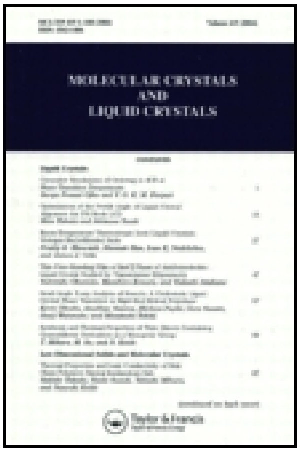

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Condis Crystals of Small Molecules II. The Polymorphs of N, N'-bis(4-n-octyloxybenzal)-1,4-phenylenediamine (OOBPD)

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Condis Crystals of Small Molecules II. The Polymorphs of N,N′-bis(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD)

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The high temperature transitions between 300 and 500 K of N,N′-bis(4-*n*-octyloxybenzal)-1,4-phenylenediamine are analyzed by scanning calorimetry, optical microscopy, light transmission measurement, thermomechanical analysis and X-ray diffraction. The prior assignment of mesophase structure K3/385.2/K2/388.2/K1/415.3/H′/422.2/G′/426.9/I/436.6/C/475.4/N/505.4/Melt (temperatures in K) has been extended by the suggestion that K1 to K3 are conformationally disordered crystals.

1. INTRODUCTION

N-N′-bis(4-*n*-octyloxybenzal)-1,4-phenylenediamine (OOBPD) has been known for some time to be an example of a liquid-crystal-forming substance of many polymorphs. It was first made by Gray et al.[1] together with the 1 to 18 carbon alkoxy-homologues of the series. Garn[2] and Arora et al.[3] showed the first thermal analyses. A similar example and the chemical formula of the octyloxy-homologue are shown in Figure 1. Five smectic and one nematic liquid crystal phase were originally designated and separated from the crystal phases by their negligible supercooling at the transitions.[3] Petrie et al.,[4]

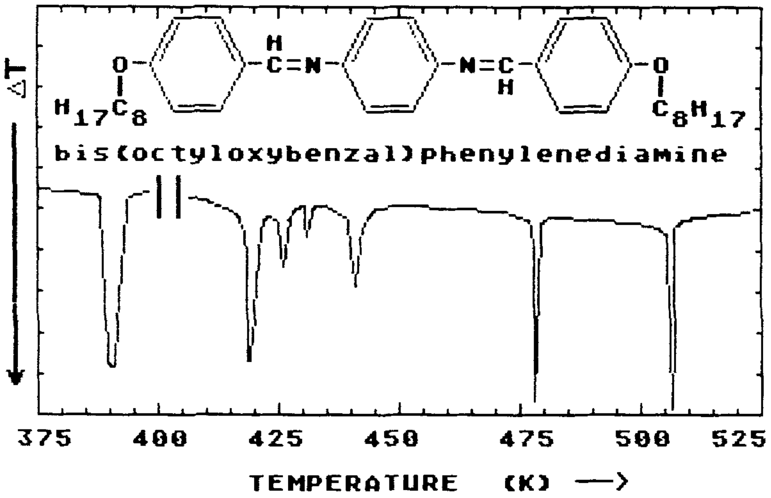


FIGURE 1 Typical DSC-traces of OOBPD crystals heated at 5 K/min (Perkin-Elmer DSC 2). For transition parameters see Table I. At the double-line, the sensitivity is increased by a factor 2. The lowest temperature transition is K3 to K1 with a combined ΔH of 17.6 kJ/mol.

Spratte and Schneider[5] and Barrall et al.[6] provided calorimetric and volumetric information on OOBPD. A critically selected list of data is presented in Table I. It differs somewhat from the recent data

TABLE I

Transition parameters of OOBPD

Phase:	Transition T:[a] (°C)	Transition T:[a] (K)	Enthalpy:[b] (kJ/mol)	Entropy:[c] [J/(K mol)]	Volume Change:[d] (cm^3/mol)
K3					
K2	112.0	385.2	10.5	27.3	8.2
K1	115.0	388.2[e]	7.1	18.3	9.2
H'	142.2	415.3	6.7	16.1	4.3
G'	149.0	422.2	2.1	5.0	1.0
I	153.7	426.9	0.4	0.9	0.4
C	163.4	436.6	3.2	7.4	2.2
N	202.2	475.4	3.6	7.6	2.1
Melt	232.2	505.4	2.3	4.6	1.8

[a] Values of Refs. 10, 11; are in agreement with our DSC experiments on heating at 1 K/min within −0.15 ± 0.9 K.

