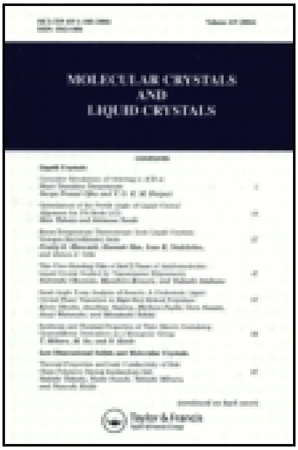


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

The Nature of Phase Transitions in Reentrant CBOBP: 4-Cyanobenzoyloxy-4′-Octylbenzoyloxy-p-Phenylene

April E. Hassel [a] & Gerald R. van Hecke [a]
[a] Department of Chemistry, Harvey Mudd College, Claremont, CA, 91711, USA

Version of record first published: 24 Sep 2006

To cite this article: April E. Hassel & Gerald R. van Hecke (1999): The Nature of Phase Transitions in Reentrant CBOBP: 4-Cyanobenzoyloxy-4′-Octylbenzoyloxy-p-Phenylene, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 330:1, 53-63

To link to this article: http://dx.doi.org/10.1080/10587259908025576

Mol. Cryst. Liq. Cryst., 1999, Vol. 330, pp. 53-63
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

The Nature of Phase Transitions in Reentrant CBOBP: 4-Cyanobenzoyloxy - 4'-Octylbenzoyloxy-*p*-Phenylene

APRIL E. HASSEL and GERALD R. VAN HECKE

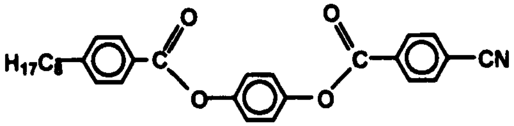
Department of Chemistry, Harvey Mudd College, Claremont, CA 91711 USA

The phase transitions of 4-cyanobenzoyloxy-4'-octylbenzoyloxy-*p*-phenylene (CBOBP) were proposed to be doubly reentrant with the phase sequence: crystal to S_{A1} to N to S_{Ad} to N to I. We have reinvestigated the thermal behavior of CBOBP in light of the theory of Navard and Haudin. According to the theory, the peak height of a differential scanning calorimetry DSC signal obtained at different heating rates may be used to determine whether the order of the phase transition is 1st or 2nd order. Our calorimetric data combined with previous characterization of the S_A phases by X-ray and NMR experiments show that the S_{A1} and the S_{Ad} are different phases which must not be considered thermodynamically the same phase. Thus, since only the N is reentrant, the term doubly reentrant incorrectly describes the phase behavior. We propose the phase behavior to be crystal to S_{A1} 1st order, S_{A1} to N 2nd order, N to S_{Ad} 1st order, S_{Ad} to N 1st order, and N to I 1st order.

Keywords: reentrant; phase transition; DSC; CBOBP; nematic; smectic

INTRODUCTION

Multiple reentrant phase behavior, though only first observed in 1979 by Hardouin *et al*[1], already has a rich literature. The first multiply reentrant compound, commonly called T8, 4-octyloxybenzoyloxy-4'-cyanostilbene, exhibits the phase sequence K-S_{A1}-N-S_{Ad}-N-I (K=crystal) suggesting that both the smectic A and the nematic phases are reentrant. However, in T8, the S_{A1} phase is metastable and only observed through a monotropic phase transition. The first truly enantiotropic reentrant compound exhibiting behavior similar to T8 was reported by Tinh and Destrade to be 4-cyanobenzoyloxy-4'-octylbenzoyl-*p*-phenylene, CBOBP[2].



4 - cyanobenzoyloxy - 4'- octylbenzoyloxy - *p* - phenylene

K-124°C-S_{A1}-140°C-N-160°C-S_{Ad}-185°C-N-236°C-I

The thermotropic phase sequence of CBOBP is the same as that of T8 except all the phase transitions are enantiotropic. These reentrant phase sequences have been the subject of several investigations seeking to discover the nature and origin of the reentrant transitions. Miyajima and Chiba used DTA to elucidate the thermal anomalies associated with the phases in T8 and CBOBP[3]. Van Hecke and Sorai investigated CBOBP by adiabatic calorimetry looking to demonstrate that S_{A1} and S_{Ad} were the same phase from a thermodynamic point of view[4]. Miyajima and Hosokawa used ^1H and ^2H NMR to better understand the factors differentiating the S_{A1} and S_{Ad} phases in CBOBP[5]. Evans-Lutterodt *et al* conducted detailed X-ray scattering and heat capacity studies on T8 also seeking not only to discover the factors differentiating the S_{A1} and S_{Ad} phases, but also to describe the order of the smectic A - nematic phase transitions[6].

