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Hexagonal columnar *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates

Thermal behaviour and water absorption

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The thermal behaviour of freeze dried and water saturated samples of a homologous series of hexagonal columnar, liquid-crystalline *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates (three chain diols) is discussed. The water absorption from a saturated atmosphere as well as in direct contact is also described.

1. Introduction

Polyhydroxy liquid-crystalline compounds, known for a long time [1, 2], have only received considerable attention in the last decade [3–10]. Mesogens with only two terminal hydroxy groups were described in former times as possessing either a lamellar [11] or a discotic [12] mesophase. Later, different series of diol mesogens have been examined more extensively. Together with their lyotropic liquid-crystalline behaviour, the thermotropic mesomorphism of diol compounds, showing bilayered lamellar or smectic structures, was described [13–17].

We have found that certain 1,3-diols containing cyclohexane moieties, i.e. three chain and two chain diols, built up a hexagonal columnar mesophase of the D_{hd} type [18–22]. Their mesogenic unity is not formed, as classically known [23], by a disc-like single molecule (molecular mesogen), but by an aggregation of six single molecules via hydrogen bonding. Therefore we refer to this case as a supramolecular mesogen. In this paper we want to give, in addition to previous results [18, 19, 21], a more detailed analysis of the thermal behaviour of the homologous series of *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates in the dry as well as in the state after water absorption from either a water saturated atmosphere or from direct contact with water.

2. Experimental

The synthesis of the *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates (three chain diols) with the general formula shown in figure 1 is described elsewhere

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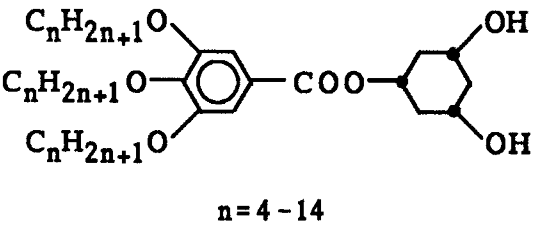


Figure 1. General formula of the three chain diols.

Table 1. Purification process, yields and optical appearence of the three chain diols.

Number of carbon atoms *n*	Purification process	Yield (%)	Optical appearance
4	Recrystallized from toluene	80	White powder
5	Recrystallized from toluene	72	White powder
6	MPLC, eluent: ethylacetate	76	Colourless waxy
7	Recrystallized from toluene	75	White powder
8	Recrystallized from toluene	71	White powder
9	Twice recrystallized from toluene	63	White powder
10	Twice recrystallized from toluene	67	Colourless waxy
11	MPLC, eluent: ethylacetate	69	White powder
12	MPLC, eluent: ethylacetate	79	White powder
13	MPLC, eluent: ethylacetate	28	White powder
14	MPLC, eluent: ethylacetate	35	White powder

MPLC: middle pressure liquid chromatography (Kronwald Separationstechnik), pump Sepapress HPP 100/50, gradient control Sepacon GCU 311, UV detector Sepachrom UV/VIS-400, Sepachron HPP column of 539 mm length, filled with HD-SIL 30–60 (particle size: 20–45 μm).

[19, 24]. The etherification of the 3,4,5-trihydroxybenzoic acid methylester was performed, instead of in acetone, in cyclohexanone with potassium carbonate for 4 h under reflux, in analogy to [27]. The products were characterized by means of ^{1}H NMR, ^{13}C NMR, IR and mass spectrometry, their purity was checked by means of GPC and elemental analysis, the data confirmed the structure in each case [25]. Table 1 summarizes the conditions of the purification process, the yield with respect to the last reaction step including the purification and the optical appearance of the three chain diols synthesized. The liquid-crystalline behaviour was investigated by means of DSC measurements and polarizing microscopy. The experimental details of the analytical methods used are given in [19]. A detailed description of the water absorption procedure is given in § 4.1 and 4.2.