[b] Values of Refs. 4–6; in agreement with our DSC experiments on heating.

[c] Calculated from columns 2 and 3.

[d] Data of Ref. 5 in qualitative agreement with Figure 5.

[e] Since we could not separate the K3-K2-K1 transitions the listed value is from Refs. 10 and 11.

compilation of Beguin et al.[7] who quoted only one of the above references. The classification of the various polymorphs went through a number of changes and are now identified as given in Table I.[8–12] Only four of the polymorphs are smectic phases, while earlier as many as six were designated as smectic.[6]

In this paper we report on microscopy, X-ray diffraction, dilatometry, and scanning calorimetry. An early report was given at the 12th NATAS meeting.[13] In particular, we want to address the question which of the polymorphic phases can be classified as a conformationally disordered (condis) phase.[14] This is the second publication in the series on condis crystals of small molecules.[15]

2. EXPERIMENTAL

The optical microscopy and thermal analysis were carried out with the Mettler FP800 Thermosystem and a Wild-Leitz Orthoplan microscope.[13] The FP84 hotstage was connected through the FP80 control unit and a RS232 interface to a personal computer. A video camera and recorder preserved both, field of view and thermal analysis plots. Light-intensity was continuously monitored.

Dilatometry was performed with a thermomechanical analyzer of type Mettler 3000/TMA 40. The specially adapted dilatometer head is shown in Figure 2.

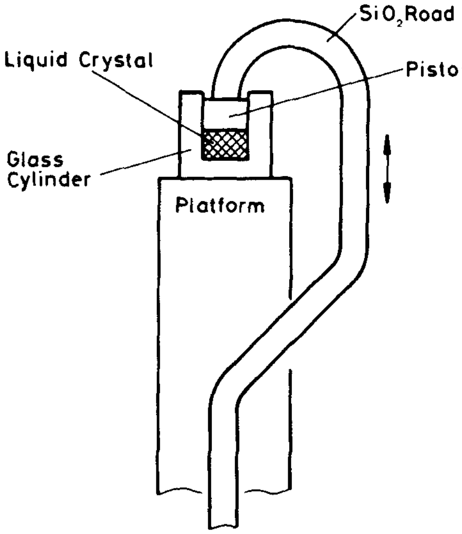


FIGURE 2 Drawing of the dilatometer head of the Thermochemical Analyzer.

X-ray diffraction was carried out as a function of temperature using a Guinier-Simon Camera with CuKα-radiation.

The OOBPD was purchased from the Eastman Kodak Company and used without further purification (for DSC-trace see Figure 1).

DSC data were taken at 1 to 10 K/min heating rate. All transition data listed and discussed are extrapolated to the onset of the transition, using the straightline-portion of the transition peak making use of the 1 K/min experiments.

3. RESULTS

Selected micrographs of the heating and cooling sequence of OOBPD are shown in Figure 3. They are representative of the nematic phase (3–5), the various smectic phases (1, 2, and 6–8) and the crystal phases (9–12). A video-film was made of these sequences and shown at the 12th NATAS meeting.[13] Figure 4 shows a comparison of the light transmission on heating and cooling.

Figure 5 displays the thermomechanical analysis data and Figure 6 the X-ray data observed on cooling the sample with crystal morphologies as displayed in Figure 3 (micrographs 5–12).

Table II gives a listing of the various transition temperatures on cooling as taken from the original traces.