The nature of the smectic A - nematic phase transition, whether it is first or second order, has been the subject of extensive studies on a large number of liquid crystalline compounds. In earlier work[4], our calorimetric results were interpretated from the point of view that all smectic A - nematic transitions were first order and that the S_{A1} and S_{Ad} phases were the same phase from a purely thermodynamic point of view. We have re-investigated CBOBP using the most sensitive differential scanning calorimeter now available and have analyzed the results using the theory of Navard and Haudin[7]. In light of our new analysis we offer a modified view of the reentrant phase behavior in CBOBP.

THEORY

In 1984 Navard and Haudin introduced a theory to predict the DSC signals expected for 1st and 2nd order phase transitions[7-10]. The essence of the theory lies in the analysis of the DSC signal peak heights expected for 1st and 2nd order phase transitions. The procedure is illustrated in Figure 1. Calorimetric data is obtained for various scan conditions and the signal peak heights are compared. A particularly convenient procedure is to conduct two DSC experiments whose heating rates differ by a factor of two. For the same mass, m, use the heating rates $dT/dt = T_p$ and $2T_p$.. In such a case the magnitude of the peak height ratio then suggests the order of the phase transition by:

1st Order: $$1 < \frac{h_2(2T_p,m)}{h_1(T_p,m)} < \sqrt{2}$$

2nd Order: $$\frac{h_2(2T_p,m)}{h_1(T_p,m)} = 2$$

Changing the sample mass by a factor of two for the same heating rate gives the same criterion but requires two samples. We have used the procedure of Navard and Haudin to examine the phase transitions of CBOBP by DSC.

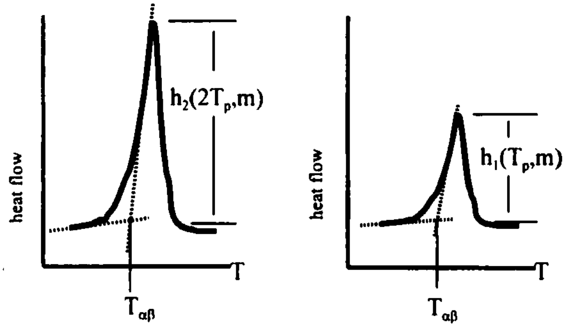


FIGURE 1. The procedure of Navard and Haudin[1].

EXPERIMENTAL

The CBOBP used was synthesized using the procedures detailed earlier[2-4].

A Perkin-Elmer Differential Scanning Calorimeter Model 7 was used to obtain the calorimetric data. Large sample sizes, ~ 12-17 mg, were used to enhance the detection of weak signals. Generally the Al sample pan was filled several times by melting sample into the pan. No lid was used on sample pan. A baseline correction was applied to the DSC data to correct for drift often observed at the high heat flow sensitivities necessary in these experiments to detect signals. The representative thermograms shown in Figures 2-4 are single examples of many scans. The peaks identified on the thermograms are those that consistently appear while any other apparent signals are noise. Heating rates varied from 5 to 20 °C/min with specific rates noted in Figures. The "fast" heating rates were used to take advantage of the increased DSC signal sensitivity at higher scan rates. Using such fast scan rates reduces the resolution of closely spaced temperature events but since all the transitions of interest here are quite separated in temperature, the gain in signal sensitivity was a good trade-off.

The DSC was additionally equipped with a high pressure cell. However, no effect of pressure on the DSC results was noticed up to 9 atm which was the limit of the measurements. Moreover, the thermograms were very noisy and essentially useless for the detection of small signals.

Polarized light microscopy was studied by means of an Olympus BH2 microscopy equipped with a Mettler FP52 hot stage.