3. Results and discussion of the thermal behaviour

3.1. *Freeze dried products*

3.1.1. *DSC measurements*

All DSC measurements of the three chain diols (freeze dried as well as water saturated) were carried out with a heating and cooling rate of 10 K min^{-1} in the range

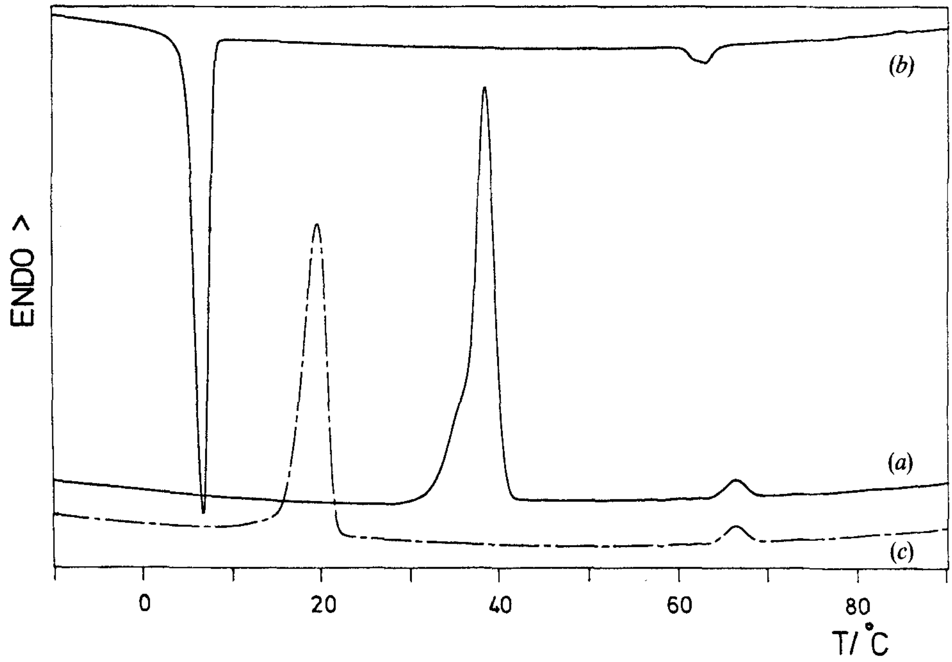


Figure 2. DSC thermogram of the three chain diol with $n=12$. (*a*) Heating curve (first heating), (*b*) cooling curve, (*c*) heating curve (second and further heating).

from −50°C to 150°C. Figure 2 shows as an example the DSC thermogram of the three chain diol with $n=12$. The transition temperatures and enthalpies of all *cis,cis*-(3,5-dihydroxycylohexyl)-3,4,5-tris(alkoxy)benzoates are summarized in table 2. As can be seen from table 2, there is no completely regular phase behaviour of the *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates. The compound with the shortest alkyl chains ($n=4$) exhibit a stable crystalline phase and a monotropic mesophase. The three chain diols with $n=5$–9 show crystalline phases on the first heating. Because of a strong hindrance of recrystallization, these phases reappear only after a period of nine to twelve months. Therefore, on second and further heating cycles only transition temperatures at the clearing point and glass transition temperatures can be estimated. The same phenomenon can be observed with the decyl derivative ($n=10$), except that no crystalline phase exists [19]. The glass transition temperatures of the freeze dried compounds with $n=4$–10 are summarized in table 3.

The higher homologues ($n=11$–14) exhibit a crystalline phase even in the second and further measuring cycles. These metastable crystalline phases are formed by recrystallization from the mesophase, whereas the stable crystalline phases, detectable on the first heating, reappear only within several months. The classification of the crystalline phases as C_1, C_2 and C_3 results from the transition temperatures, supposing an odd-even effect and a regular dependence of the transition temperatures with respect to the increasing length of the alkoxy side chains.

Summarizing all the results from the DSC measurements as shown in figure 3, we can divide the homologous series of *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy) benzoates into three parts. The compounds with the short alkoxy side chains ($n=4$–6) exhibit a monotropic liquid-crystalline mesomorphism (for $n=5$ or 6 related to the first

Table 2. Transition temperatures (in °C) and in brackets enthalpies (kJ mol^{-1}) of the freeze dried three chain diols.

n	C_1		C_2		C_3		D_{hd}		I
4	—		—		●	90·0(38·1)	●	[42·5(0·5)]	●
5	—		—		●	71·0(10·5)†	●	[62·5(0·8)]	●
6	—		—		●	63·0(10·5)†	●	[54·0(0·6)]	●
7	—		●	61·5†	●	68·0(32·7)†‡	●	80·0(1·4)	●
8	—		—		●	72·5(41·4)†	●	86·5(1·6)	●
9	—		—		●	63·0(42·2)†	●	92·0(1·5)	●
10	—		—		—		●	87·5(1·6)	●
11	—		●	12·0(17·0)§	●	56·0(22·0)†	●	86·5(1·4)	●
12	●	19·0(19·8)§	●	34·0(29·7)†	—		●	67·0(1·2)	●
13	—		●	35·5(32·2)	—		●	75·0(1·6)	●
14	—		●	45·0(52·9)§	●	72·5(96·8)†	●	[71·5 (2·0)]	●

n: Number of carbon atoms in the side chain.
C_1, C_2, C_3: Crystal phases.
D_{hd}: Hexagonal columnar disordered mesophase.
I: Isotropic phase.
† Only on the first heating.
‡ Transition enthalpy for C_2 and C_3.
§ Only on second and further heating.
[ ]: Monotropic liquid crystal.

