequently the case in the parallel relaxation.[7] As the temperature varies, one observes a change in the shape of the diagram. At low temperature it is the superposition of two relaxations

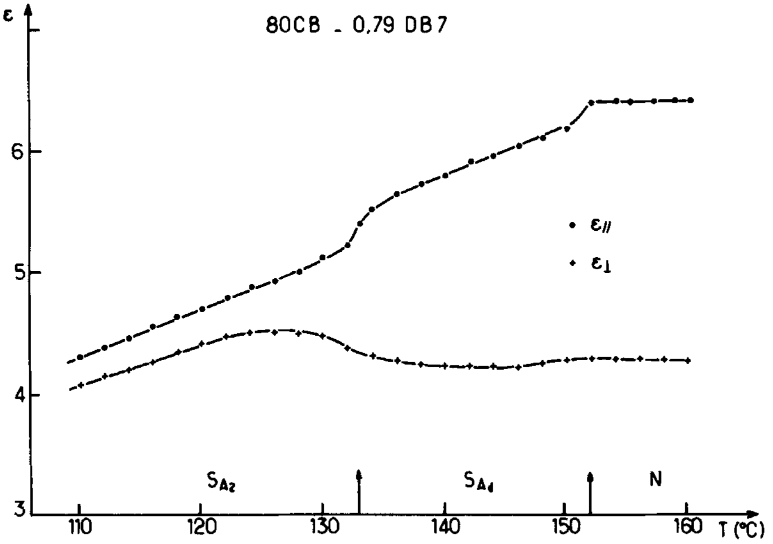


FIGURE 1 Temperature dependence of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ in the nematic, S_{A_d} and S_{A_2} phases of the 8OCB-0.79DB7 mixture (20 KHz).

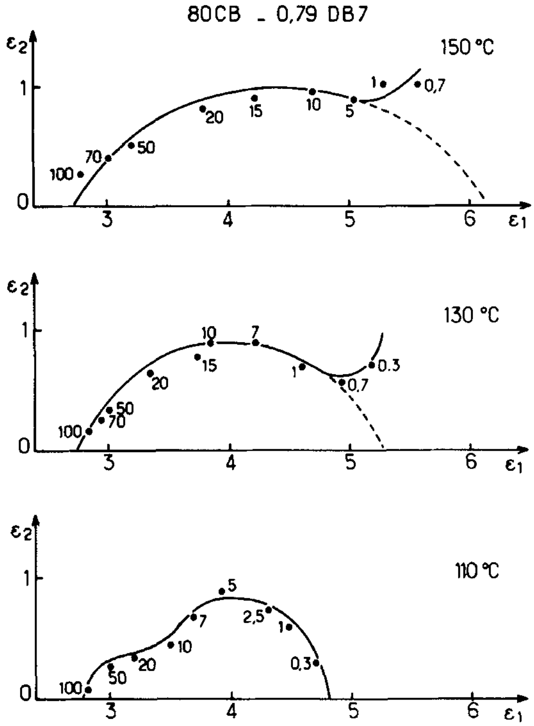


FIGURE 2 Cole-Cole diagrams at different temperatures for the 8OCB-0.79DB7 mixture. Frequencies in MHz.

but at higher temperature one has the feeling that it corresponds to a distribution of relaxation times.

In order to get a more quantitative analysis we fitted the experimental results with the two possibilities a) the relaxation spectrum is the sum of two Debye relaxations and the complex dielectric constant is given by:

$$\epsilon^* = \epsilon_\infty + \frac{\Delta_1}{1 + i\omega\tau_1} + \frac{\Delta_2}{1 + i\omega\tau_2} \tag{1}$$

b) the spectrum is a Cole-Cole distribution with:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \tag{2}$$

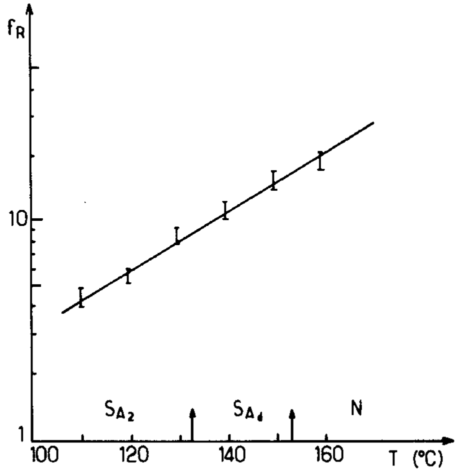


FIGURE 3 Thermal variation of the relaxation frequency f_R for the 8OCB-0.79DB7 mixture.