RESULTS

Figure 2 is a thermogram for the full temperature range of CBOBP's phase transitions which covers 120 to 240 °C. Figure 3 shows a slightly narrower temperature range but with a highly magnified heat flow axis for increased sensitivity. Signals for the S_{A1} - N, N - S_{Ad}, and N - S_{Ad} transitions are readily identified from optical microscopy and literature reports. The signal at 150 °C

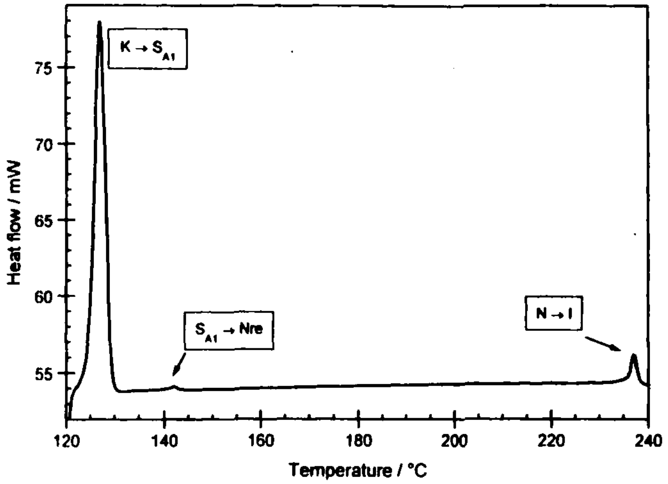


FIGURE 2. Thermogram of CBOBP full temperature range.

will be discussed below. Noteworthy is the observation that the heat flow signal for the S_{A1} - N transition at 136 °C is significantly larger than either of the N - S_{Ad}, or N - S_{Ad} signals at 156 °C and 185 °C. Figure 4 is a high resolution

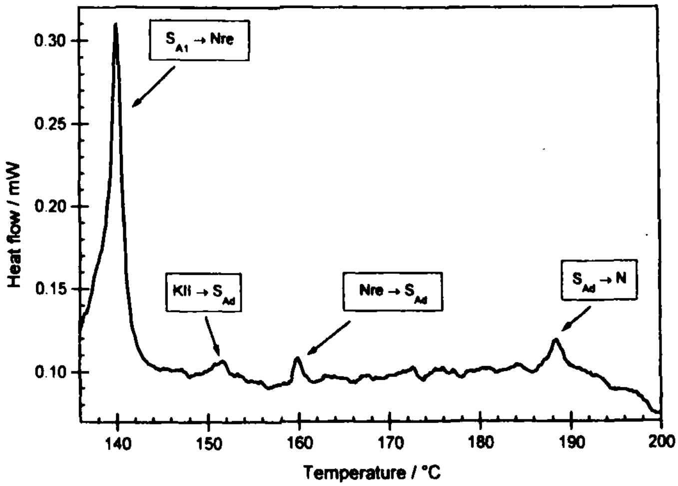


FIGURE 3. Thermogram of CBOBP high heat flow sensitivity.

thermogram for two heating rates, 10 °C and 20 °C, concentrating on the phase transitions around 135 °C and 156 °C which are the S_{A1} - N and the N - S_{Ad} transitions. The peak height analyses for several experiments using different masses and heating rates are collected in Table 1. The reported uncertainties were obtained by estimating the minimum and maximum height values for each measurement and then propagating the error in the ratio.

DISCUSSION

From the results presented in Table 1, the S_{A1} - N transition can be described as 2nd order while the N - S_{Ad} transition is 1st order. Qualitatively 1st and 2nd order phase transitions can be described by the isobaric Gibbs potential - temperature phase diagrams shown in Figure 5. Figure 5a presents typical 1st order behavior as the intersection of G - T lines for each phase with the intersection defining the transition temperature. Figure 5b presents the G - T lines for a 2nd order

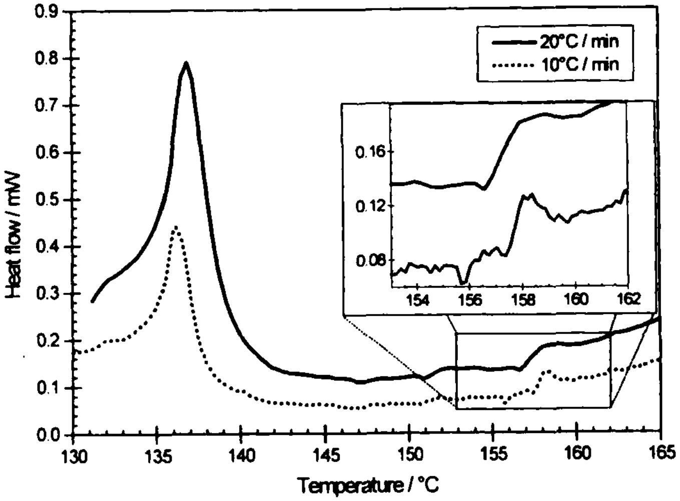


FIGURE 4. Thermograms of CBOBP at 20 and 10 °C/min .