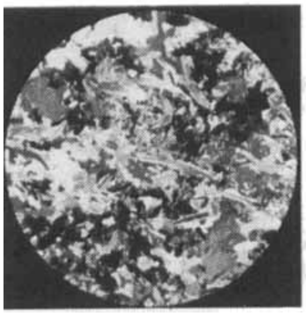
4. DISCUSSION

Purely on the magnitude of the heats and entropies of transition the assignments as given in Table I appear likely. Adding all transition entropies from K1 to Melt results in 41.6 J/(K mol). According to a survey of entropies of fusion, this falls into the range of values observed for a group of molecules of single, rigid, nonspherical motifs. The average of 27 arbitrarily chosen molecules ranging in complexity from molecules like Cl_2 and CO_2 to diphenyl and phenanthrene is 36 ± 10 J/(K mol).[16] This match of transition entropy allows, in addition, the conclusion that over this path from K1 to Melt only *one* motif, the mesogen, achieves translational and rotational freedom. For the remaining 16 CH_2- and -CH_3 groups, conformational freedom must have existed already in state K1. Judging from paraffins and macromolecules[16] these 16 motifs would need each 9.5 ± 2 J/(K mol) to go from a well-ordered crystal to the melt. The K3 to K1 transition entropies yield only 45.6 J/(K mol) instead of the expected

152 J/(K mol). One must thus conclude that *all* three crystal phases K3, K2, and K1 are mesophases of the condis type.[14,15] An increasing number of paraffinic groups becomes mobile as the temperature increases and K1 must have practically full conformational freedom for the alkoxy groups, while the mesogen is still fully rigid. The analysis of the thermodynamic data supports thus two points made in the introduction to this series of publication.[15] First, the liquid crystals, nematic as well as smectic, have a large degree of conformational freedom in the flexible parts of their molecules. Second, the existence range of liquid crystals is not necessarily limited by rigid, fully-ordered crystals, but may lead to condis crystals, which, in turn, may show polymorphism. It would be of interest to follow the OOBPD to absolute zero and derive a full characterization through heat capacity as well as transition analysis. One would expect further transitions at low temperatures or a CD-glass transition. Direct study of the paraffinic mobility through solid-state NMR would also be of interest.

The cooling experiments displayed in Figures 3 to 6 are interpreted next. The actual transition temperatures are collected in Table II. Most straight-forward is the interpretation of the DSC-data which show a reverse trace of Figure 1 with clearly indicated supercoolings from the heating curves (last column of Table II). As usual, the cooling traces show the transitions as somewhat narrower peaks and, in the present case, the transitions K1 to K2 and K2 to K3 are always separated on cooling, but often not on heating (see Figure 1). The assignments of the phases is done strictly on the correspondence of the heats of transition with the heating trace of Figure 1. The thermomechanic analysis (Figure 5) and the light transmission measurement (Figure 4) correspond well with the DSC data in Table II. It is of interest to note that on cooling the change to the nematic texture N (picture 5 of Figure 3), to the smectic texture C (picture 6 of Figure 3), to the smectic texture G′–H′ (picture 8 of Figure 3) and to the condis crystals K_2–K_3 (pictures 11 and 12 of Figure 3) are the four large events for microscopy and light transmission (Figure 4). The almost instantaneous change from I to G′ is particularly impressive on the video tape. Calorimetrically this transition is, however, rather small (see Table I). The next larger calorimetric step, in contrast (H′ to K1, picture 9 in Figure 3), is small in change of transmitted light intensity and hardly visible on the video tape. The supercooling for the transitions increases as the order of the phases increases, with definite steps on going from I to G′ and K_1 to K_2 (see Table II).