Table 3. Glass transition temperatures (in °C) of the freeze dried and water saturated three chain diols with $n=4$–10.

n	4	5	6	7	8	9	10
T_g/°C							
Freeze dried	−3	−2	−8	−7	−6	−2	−2
Water saturated	−7	−20	−33	−1	−1	−1	−5

heating). The corresponding melting points decrease and the clearing temperatures increase strongly with increasing chain length. The glass transition temperature remains more or less constant. The second part ($n=7$–10) shows an enantiotropic mesomorphism with a decrease of T_m (melting temperature on first heating) and a maximum of the clearing temperature T_c at 92·0°C for the three chain diol with $n=9$. The glass transitions still remain in the same region as for the compounds with $n=4$–6. The third part is formed by the homologues with $n=11$–14. Here, the crystalline phases C_1 and C_2 appear at every heating run. The melting or crystalline transition temperatures increase but the clearing temperatures decrease with increasing chain length. With respect to the melting temperature of the crystalline phase C_3 (first heating run), the diol mesogen with $n=14$ is even monotropic again.

To summarize, we observe, in general, that the mesophase stability, i.e. the temperature range of the mesophase increases with increasing chain length n in the first group of the three chain diols ($n=4$–6), remains more or less constant in the second group ($n=7$–10) and decreases in the third group ($n=11$–14).

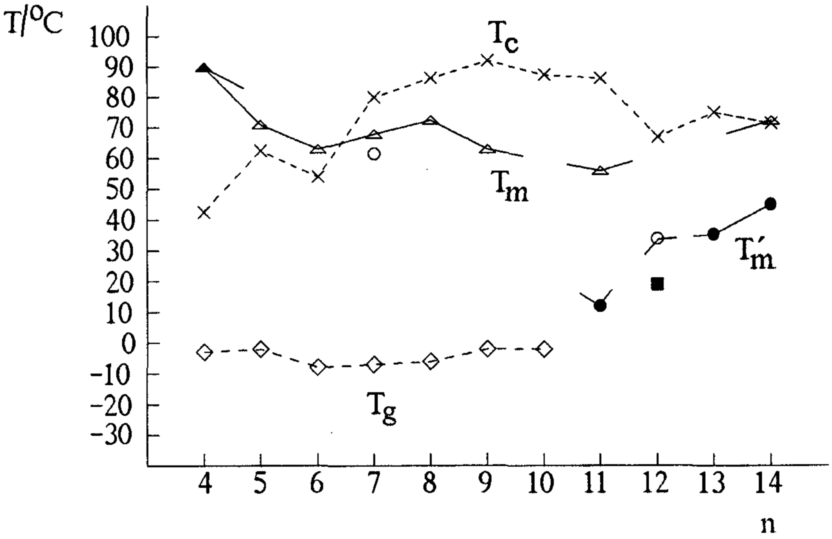


Figure 3. The dependence of the transition temperatures (in °C) of the freeze dried three chain diols on the number of carbon atoms n; (×) clearing temperature T_c; (△) melting temperature T_m of modification C_3, only on first heating; (○) transition or melting temperature of modification C_2, only on first heating; (●) melting temperature T'_m of modification C_2, on second and further heating; (■) transition temperature of modification C_1; (◇) glass transition temperature T_g.

3.1.2. *Polarizing microscopy*

All *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates exhibit similar textures (see figure 4). For the compound with $n = 10$, pronounced pseudo focal conic textures together with small areas of homeotropic domains can be observed [19]. Further cooling only causes a slight change in the colour of the texture for the compounds with $n = 4$–10, whereas for $n = 11$–14 recrystallization could be observed. Only on heating, do streak like defects appear in the focal conic domains. The formation of these defects is reversible depending on the heating and cooling cycles [19].