TABLE I Peak height analyses for variable heating rates and sample sizes of CBOBP

Sample (mg)	Height ratio 135 °C	2nd order ratio	Height ratio 156 °C	1st order ratio
12.927	1.67 ± 0.13	2.0	1.15 ± 0.12	1.1 - 1.4
12.927	1.84 ± 0.11		0.79 ± 0.14	
9.468	1.82 ± 0.12		1.30 ± 0.16	
17.537	1.78 ± 0.08		1.20 ± 0.15	

transition following Stanley[11]. Recalling that the slope of a G - T line is -S, (a), the 1st order transition shows a discontinuity in the entropy at the phase transition, while (b) the 2nd order shows the entropy change to be continuous. Two important observational facts can be explained by reference to these Figures. One, 1st order transitions can exhibit supercooling (and superheating).

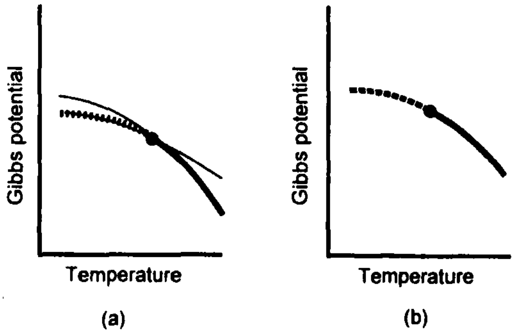


FIGURE 5. Gibbs potential versus temperature phase diagrams for pure substances undergoing a 1st order phase transition (a) and a 2nd order phase transition (b).

Two, 2nd order transitions cannot exhibit supercooling (or superheating). In our DSC studies on CBOBP, we never observed supercooling of the 135 °C peak but did often observe supercooling of the 156 °C transition. The total of our results can be summarized in Figure 6 which is a complete isobaric G - T diagram for CBOBP. All the phase transitions for CBOBP shown on the diagram result from G line intersections except for the 2nd order S_{A1} - N transition which is only noted by a dot on a continuous line between the S_{A1} and N phases. Our new interpretation of the phase behavior is now:

$$K \text{ -(1st)- } S_{A1} \text{ -(2nd)- } N \text{ -(1st)- } S_{Ad} \text{ -(1st)- } N \text{ -(1st)- } I$$

For a phase to be reentrant from a thermodynamic viewpoint, its G - T line must be continuous and intersect the G - T line of another phase twice. For example the N G - T line crosses the S_{Ad} G - T line twice in Figure 6. For two phases to be doubly reentrant, their G - T lines have to intersect three times as shown in Figure 7 for the S_A G - T line and N G - T line. Figure 7 is the G - T diagram that would be expected if the S_A and N phases were doubly reentrant. The three intersections then define the regions labeled $S_A(S_{A1})$, N, $S_A(S_{Ad})$, and

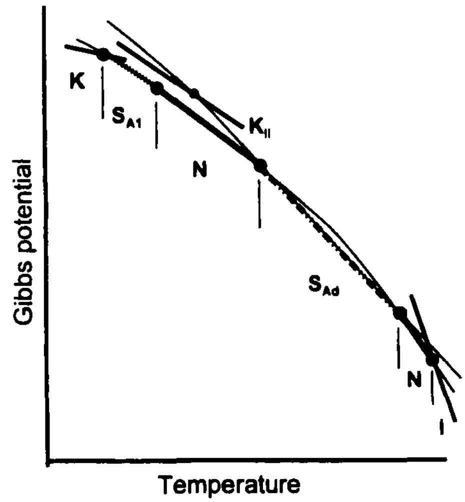


FIGURE 6. Gibbs potential versus temperature phase diagram for CBOBP for the S_{A1}-N phase transition 2nd order and the N phase reentrant.

N. If the S_A phase is doubly reentrant and the S_{A1}-N transition is 2nd order, then the "N-S_{Ad}" and "S_{Ad}-N" transitions would also have to be 2nd order or else some other G - T phase line would cross the S_{A1} N S_{Ad} N line yielding an as yet undetected phase transition. Besides the unlikely occurrence of three sequential 2nd order phase transitions, we have shown that the N-S_{Ad} phase transition is 1st order which means the N G - T line must be distinct from that of the S_{A1} phase. Thus S_{A1} and S_{Ad} are thermodynamically different phases and not reentrant.

