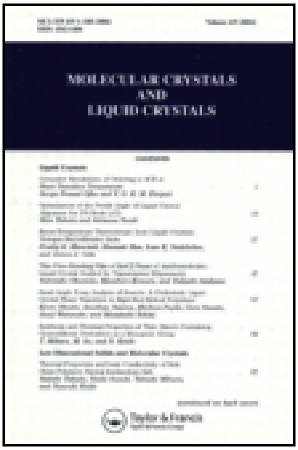

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Electro-Optical Studies on Monotropic Nematic–Smectic Phase Transitions

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The formation of nematic phases which are monotropic either with respect to a smectic A or to a smectic B phase was shown to be possible both for binary mixtures of low molar mass liquid crystals as well as for unmixed systems. The existence of these monotropic states was demonstrated experimentally by means of electro-optical Kerr effect studies.

The phase diagrams of such systems are characterized by the fact that the transition temperatures vary continuously in mixtures and in homologeous series as a function of the composition or of the chemical structure, respectively. This holds even if the nematic phase becomes monotropic with respect to a smectic phase.

Keywords: electro-optical studies, phase transitions, monotropic smectic B–nematic transition, monotropic smectic A–nematic transition, homologeous series, mixtures

I. INTRODUCTION

For molecular systems displaying multiple phase transitions it is a frequent observation that these transitions take place according to a well defined sequence.[1–3] Upon decreasing the temperature, starting from the isotropic phase, one observes the formation of phases with less and less symmetry. A typical sequence of transitions is the following: isotropic–nematic–smectic A–smectic B–crystalline state.

Exceptions from this general behavior have, however, been reported in the literature.[1–31] The occurrence of liquid crystalline phases which are monotropic with respect to the crystalline state is an example in case. It thus seems conceivable that other deviations from the generally observed sequence of phase transitions occur, for instance that a higher symmetrical liquid crystalline phase may be monotropic with respect to a lower symmetrical liquid crystalline state. This is the topic of this paper. Relying primarily on electro-optical relaxation studies it reports the occurrence of such a monotropic behavior of a nematic phase relative either to a smectic A or to a smectic B phase.

In our search for appropriate model systems we started conceptionally from the McMillan treatment of the transition into the smectic A phase either from the isotropic phase or from the nematic phase.[4] The lesson to learn from this treatment is that one should be able within a homologous series of substances to narrow the gap between the nematic and the smectic transition temperatures by a suitable variation of the length of the aliphatic part of the molecules at constant aromatic part, for instance. One should even be able to approach the case that the isotropic–nematic and isotropic–smectic A transition occur at the same temperature. We speculated that the nematic transition will become monotropic with respect to the smectic A transition if the chemical variation is continued along the same direction.

We thus looked for a homologous series of substances for which the smectic phase transition increases continuously with respect to the nematic phase transition as a function of the length of the aliphatic part of the molecule and for which the smectic transition is the only one which seems to take place for sufficiently long aliphatic parts. Based on these considerations we selected for our studies two different homologeous series and we studied the pure components as well as mixtures of appropriately selected members of such homologeous series.

One important requirement for the investigation of monotropic behavior in liquid crystalline phases is the selection of experimental techniques which are able to detect such monotropic phases. It is known from studies on liquid crystalline phases which are monotropic with respect to the crystalline state, that calorimetry is often the technique of choice.[1] On cooling one is able to observe the monotropic phase due to the vast differences between the supercooling which take place for liquid crystalline and crystalline phases. Now, obviously for the purpose of studying liquid crystalline phases which are monotropic with respect to another liquid crystalline phase this technique will fail in general, due to the small differences in the supercooling which can be achieved for liquid crystalline phases. (This topic will be considered in the appendix I.)

We will show in the following that the technique of electro-optical (Kerr-effect) studies is able to solve this particular problem. This technique is capable, as we will demonstrate below, to prove the existence of a nematic phase transition on the basis of experimental results which are obtained at temperatures up to 30°C above the actual phase transition temperature.

II. THE ELECTRO-OPTICAL KERR-EFFECT

This technique involves, in principle, the application of a static or dynamic electrical field to a fluid or solid phase and the detection of the optical birefringence resulting from the electric field.[5–9] The basic mechanism which gives rise to the occurrence of birefringence is a reorientational motion of anisotropic molecules. The Kerr law states that a linear relationship should exist between the induced birefringence and the square of the applied electrical field E:

$$\Delta n = \mathrm{B}\,\lambda\,\mathrm{E}^2$$

where B is the so-called Kerr constant. It is a function of the molecular optical and electrical anisotropy.[5-9] It depends, in addition, however, on the correlations which exist between the molecules which reorient due to the external electrical field.

This is obvious if one considers the dependence of the Kerr constant on the temperature.[6-14] The Kerr constant is found to increase slightly with decreasing temperature for normal isotropic fluids, like azobenzene or water. The reason is that the thermally induced disturbances decrease with decreasing temperature. On the other hand, one observes for the isotropic phase of fluids which possess a nematic phase at lower temperatures, that the Kerr constant increases very strongly with decreasing temperatures and even seems to diverge at a temperature close to the isotropic nematic phase transition temperature T_{ni}.[10-14]

This behavior was interpreted by de Gennes on the basis of a Landau theory of phase transitions.[3,15] The assumption is that the divergence of the Kerr constant results from a divergence of the correlation length for fluctuations of the orientational order and thus of the reorientational motions. The occurrence of the divergence is attributed to the existence of a critical supercooling temperature T^* which is located close to but below the first order phase transition T_{ni}. The isotropic phase becomes totally unstable with respect to the nematic phase below this temperature.

The basic step consists in expanding the free energy of the liquid crystalline material with respect to the orientational order parameter S:

$$F(T) = F_0(T) + (a(T)/2)S^2 - (b(T)/3)S^3 + (c(T)/4)S^4 + \dots$$

Taking the symmetry of the nematic phase into account one comes to the conclusion that the first order expansion term has to be zero and that the third order term has to be nonzero. In addition, the second order coefficient is expressed by:

$$a(T) = a_0\,(T - T^*)^{\gamma}; \qquad \gamma = 1 \text{ (mean field approx.)}$$

according to the Landau theory, where T^* corresponds to the temperature below which the isotropic phase becomes unstable and has to transform into the nematic phase. This results in the following expression for the dependence of the Kerr constant on the temperature:

$$B(T) \sim 1/a_0\,(T - T^*)$$

and thus

$$B(T)^{-1} \sim (T - T^*)$$

So it is obvious that one is, in general, able to predict the occurrence of a nematic transition from experimental results obtained within the isotropic phase at temperatures as far as 30°C above the actual transition temperature.