At 110°C the best fit is effectively given by eq (1) and we get the following values of the parameters: $\Delta_1 = 1,5$, $\tau_1 = 4.10^{-8}$s, $\Delta_2 = 0,5$, $\tau_2 = 3,8.10^{-9}$ s.

However for $T \geqslant 120$°C the best fit is given by the Cole–Cole distribution with the parameter α increasing with T (Fig. 4). In figure 3, we give the variation of the characteristic frequency $f_R = 1/2\pi\tau$ with T. One notes that there is no anomaly in f_R or α neither at the N-S_{A_d} transition nor at the S_{A_d}-S_{A_2} transition.

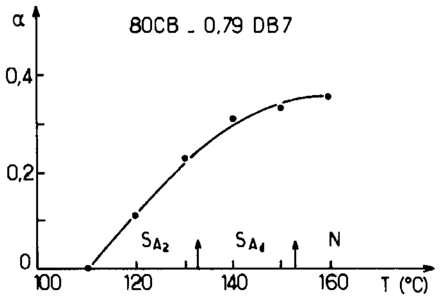


FIGURE 4 Distribution parameter α versus temperature for the 8OCB-0.79DB7 mixture.

b. T_8-T_5NO_2 system. We have studied three samples:

T_8-0,20 T_5NO_2 $\quad S_A \xrightarrow{97} N \xrightarrow{138} S_A \xrightarrow{198} N$

T_8-0,25 T_5NO_2 $\quad S_A \xrightarrow{182} N$

T_8-0,35 T_5NO_2 $\quad S_A \xrightarrow{171} N$

We choose these three concentrations for the following reasons: for $x = 0,20$ we have the same sequence as in the pure T_8; for $x = 0,35$ the reentrant phase has disappeared and with it the double reentrant phenomenon; and the concentration $x = 0,25$ is just that for which the intervall temperature of the reentrant nematic phase shrinks to zero. For the first mixture the dielectric properties are very similar to those of the pure T_8: we observed two relaxations in the $E \| n$ geometry each of them characteristic of one S_A phase and coexistence of both relaxations in the reentrant nematic phase. The fact that we have now a mixture of two compounds does not modify the dielectric behavior. Thus we can relate, as in the pure T_8, each relaxation to a particular short range order.

For $x = 0,35$ the measurements show only one relaxation mode. From the dependence of its characteristic frequency with the temperature this relaxation seems analogous to the LF relaxation of the samples exhibiting the two relaxations.

The important and very interesting result is that in the T_8-0,25T_5NO_2 mixture the dielectric measurement does reveal the presence of two relaxations although there is no reentrant nematic phase and only one S_A phase (Fig. 5). Indeed, at the higher temperature (148°C) one sees two relaxations. At lower temperature (140°C, 130°C, 120°C) there is always two relaxations but the LF relaxation amplitude increases, whereas the HF relaxation amplitude decreases. At 110°C only one relaxation remains.

The experiments on the pure compound T_8 and on the mixture T_8-0,35 T_5NO_2 show clearly that the appearance of two relaxations is not due to the existence of two different molecules but is rather related to the local structure. Thus we conclude that the coexistence of the two relaxations is not a phenomenon characteristic of the reentrant nematic phase, but appears to be related to the gradual passage from S_{A_d} to S_{A_1}.