In Figure 3 the signal at ~ 150 °C appears frequently in replicate experiments but not always. It is not considered to be noise but a metastable crystal to S_{Ad} transition. The G - T line labeled K_{II} is drawn to intersect the S_{Ad} G - T line and explain the transition. The random occurrence of the transition depends on the sample history. Supercooling the S_{Ad} phase allows for a fraction of the room

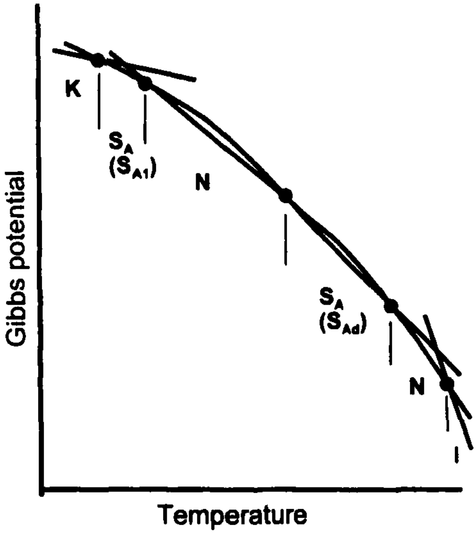


FIGURE 7. Gibbs potential versus temperature phase diagram for CBOBP for all transitions 1st order and both the S_A and N phases reentrant.

temperature crystalline sample to be K_{II}. The thermogram shown in Figure 3 actually results from heating a mixture of K and K_{II}. Once the K_{II} portion of the sample melts to S_{Ad}, the observed phase transitions follow the same G - T sequence as starting from K.

Our evidence, along with the NMR and X-ray studies, strongly suggests that S_{A1} and S_{Ad} are structurally and thermodynamically distinct phases. Thus only the N phase is reentrant and while CBOBP is a fascinating compound, it is not doubly reentrant.

CONCLUSIONS

- The theory of Navard and Haudin is easy to apply and has been neglected too long.

- The S_{A1} - N transition is 2nd order in agreement with others[5, 6].
- CBOBP is not a doubly reentrant compound since the S_{A1} and S_{Ad} phases are distinct. Only the N phase is reentrant.
- At least two crystal forms exist, one of which is always metastable with respect to the room temperature crystal. The metastable K_{II} undergoes an enantiotropic phase transition to S_{Ad}.
- Use of large, ~ 12-17 mg, size samples greatly aids the detection of weak DSC signals..

Acknowledgments

The National Science Foundation funds from the Instructional Laboratory Improvement grant 9551572 to purchase the DSC 7 are gratefully acknowledged. The authors also thank the Research Corporation, the Camille and Henry Dreyfus Foundation, and the Harvey Mudd College Research Committee for additional funding. These remarks cannot be concluded without acknowledging the contributions and leadership of the late Christian Destrade to the field of reentrant liquid crystals.

References

[1] F. Hardouin, G. Sigaud. M.F. Achard, and H. Gasparoux, *Physics Lettr. A.*, **71**, 347; (1979), *Solid St. Commun.*, **30**, 265 (1979).
[2] N.H. Tinh, and C. Destrade, *Nouv. J. Chim.*, **5**, 337 (1981).
[3] S. Miyajima. and T. Chiba, *J. phys. Soc. Jap.*, **54**, 2793 (1985).
[4] G.R. Van Hecke, and M. Sorai, *Liq. Cryst.*, **12**, 503 (1982).
[5] S. Miyajima, and T. Hosokawa, *Phys. Rev. B*, **52**, 4060 (1995).
[6] K.W. Evans-Lutterodt, J.W. Chung, B.M. Ocko, R.J. Birgeneau, E. Chin, J. Goodby, and N.H. Tinh, *Phys. Rev. A*, **36**, 1387 (1987).
[7] P. Navard, and J.M. Haudin, *J. Thermal Anal.*, **29**, 405 (1984).
[8] P. Navard, and J.M. Haudin, *J. Thermal Anal.*, **29**, 415 (1984).
[9] P. Navard, and R. Cox, *Mol. Cryst. Liq. Cryst. (Letters)*, **102**, 261 (1984).
[10] P. Navard, and R. Cox, *Mol. Cryst. Liq. Cryst. (Letters)*, **102**, 265 (1984).
[11] Stanley, H.E., *Introduction to Phase Transitions and Critical Phenomena*, (Oxford University Press, Oxford 1971) Chap. 2, p. 32.