The textures of the smectic phases, G′, H′, and the condis crystal K1 show surprising similarity. In the same way, the X-ray patterns



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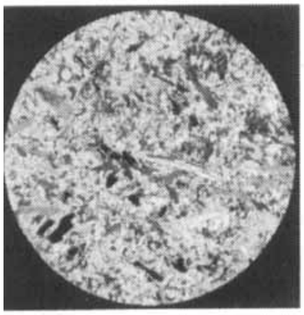

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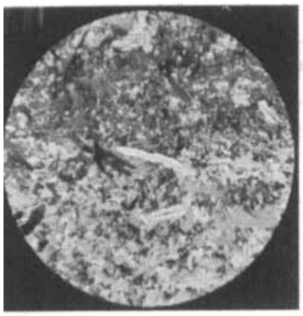

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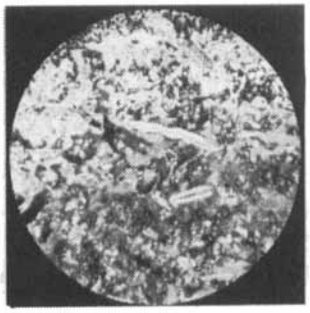

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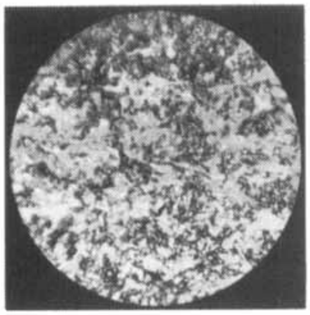

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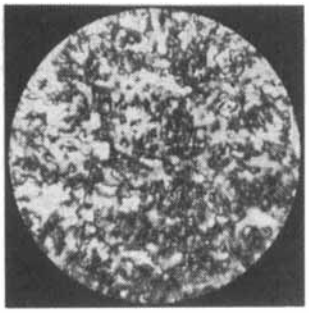