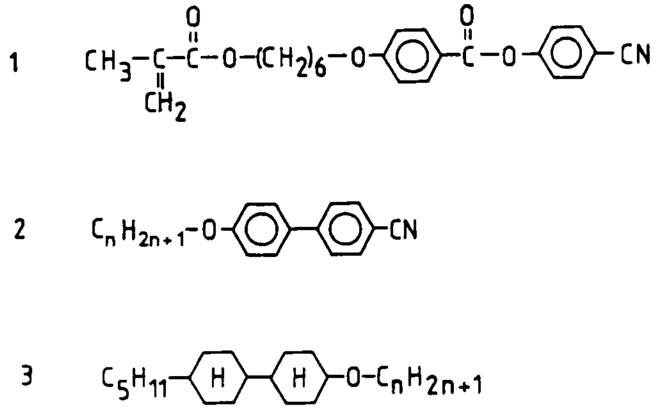

FIGURE 1 Structure of the model systems studied.

III. EXPERIMENTAL

The model systems considered in this paper are displayed in Figure 1. One of the systems, namely system 1, used for the electro-optical studies consisted of a monomer which has been used to build up oligomeric and polymeric side chain liquid crystal polymers. This system was obtained from Röhm GmbH, Darmstadt. We furthermore studied members of the homologeous series *n*OCB (system 2, Figure 1) with *n* varying from 7–12. These substances were provided by Merck & Co Darmstadt as well as by BDH, Great Britain. We finally studied members of the homologeous series CCH50*n* (system 3, Figure 1) with *n* varying between 1 and 4. The transition temperatures and the phases displayed by these systems will be discussed below.

The calorimetric investigations were performed with a DSC 4 (Perkin Elmer) calorimeter. The Kerr studies were done with an experimental set-up, constructed by us. Details of the set-up have been published previously.[12–14] In each of the experiments described below we checked whether the induced birefringence depended linearly on the square of the electric field (Kerr law), as required by theory.

IV. RESULTS AND DISCUSSIONS

a) A nematic crystalline monotropic transition

In order to demonstrate the usefulness of the electro-optical relaxation method we have investigated the phase behavior of the low molar mass system 1, which serves as a monomer for the synthesis of liquid crystalline side chain polymers. It is characterized by a crystalline state up to a temperature of 59°C as is obvious from the DSC trace displayed in Figure 2. On cooling down the sample one observes a strong supercooling of the isotropic melt by as much as 38 K even for a relatively moderate cooling rate of 20 K/min, as judged from the peak locations for cooling

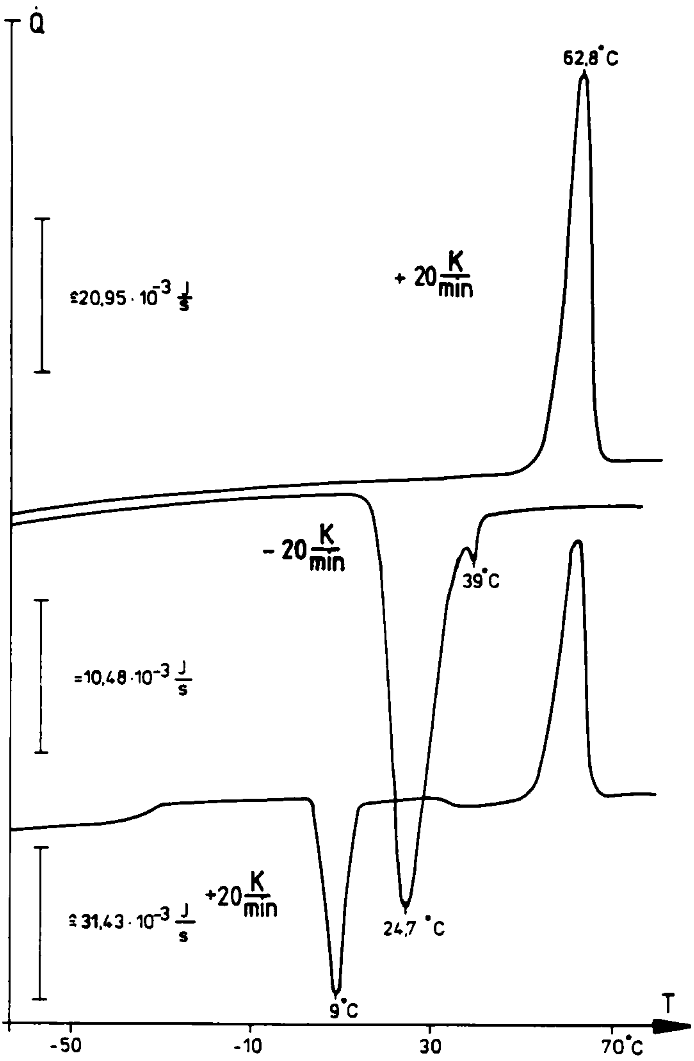

FIGURE 2 DSC heating and cooling traces obtained for model system 1.

and heating. The DSC trace obtained on cooling displays, in addition, a tiny exothermic peak at a temperature of about 39°C, indicative of the occurrence of another phase transition. The heating curves obtained for a rapidly quenched sample reveals that the quenching gives rise to the formation of a glassy state. This is obvious from the occurrence of a stepwise increase of the specific heat at a temeperature of −33°C (the glass transition temperature) as well as from the occurrence of a recrystallization exotherm above the glass transition. The DSC curve does, however, not contain any indication of another phase transition. These results point thus out that a monotropic phase exists, probably a liquid crystalline one.