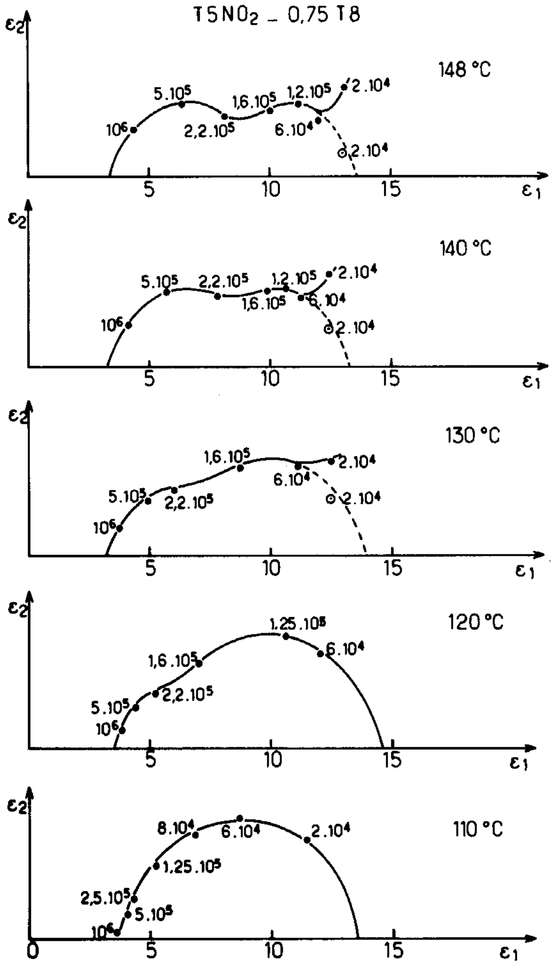


FIGURE 5 Cole–Cole diagrams at different temperatures for the T_8-0.25 T_5NO_2 mixture. Frequencies in Hz. "." point corrected from the conduction.

3. DISCUSSION

3.1. 8OCB-DB$_7$ system

From the results of the previous section we can say that in the nematic phase we have a distribution of relaxation times of the Cole–Cole type. When passing to the S_{A_d} phase this distribution becomes narrower. In the S_{A_2} phase this trend continues but a second relaxation appears until that at 110°C the spectrum consists in two Debye relaxations.

Our results are very different from those of Druon et al.[10] who reported dielectric measurements on a binary system which exhibits the N-S_{A_1}-$S_{\tilde{A}}$-S_{A_2} sequence. In particular when T increases they observed a narrowing of the distribution giving an almost pure Debye relaxation in the nematic phase. In the S_{A_2} phase their results may be also interpreted as the sum of two relaxations. In their interpretation the dielectric behavior reflects only the fact that there are two types of molecules, the structure influencing only the activation energy.

In our case we have a rather broad distribution of relaxation times which strongly depend on T and we think this can be interpreted in a quite different way than in ref.[10] A distribution of relaxation times implies that they are many possibilities of local order for the molecules. Each molecule *sees* a different surrounding. We have important fluctuations of the nematic order parameter.

One can ask if this situation is due a) to the fact we have a mixture of two compounds with different lengths (8OCB has two benzene rings but DB_7 three), b) to the nature of the S_{A_d} itself. We think that the answer to this two questions is *no* and we explain why:

— Zeller[7] studied the parallel relaxation in the mixture of two compounds with also different lengths (5CP with two benzene rings and 5CT with three). He observed two distinct relaxations related to the two components and not a distribution of relaxations.

— The parallel relaxation was measured in several short molecules with a S_{A_d} phase (8CB,[8] CBOOA[9]). It was always found that the relaxation is an almost perfect Debye relaxation.

We think that the relaxation distribution in the S_{A_d} phase must be related to the particular properties of the systems which exhibit two different modulations.[4,10] The condensed mode gives in S_{A_d} a layer thickness incommensurable with any of the two molecular lengths and the second one which will be condensed in the S_{A_2} phase but already exists as fluctuations. The coexistence of the two layering modulations is possible only if there is an important local disorder. In other words, on a very short scale the general structure is not perceptible. Only with a technique probing the rather long range order (like X-ray diffraction) this structure can be revealed. If one try to imagine a system of a S_{A_d} modulation with S_{A_2} islands (taking into account that the local order is not modified at this S_{A_d}-S_{A_2} transition), one sees that it is possible only with numerous *defects*. From the above discussion, it seems that in the 8OCB-DB_7 system we have to rule out a simple and naive picture of this type of S_{A_d}-S_{A_2} transition, that of dimers with the overlapping of molecules varying continuously from the S_{A_d} to the S_{A_2} phase.