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See Color Plate I

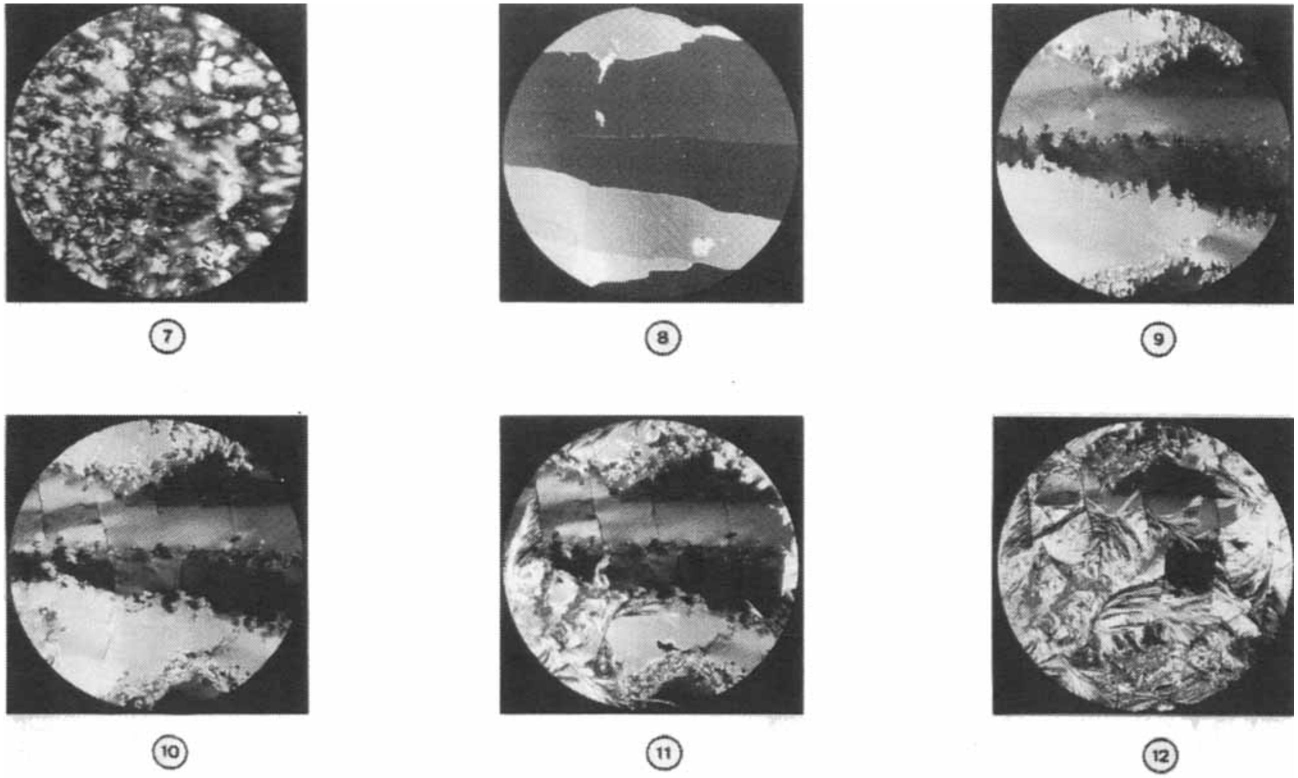

FIGURE 3 Selected photomicrographs of OOBPD
A. On heating at 10 K/min. 1. G′ at 426 K; 2. I at 434 K; 3. N at 497 K; 4. N at 505 K.
B. On cooling at 10 K/min. 5. N at 488 K; 6. C at 466 K; 7. I at 421 K; 8. H′ at 410 K; 9. K1 at 408 K; 10. K1 at 376 K; 11. K2 at 367 K; 12. K3 at 363 K.
For corresponding light transmission see Figure 4. See Color Plate II

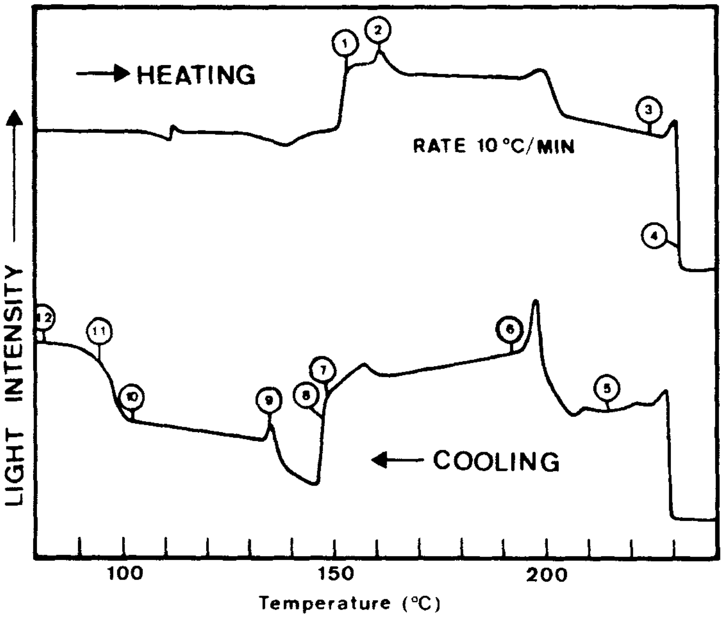

FIGURE 4 Light transmission curves of OOBPD on heating and cooling at 10 K/min. The marked numbers refer to the micrographs in Figure 3.

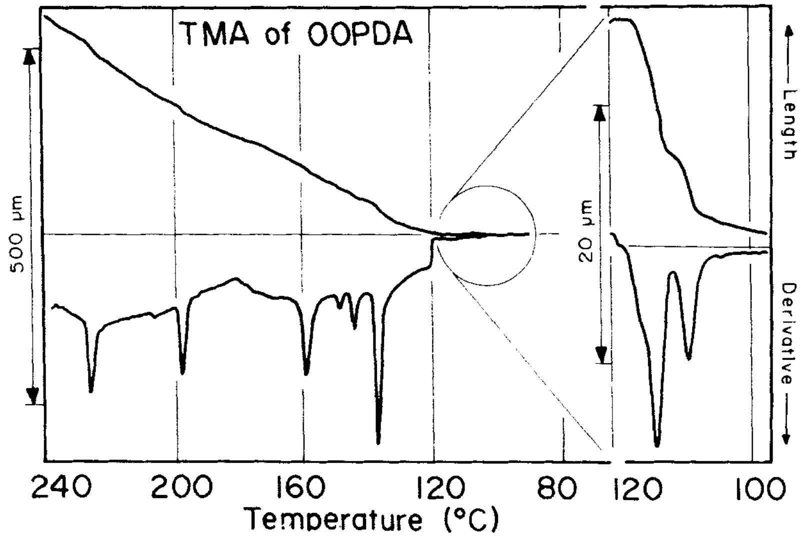

FIGURE 5 Thermomechanical analysis of OOBPD on cooling. Upper curve piston position of the head of Figure 2. Lower curve derivative. (Note the expanded scale repeat of the 120 to 100°C region).