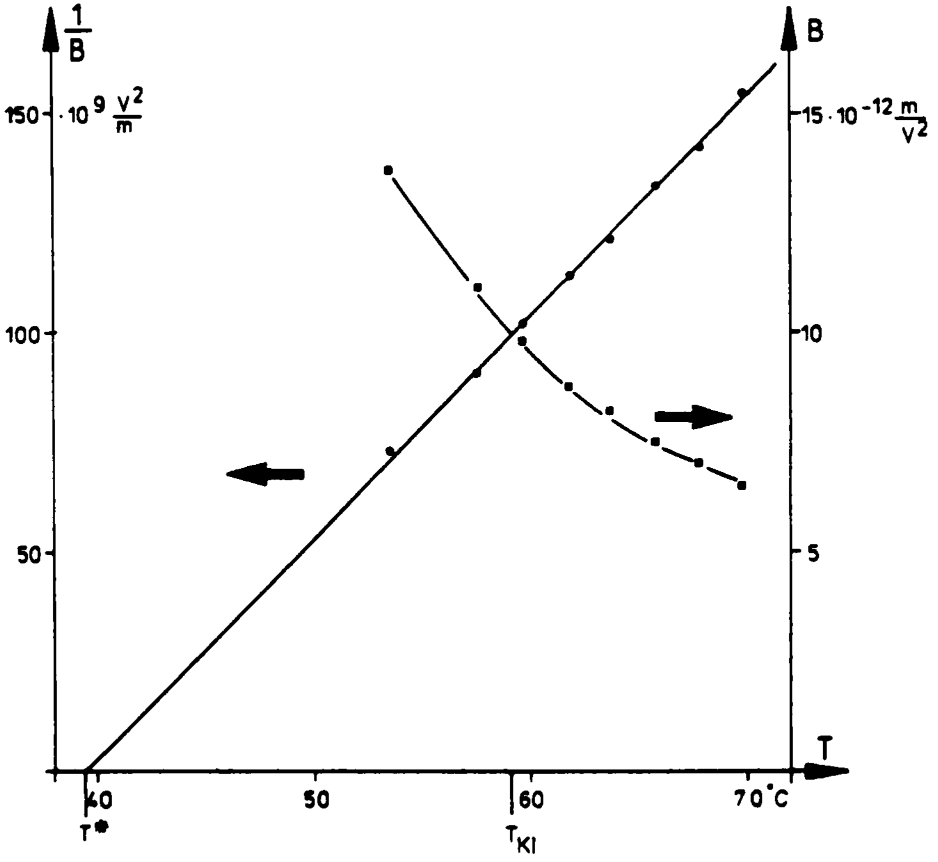

FIGURE 3 Kerr-effect results obtained for model system 1.

Figure 3 shows the results of the electro-optical Kerr-effect studies. It displays both the dependence of the Kerr constant B as well as of the reverse Kerr constant on the temperature within the isotropic fluid state. It is evident that the Kerr constant increases very strongly with decreasing temperature and tends to diverge at a characteristic temperature T*, which amounts to 39.4°C. This corresponds to the transition detected in the DSC cooling trace. When comparing the absolute values of the transition temperatures obtained from the DSC and the Kerr investigations one has to keep in mind that the difference between T* and the first order phase transition temperature T_{ni} is in general of the order of 1 K.

So we conclude from these studies that actually a nematic monotropic phase exists in the system studied here. This finding is in agreement with the observation, that oligomers and side chain liquid crystalline polymers derived from this monomer actually display an enantiotropic nematic phase. So these investigations have shown that the method works in predicting the onset of a nematic phase transition from results obtained well within the isotropic phase as much as 20 to 30 K above the actual phase transition.

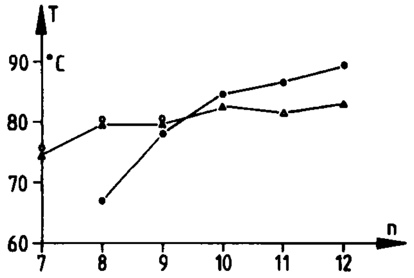

FIGURE 4 Transition temperatures for model system 2 (nOCB) as a function of n: (○) nematic-isotropic transition T_{ni}, (△) temperature T* and (●) smectic transition.

b) A nematic–smectic A monotropic behavior

We have recently reported experimental results of electro-optical Kerr-effect studies on a homologeous series of nOCBs, varying n from 7–12.[16] We were able to show that the nematic phase which is enantiotropic for n = 7–9 becomes monotropic with respect to a smectic A phase for n larger than 9. The transition temperatures of the two phases are displayed in Figure 4. The monotropic transition temperatures were obtained in this case from Kerr effect studies, as described above. Figure 5 gives an example for the dependence of the inverse of the Kerr constant B on the temperature for the case of nOCB with n = 10. The smectic transition evidently takes place 2.1 K above the characteristic temperature T*. It is gratifying to note that the monotropic nematic transition temperatures are located

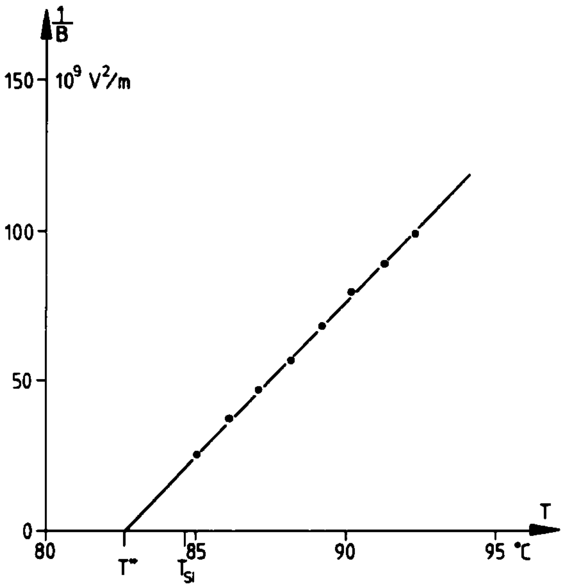

FIGURE 5 Kerr-effect results obtained for model system 2 (nOCB) for n = 10.

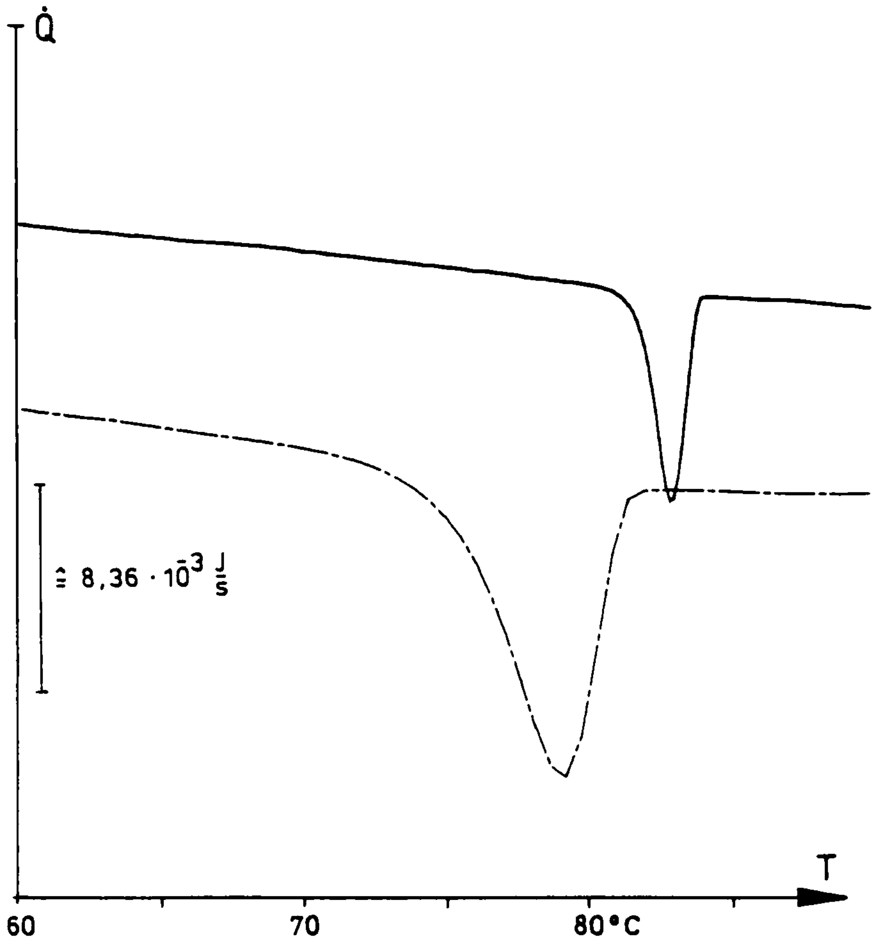

FIGURE 6 DSC-cooling traces obtained for model system 2 (*n*OCB) for $n = 10$: (———) cooling rate 10 K/min, (—·—) cooling rate 40 K/min.

exactly where one would expect them to be from a direct extrapolation of the data obtained for the enantiotropic nematic phases. This suggests that the smectic and the nematic phase transitions happen independently of each other. This point will be discussed later in more detail.