Decreasing the temperature the number of defects decreases, the long range S_{A_2} bilayer order is allowed to establish, and it is essentially controlled by the DB_7 molecules. In such a case, the 80CB molecules cannot be *integrated* to the structure and tend to form a new local order. We believe that it is the origine of the second relaxation at 110°C (Fig. 2).

3.2. T_8-T_5NO_2 system

The S_{A_d}-S_{A_1}transition seems to be the most problematic transition between S_A phases from an experimental point of view.[1] In some cases a true transition is claimed. Nevertheless a more subtle experimental interpretation is suggested from the existence of an intermediate reentrant nematic phase.[1] In other cases the S_{A_d}-S_{A_1} passage is gradual and it is the situation of the mixture T_8-$0.25T_5NO_2$ taking into account microscopic observations,[3a] DSC measurements[3b] and X-ray analysis.[1] In particular the variation of the layer thickness d was measured as a function of T.[1] There is no anomaly in d, it decreases regularly with T but there is a slight increase of the slope around 140°C which is also the temperature where the two relaxations have approximately the same amplitude. Thus from our dielectric results we have to conclude that the same S_A phase with only one possible layering modulation can possess two short range local orders. The analogy with the fluid may be useful.[1] As in a liquid-gas transition one can have either a first order transition or gradual passage from one phase to another. Prost[11] has proposed a model to describe this behavior.

Moreover we note that the frequency relaxation of the high temperature side (S_{A_d} like phase) is higher than that of the low temperature side (S_{A_1} like phase). Accordingly to the interpretation of the relaxation mechanism proposed independently by Zeller[12] and by Diogo and Martins,[13] it means that the S_{A_d} phase has a larger free volume than that of the S_{A_1} phase. The S_{A_d} is a more open structure. May be the S_{A_d}-S_{A_1} transition is a process of densification coupled to a S_A antiferroelectric ordering. As above, we believe that the simple picture of dimers with variable overlapping has to be excluded but we can retain the general picture of a dimer. May be it is an useful picture since it is a local one. Two molecules may have the possibility to form a dimer with overlapped cores only if the free volume is big enough ie. at high temperature. At lower temperature, to fit the contraints due to thermal contraction, this kind of associations is more unlikely. Nevertheless, if one takes in account that the system still wants to achieve a stronger antiferroelectric ordering in S_{A_1} phase (as shown by previous static measurements[4]) a new possibility arises which is to form head to head dimers (S_{A_2}*-dimers*) in a certain quantity which goes increasing with lowering temperature. We recall that a S_{A_1} symmetry is not incompatible even with complete dimerization of that type, provided that there is a disorder of the dipoles inside the layers[13] (an additional transverse interaction seems necessary to lead to the long range S_{A_2} stacking[10]).

Although this interpretation is only speculative, it permits to understand the process of the passage from the S_{A_d} to the S_{A_1} phase.

4. CONCLUSION

The study of the short range order by means of dielectric relaxation permits to gain new insight about the difference between long range and short range order. In the case of the S_{A_d}-S_{A_2} transition we saw that the local order does not suffer drastic change although the general structure has passed from one to another type of S_A phase. We believe that is due to the very particular nature of these phases for which two different longitudinal modulations may appear. In the second case investigated there is no S_{A_d}-S_{A_1} phase transition (in the thermodynamic meaning) but the dielectric relaxation show the presence of two distinct types of local order: one of them disappears when we go toward one of the two phases.

This work gives an example how the local order, controled by the fluctuations, may be very different from the long range order in the S_A phases. Thus such a study recommends carefulness in the microscopic description of the peculiar phase transitions encountered in these chemical systems.

Acknowledgements

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