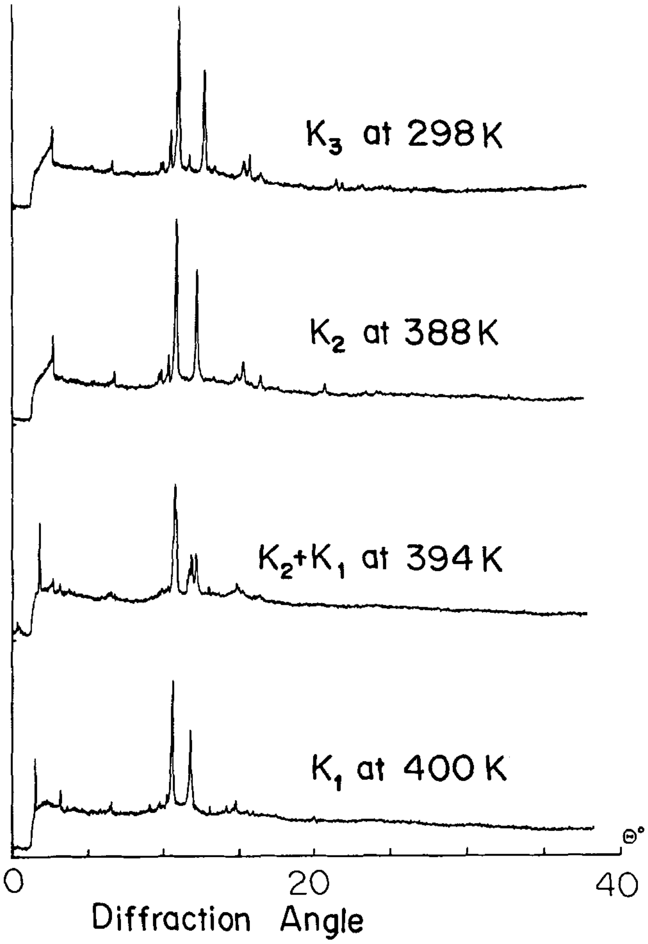

FIGURE 6 Densitometer traces of the X-ray diffraction of OOBPD on cooling from 473 to 295 K in 40 h. Traces shown at 298, 388, 394 and 400 K (A), and 454, 441, 430 and 426 K (B).

of these three states do not differ drastically (compare the 400 and the 426 K diffraction patterns of Figure 6). The larger volume change in the H′ to K1 transition than in the smectic-smectic transitions is revealed by the cracking of the crystals. All this supports the suggestion that during the transition into the K1 condis phase minor structure changes occur, but the mobility of the mesogen is lost. Bigger structure changes are found on crystallizing structures K2 and K3 which start, as shown as an example in Figure 3, from new nuclei and grow in a typical spherulitic pattern (see pictures 11 and 12).

The X-ray patterns when viewed under the continuous recording of the Guinier-Simon camera shows three major structure patterns with two short temperature range intermediate structures. The K_3-structure is clearly highly crystalline with 14 discernible diffraction lines (see Figure 6). The K_2-structure is clearly an intermediate to the basic K_1-structure. In the diffraction photograph it exists at best for 4–5 K, overlapping on both sides with the K_1 and K_3 structures. The K_1-structure, in turn shows hardly observable changes when changing to H′ and G′. The major structure change is the transition to I. The structure of I changes, however, more or less continuously