The DSC analysis failed in this particular case to give any indication of the existence of a monotropic phase for $n = 11$ and 12, for which the gap between the smectic and the nematic monotropic transition temperature is about 5–6 K. Very weak indications for the existence of the monotropic phase were available from polarizing microscopical studies as well as DSC-cooling studies (Figure 6) only for the case of $n = 10$, where the gap between the equilibrium transition temperatures is about 1 K. In the DSC cooling curve one observes a slight deviation from the smooth shape of the exotherm on the high temperature tail of the exotherm. Still larger cooling rates had the disadvantage that the transition was broadened and smeared out over a large temperature range. This evidently results both from the kinetics of the phase transition as well as from the limited heat conduction characteristic of the organic systems used here. Fast cooling gives, in addition rise to the formation of a inhomogeneous texture, containing both features characteristic of a nematic Schlieren texture and a smectic fan shaped texture.

c) A nematic–smectic B monotropic behavior

So far we have discussed the occurrence of a nematic phase which was either monotropic with respect to a crystalline or a disordered smectic (smectic A) phase. So it was of interest to look for homologeous series displaying an ordered smectic phase in addition to a nematic phase. Such a homologeous series is the CCH50*n* series. For $n = 1, 2$ it displays a nematic and at lower temperatures a smectic B phase and for the members of this series with $n = 3, 4$ it displays just a smectic B phase. The transition temperatures are shown in Figure 7. The DSC diagrams do not give any indications of the existence of a monotropic nematic phase for the members with $n = 3, 4$.

Figures 8 and 9 on the other hand clearly point out the existence of such a monotropic phase. It displays the results of Kerr effect studies for two members of this series, namely 501 (Figure 8) and 503 (Figure 9). It is apparent that the Kerr constants diverge in all cases. The characteristic temperatures T* obtained from these investigations allow us to determine also the first order phase transition temperatures for the monotropic phase. They are shown in Figure 7. The variation of the nematic transition temperature as a function of *n* is continuous and not

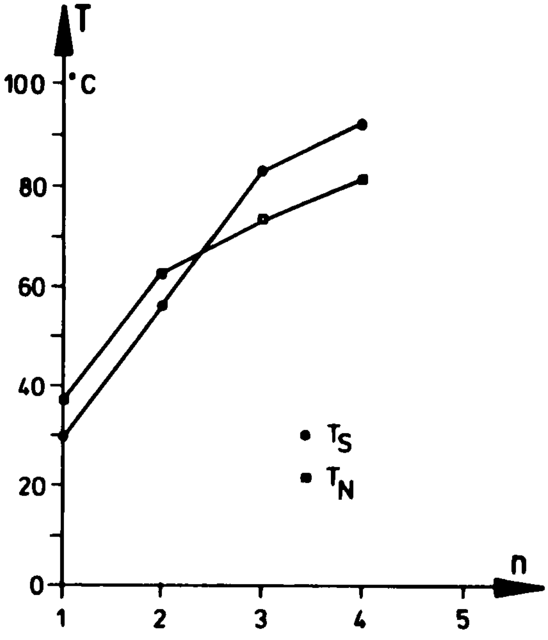

FIGURE 7 Transition temperatures for model system 3 (CCH 50*n*) as a function of *n*.

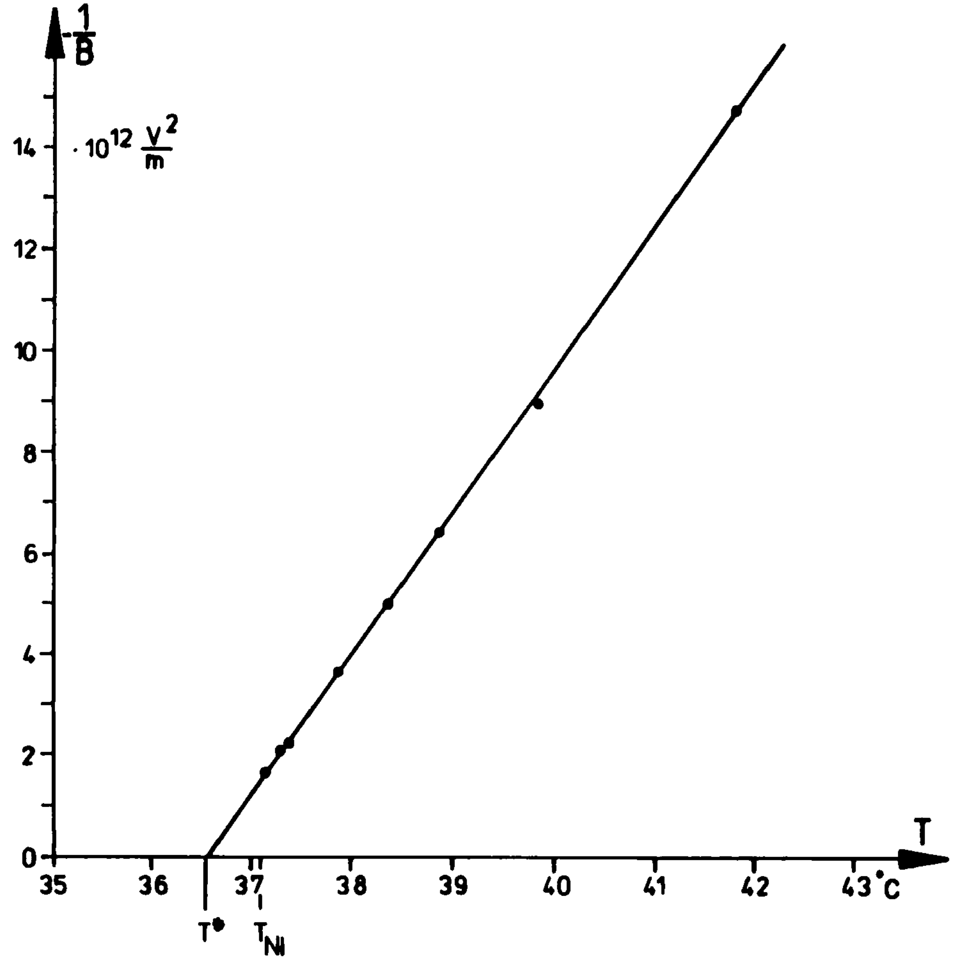

FIGURE 8 Kerr-effect results obtained for model system 3 (CCH 50*n*) for *n* = 1.

sensitive to the transition from an enantiotropic to a monotropic phase, in agreement with similar findings reported above.

d) A monotropic nematic–smectic B behavior in mixtures

So far we have investigated the transition of the nematic phase from an enantiotropic one to a monotropic one within a homologeous series as a function of the chemical structure of the molecules. Next we will consider the case of mixtures where one of the components displays an enantiotropic and the other a monotropic nematic phase in addition to a smectic B phase. We would like to know whether the phase diagram is characterized by continuous transition lines.