Resulting from X-ray and other measurements [21], the mesophase of the three chain diols was determined to be hexagonal columnar (D_{hd}). The discoid mesogenic unit is formed by the aggregation of six non-discoid single molecules. The interaction force responsible for this behaviour is provided by hydrogen bonding between the hydroxy groups of the diol compounds.

3.2. *Water saturated products*

3.2.1. *DSC measurements*

Due to their amphiphilic nature (hydrophilic hydroxy groups, hydrophobic alkoxy side chains) the *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates exhibit a strong affinity towards water. The transition temperatures of the compounds having absorbed water from a saturated atmosphere (cf. Section 4.1) differ strongly from those of the freeze dried three chain diols. Figure 5 shows the DSC thermogram of the compound with $n = 12$ (cf. figure 2). The results from DSC measurements for all water saturated three chain diols are summarized in table 4.

Figure 4. Optical texture of the freeze dried three chain diol with $n=12$, between crossed polarizers after cooling from the isotropic melt, at 60°C.

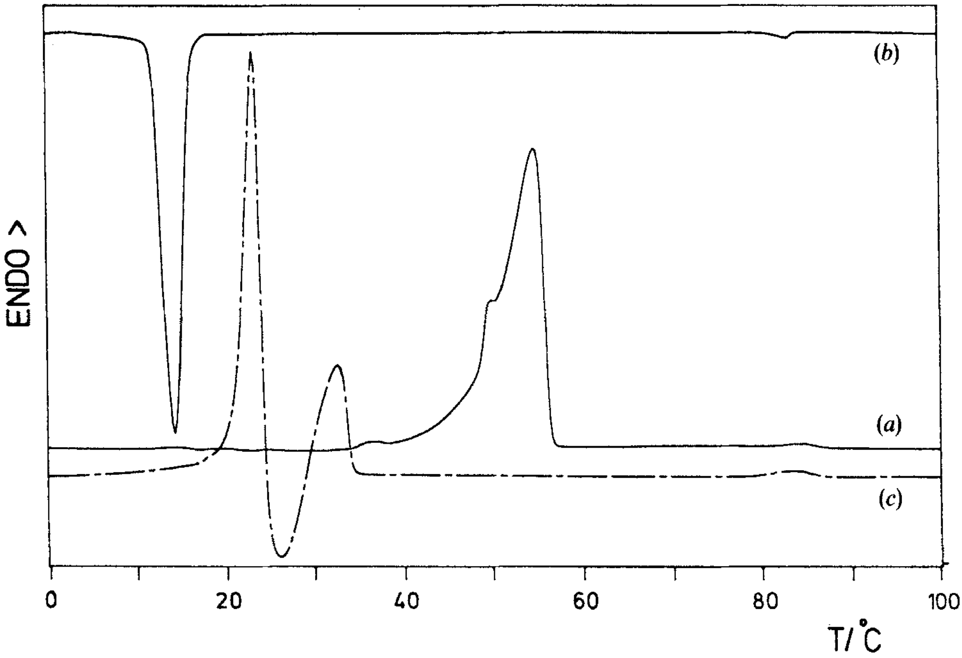


Figure 5. DSC thermogram of the three chain diol with $n=12$, having absorbed water from a saturated atmosphere. (*a*) Heating curve (first heating), (*b*) cooling curve, (*c*) heating curve (second and further heating).

Table 4. Transition temperatures (in °C) and in brackets enthalpies ($kJ\,mol^{-1}$) of the water saturated three chain diols, having absorbed water from a saturated atmosphere.

n	C_1		C_2		C_3		D_{hd}		I
4	—		—		●	88·5 (40·1)	●	[44·5 (0·5)]	●
5	—		●	48·5 (24·7)†	—		●	70·5 (0·8)	●
6	—		—		—		●	86·0 (0·7)	●
7	—		●	66·0†	●	71·0† (35·6)‡	●	90·0 (1·4)	●
8	—		—		●	74·5 (41·7)†	●	89·0 (1·4)	●
9	—		—		●	66·0 (43·0)†	●	95·0 (1·5)	●
10	—		—		●	53·5 (62·3)†	●	96·5 (1·6)	●
11	—		●	19·0 (26·5)§	●	64·5 (63·6)†	●	94·5 (0·9)‖	●
12	●	25·0 (27·7)	●	34·0 (27·6)	●	55·0 (72·5)†	●	86·0 (1·1)	●
13	—		●	39·0 (42·6)§	●	73·0 (99·5)†	●	[67·5 (0·7)]	●
14	—		●	48·0 (48·7)§	●	74·5 (99·7)†	●	75·5 (1·7)	●

n: Number of carbon atoms in the side chain.
C_1, C_2, C_3: Crystal phases.
D_{hd}: Hexagonal columnar disordered mesophase.
I: Isotropic phase.
† Only on the first heating.
‡ Transition enthalpy for C_2 and C_3.
§ Only on second and further heating.
‖ Average value.
[ ]: Monotropic liquid crystal.