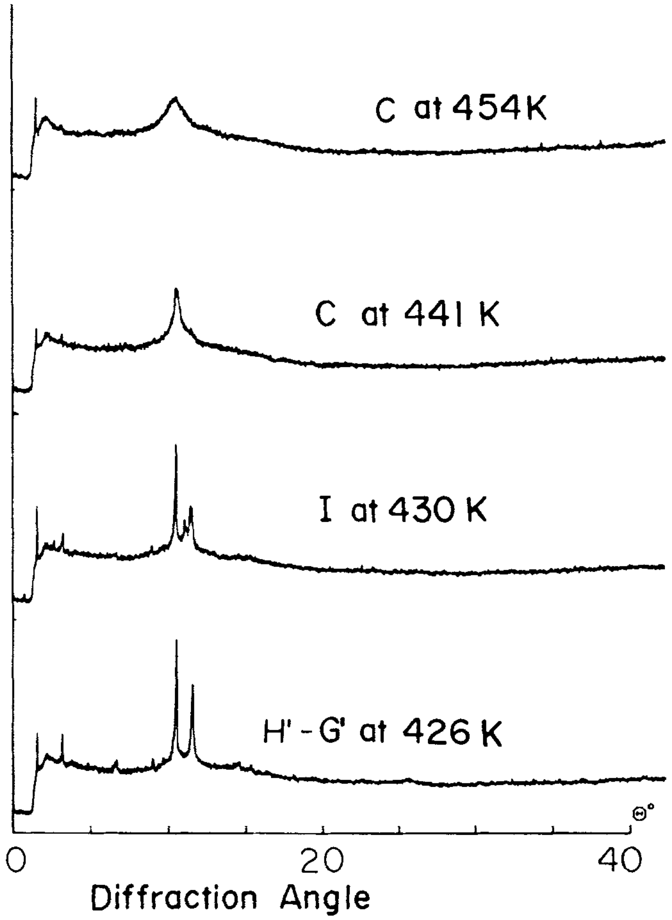

FIGURE 6 (continued)

TABLE II

Transitions observed on cooling of OOBPD in kelvin

	TMA[a]	DSC[b]	Video[c]	X-ray[d]	Light T.[e]	ΔT[f]
1. Melt → N	500	504.9	498		500	0.5
N			(5)	—		
2. N → C	471	475.0	469		470	0.4
C			(6)	441, 454		
3. C → I	432	435.9	430		431	0.7
I			(7)	430		
4. I → G′	422	425.2	421		—	1.7
G′				426		
5. G′ → H′	418	421.1	418		420	1.1
H′			(8)			
6. H′ → K1	410	414.3	410		409	1.0
K1			(9, 10)	394, 400		
7. K1 → K2	386	381.6				6.6
K2			373	388	363–373	
			(11)			
8. K2 → K3	382	377.3				7.9
K3			(12)	298		

[a] Peak temperatures of Figure 5 (left to right), cooling rate 10 K/min.

[b] DSC curve not shown, but comparable to the inverse of the heating trace of Figure 1, particularly matching heats of transition (cooling rate 1 K/min).

[c] Temperatures taken off the video replay, numbers in parentheses refer to picture numbers in Figure 3.

[d] Temperatures of densitometer traces of Figure 6 (cooling rate 0.075 K/min).

[e] Temperatures of the original trace of Figure 4 (cooling rate 10 K/min).

[f] Supercooling as found between heating and cooling at 1 K/min (see data in Table I).

towards C. Both the smectics G′ and C, bordering I seem to also have "pretransition" structure changes anticipating the new I-structure. The smectic C-structure, finally, consists only of one sharp, low angle diffraction line and two broader lines.

5. CONCLUSIONS

The calorimetric as well as structure analysis of the transitions of OOBPD makes it likely that the prior described crystal phases K1 to K3 are condis crystals with K1 possessing great structural similarity to phases G′ and H′. For a full resolution of the phase relationships direct measurement of the mobility of the paraffin chains would be needed. Low temperature calorimetry would be of interest to resolve the question of a possible CD glass or additional low temperature transitions.

Acknowledgments

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