We selected for our studies two members of the CCH50*n* series namely one member with *n* = 1 and another member with *n* = 3. *n* is odd in both cases so that we do not have to take odd–even effects into account. The transition tem-

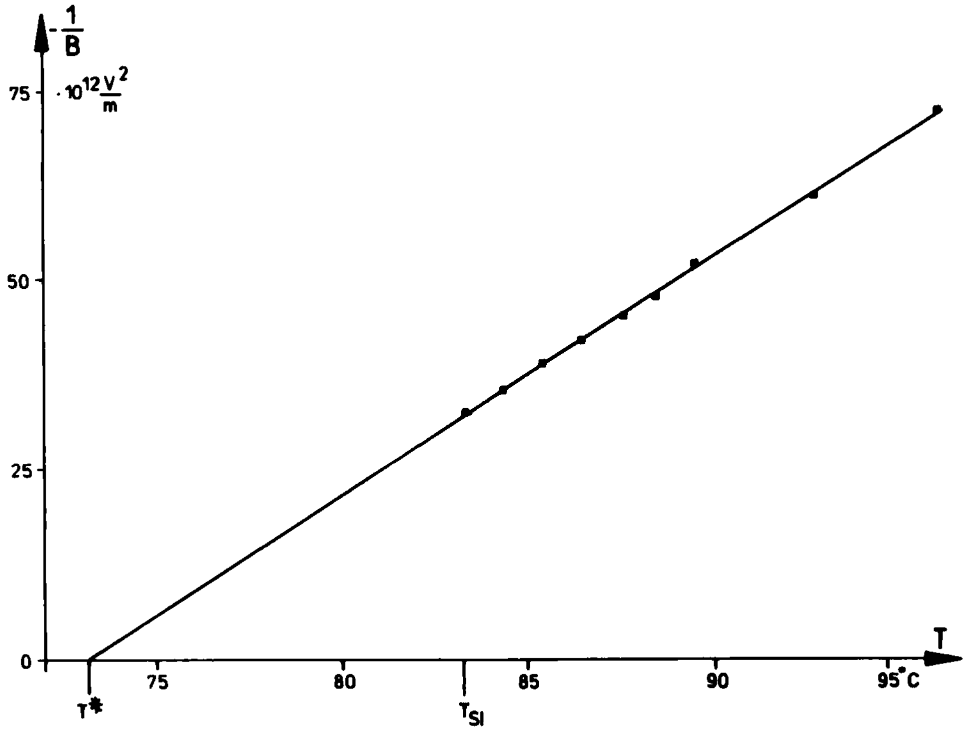

FIGURE 9 Kerr-effect results obtained for model system 3 (CCH 50*n*) for $n = 3$.

peratures of the two components are such that the nematic phase is enantiotropic with respect to the smectic phase for the system with $n = 1$ and monotropic for the case of $n = 3$.

The results of the electro-optical Kerr-effect studies are displayed in Figure 10. Again one observes a linear variation of the inverse of the Kerr constant with the temperature. These data allow to determine the characteristic temperatures T* and thus the first order phase transition temperatures T_{ni} ($T_{ni} - T^* = 0.7$ K). The results are shown in Figure 11 together with the results obtained from the calorimetric investigations. Both the smectic and the nematic phase transition temperatures are found to vary continuously as a function of the composition. The smectic and the nematic phase transition happen almost simultaneously for a composition of about 58 wt% CCH 503.

The nematic phase should be enantioptropic below 58 wt% and monotropic above this composition. The particular composition at which the two transition temperatures agree displays thus the interesting property that nematic pretransitions occur and diverge at the smectic B transition temperature T_{si}. Without prior knowledge on the total variation of the nematic and smectic transition temperatures with the composition, this would be a very disturbing result, indeed.

It should be mentioned that one is able in the case of mixtures to decrease the temperature gap between the smectic transition and the monotropic nematic tran-