The absorption of the stoichiometric amount of one mole of water per mole of three chain diol (cf. Section 4.1) leads on the one hand to the appearance of new crystalline phases for the compounds with $n=5, 10, 12$ and 13 and on the other hand to the disappearance of the crystallinity for $n=6$. This compound exhibits only a liquid-crystalline phase, which can be frozen in at −33°C. In analogy to the freeze dried products there is a strong hindrance of recrystallization of the crystalline phases, appearing on the first heating, for the compounds with $n=5$–10. Therefore, in second and further DSC measuring cycles no crystalline phase is detectable, but a glass transition can be observed. With the exception of the compound with $n=6$, the crystalline phases reappear in a period of six to twelve months depending on the length of the alkoxy side chains. Furthermore it has to be noted that all melting temperatures (except for $n=4$ and 5) are higher for the water saturated samples than for the freeze dried ones. The glass transition temperatures, observed on second and further DSC measuring cycles, are summarized in table 3. The plot of the transition temperatures versus number of carbon atoms of the alkoxy side chains is given in figure 6.

The division into three parts established for the freeze dried *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates is also applicable to the water saturated samples. In the first group ($n=4$–6) a strong stabilization of the mesophase with respect to the dry products can be observed. Whereas for $n=4$ the mesophase is monotropic, for $n=5$ and 6 mesophase becomes enantiotropic. The increase of T_c with increasing chain length is more pronounced than with the dry products. The glass transition temperatures decrease strongly until $n=6$. In the second group ($n=7$–10) an increase of all transition temperatures with respect to the dry products is observed. Because the increase of the clearing temperatures predominates over the increase of the melting temperatures, a slightly broader range of the mesophase is obtained during the

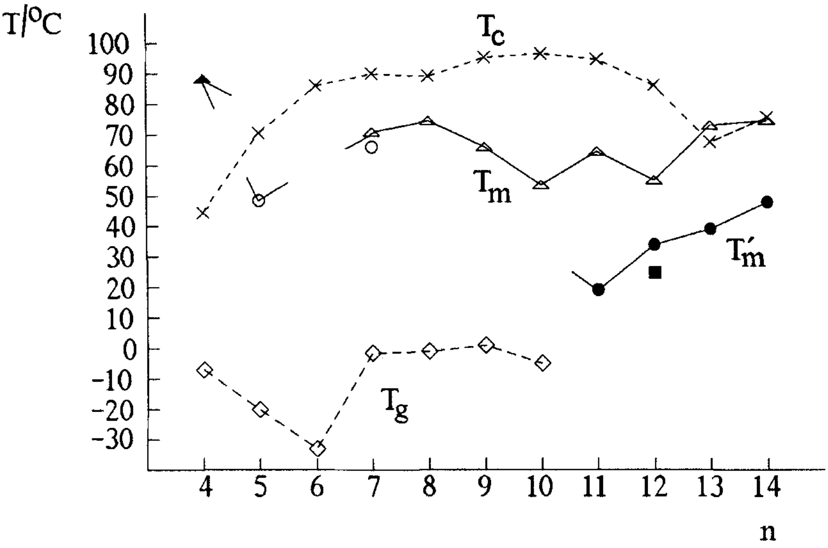


Figure 6. The dependence of the transition temperature (in °C) of the water saturated three chain diols on the number of carbon atoms n; (×) clearing temperature T_c; (△) melting temperature T_m of modification C_3, only on first heating; (○) melting or transition temperature of modification C_2, only on first heating; (●) melting temperature T'_m of modification C_2, on second and further heating; (■) transition temperature of modification C_1; (◇) glass transition temperature T_g.

first heating. The glass transitions are of the same order of magnitude as for the dry compounds. In general, the influence of water is less marked in the second group than in the first. In the third group ($n = 11$–14), beside the appearance of lower crystalline phases, the increase of the melting temperatures in the first heating predominates over the increase of T_c. So, the mesophases are destabilized up to the monotropic liquid-crystalline behaviour (with respect to C_3) for the compound with $n = 13$.