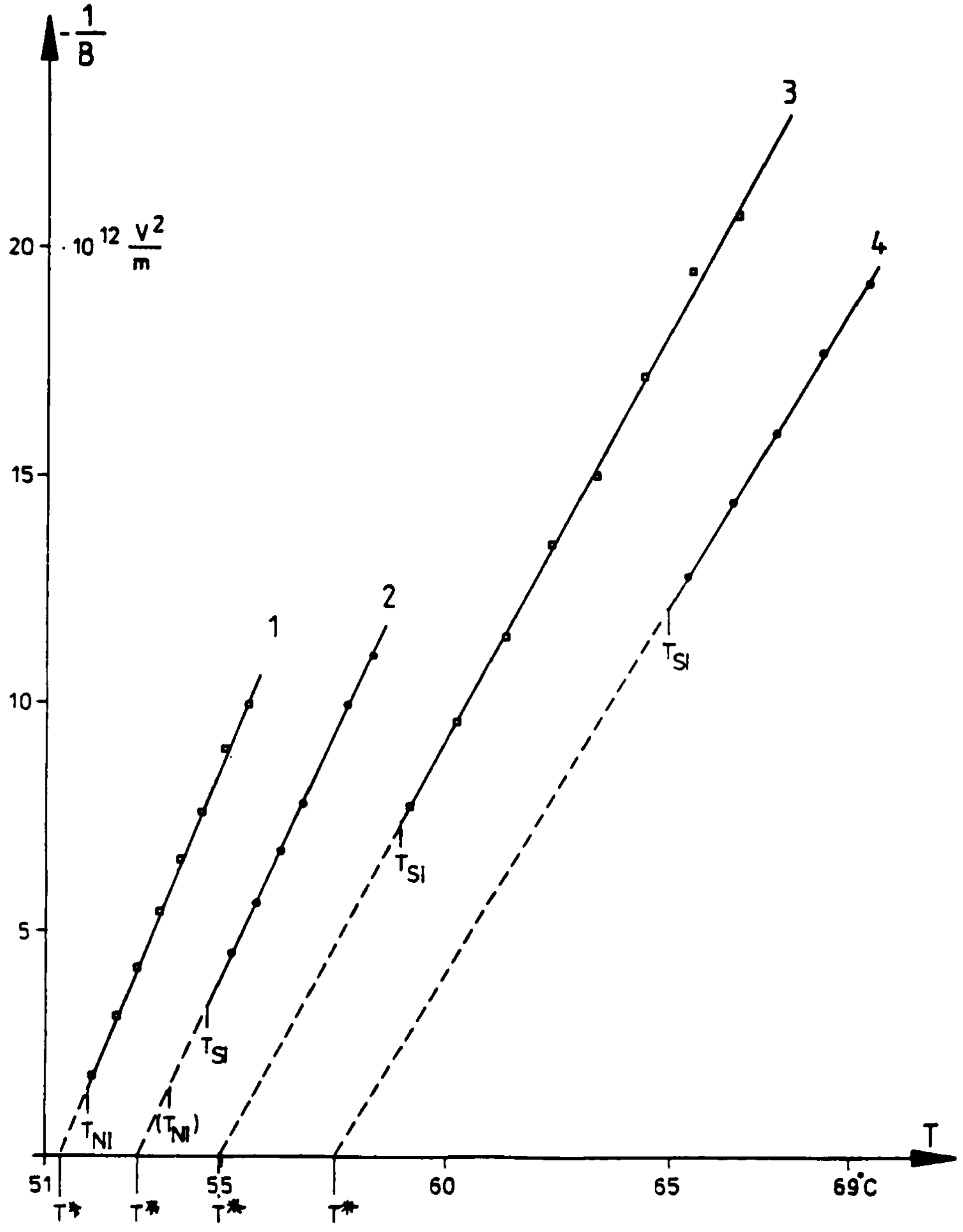

FIGURE 10 Kerr-effect results obtained for mixtures of CCH 501 and CCH 503: (1) 51.3 w%, (2) 60.3 w%, (3) 66.8 w% and (4) 75.4 w% CCH 503.

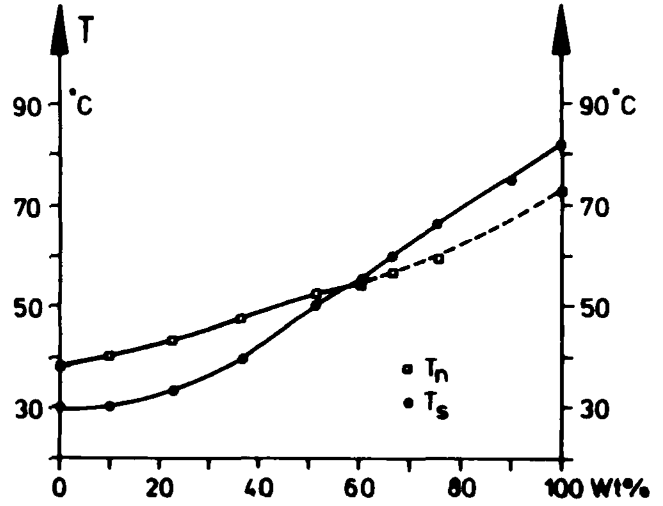

FIGURE 11 Transition temperatures obtained for the mixtures of CCH 501 and CCH 503 as a function of the wt% of CCH 503.

sition sufficiently to be able to detect this monotropic transition also by other means. We were able to observe, during cooling from the isotropic melt, by polarizing microscopical investigations first the onset of a smectic phase and suddenly at a temperature which is 0.9 K below the smectic isotropic phase transition, in addition, the formation of nematic droplets. These findings are in agreement with the electro-optical studies reported above as well as with the calorimetrical studies, the results of which are displayed in Figure 12a and b. Figure 12 contains heating and cooling cycles using a rate of 20 K/min (a) and 2 K/min (b). One is able to detect traces of the monotropic transition both on cooling and on heating. Cooling rates larger than 40 K/min failed to give any indication on the existence of the monotropic phase, due to the excessive broading of the exotherm.

CONCLUSIONS

The data discussed above have clearly shown that liquid crystalline phases may exist which are monotropic with respect to another liquid crystalline phase. The detection of such monotropic phases is not an easy task. The reason is that one cannot rely on sufficiently large differences in the supercooling which can be achieved with reasonable cooling rates, as it is the case for liquid crystalline phases which are monotropic with respect to the crystalline state (see appendix I). The electro-optical Kerr effect studies used by us have the advantage that they do not require the actual induction of the monotropic phase in order to detect it. They rely, rather, on the occurrence of pretransitional effects characteristic of such nematic phase transitions (and cholesteric ones for that matter).

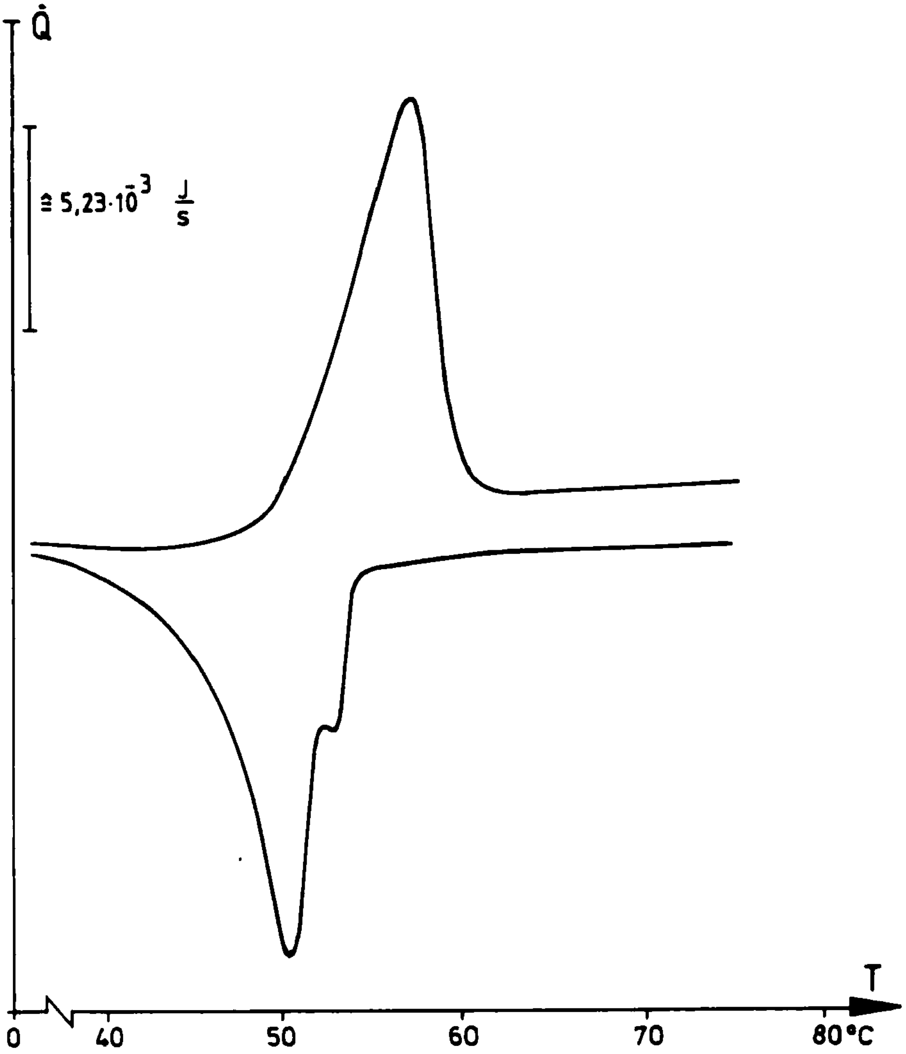

FIGURE 12a DSC heating and cooling traces obtained for mixture (2), see Figure 10. Heating and cooling rate 20 K/min.

The method, on the other hand, has the disadvantage that it is limited to the nematic and cholesteric phase. Other liquid crystalline phases such as the smectic A and smectic C phase, on the other hand, often also display pretransitional effects, which may be detected, for instance, by small angle X-ray scattering studies.[17] This would allow, for instance to study smectic A or C phases which are monotropic with respect to ordered smectic phases.

Coming back to the results reported above it is evident that they show both for series of homologeous systems as well as for mixtures that the two phase transformations considered take place independently of each other. Our experimental

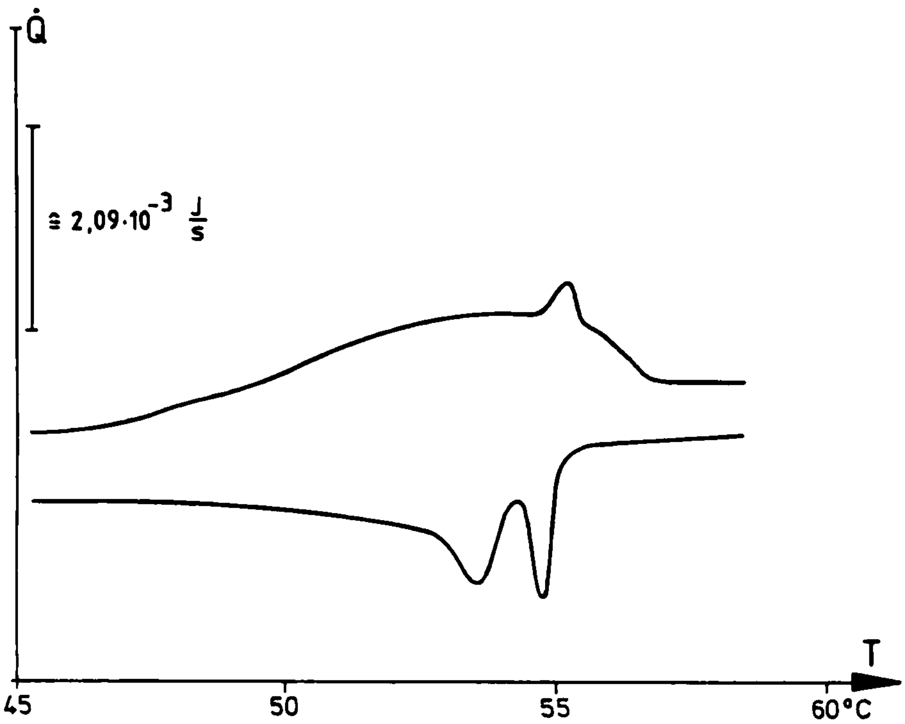

FIGURE 12b DSC heating and cooling traces obtained for mixture (2), see Figure 10. Heating and cooling rate 2 K/min.

results thus indicate that the formation of the potential minimum for the smectic A happens independently from the formation of the potential minimum characteristic of the metastable, monotropic nematic phase. Similar arguments can be used for the discussion of the independence of other liquid crystalline phase transitions.

APPENDIX I

DSC cooling studies have shown to be very effective in demonstrating the presence of liquid crystalline phases which are monotropic with respect to a crystalline phase. Since calorimetric studies are rather simple and since most laboratories possess some kind of calorimetry it seemed important to us to find out whether one is able to detect liquid crystalline phases which are monotropic with respect to other liquid crystalline phases by this technique. We performed therefore DSC investigations on the model systems for which we have demonstrated the existence of such monotropic phases by electric birefringence studies. The topic to be considered is whether different liquid crystalline phases are characterized by different degrees of supercooling.

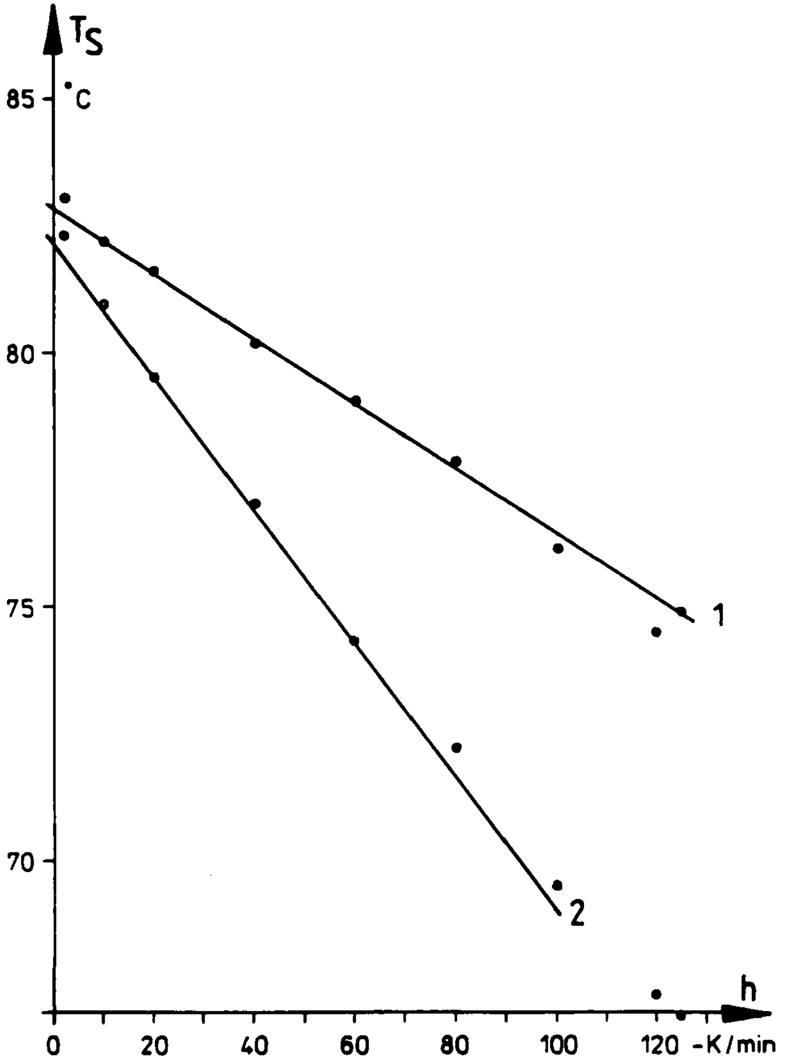

FIGURE 13 Dependence of the degree of supercooling of the smectic B model system CCH 503 on the cooling rate. 1) Location of the onset of the phase transition 2) Location of the peak maximum.

Figure 13 and Table I show the result on the dependence of the isotropic to nematic or to smectic phase transition on the cooling rate as obtained with a DSC 4 (Perkin Elmer). Displayed is the dependence of the onset of the phase transition as well as of the location of the peak maximum on the cooling rate. One obtains in both cases a degree of supercooling which increases almost linearly with increasing cooling rate. Rather large differences are observed between the variation of the onset of the transition and of the peak maximum. (Table I, Figure 13).

Our conclusion is that the variation of the onset reflects to a first approximation,

TABLE I

Dependence of the location of the onset of the phase transition and of the peak maximum on the cooling rate $-h$, as obtained by DSC calorimetry for the isotropic–nematic and the isotropic smectic B transition

Model system w% CCH 503 in CCH 501	m_n(min)	m_n(min)	m_s(min)	m_s(min)
0	0.056	0.106	0.064	0.106
51.3	0.057	0.092	0.092	0.119
monotropic 60.3	(0.056)	(0.125)	0.134	0.174
66.8			0.083	0.154
100.0			0.063	0.131

$m = -\Delta T/-h$, $-h$: cooling rate (K/min)

in principle the characteristic shift due to the apparatus and the heat conductivity of the sample, as far as the isotropic–nematic transition is concerned. The reasoning is that the isotropic phase becomes unstable at the temperature T*. The large mobility of the low molar mass systems does therefore in general not allow the occurrence of a large supercooling (in contrast to polymeric liquid crystals[18]), originating from kinetic effects related to the phase transition itself (note that cases are known where low molar mass liquid crystalline materials may also be supercooled appreciably,[19] for instance in the neighborhood of a glass transition). The kinetic control of the supercooling is manifested obviously in the shift of the peak maximum with the cooling rate.

Table I displays the effect of the cooling rate on the location both of the peak onset and of the peak maximum for the nematic and for the smectic transition in terms of the shift factor m defined by:

$$-\Delta T = -(T(h = 0) - T(h) = m\,h$$

where h is the heating rate in K/min. The data displayed were obtained for the model system 3 (CCH 50n) for the particular case of $n = 1$ and $n = 3$ and mixtures of the two components. The finding is that the onset and peak maximum positions shift differently and that the difference in the shift factor between the nematic and the smectic phase are extremely small, in most cases. This has to be taken as an indication that one will in most cases not be able to detect a monotropic phase transition unless it is as close as about 1 K below the enantiotropic phase transition. There may, of course, be larger supercooling for highly ordered smectic phases.

APPENDIX II

When discussing the results of our Kerr-relaxation studies on nematic phases which are monotropic with respect to smectic phases with Dr. Eidenschink, Merck & Co. and Prof. G. W. Gray it became apparent that experimental results on the pure

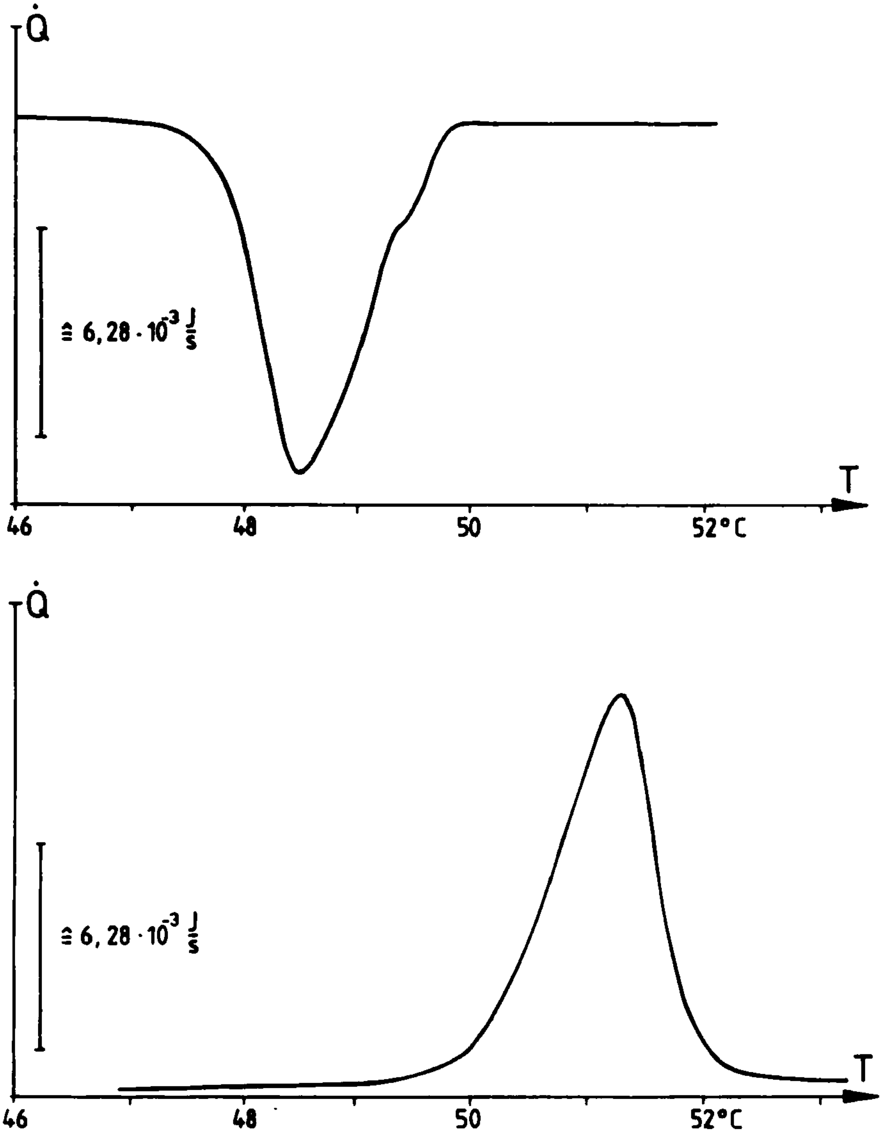

FIGURE 14 DSC heating and cooling curves obtained for the system CCH 402 (rate of heating and cooling: 5 K/min).

component CCH 402 of another homologeous series existed which might also be explained in terms of a nematic phase which is monotropic with respect to a smectic B phase. (The degree of supercooling is larger for a smectic B in comparison to the less ordered smectic A phase). Subsequent Kerr studies performed by us showed this assumption to be correct. By using DSC studies we were actually able to detect this monotropic transition (Figure 14). It gives rise to the occurrence of a shoulder on the high temperature side of the transition peak. Polarizing microscopical studies gave identical results.

Acknowledgements

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