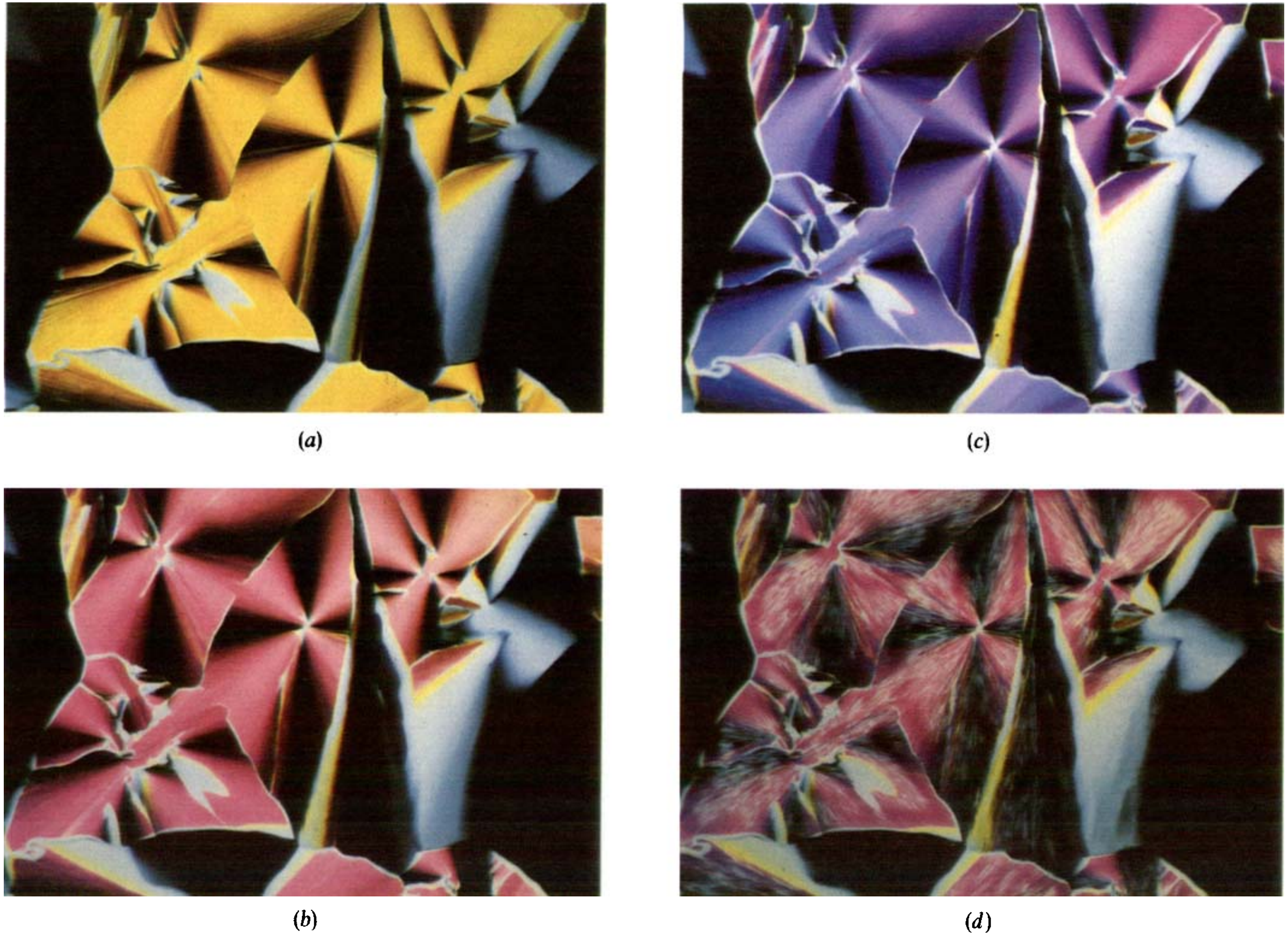
3.2.2. *Polarizing microscopy*

Water saturation has some influence on the textures observed. Whereas the freeze dried compounds show only a slight change of colour in the pseudo focal conic domains on cooling from the isotropic melt, this effect is essentially stronger for the water saturated samples, as shown for the compound with $n = 10$ (see figures 7 (*a*), (*b*) and (*c*)). Likewise, the streak-like defects, appearing on heating, are more evident than for the freeze dried samples (see figure 7 (*d*)). These defects disappear on cooling, the process is reversible on further heating and cooling cycles.

4. Results and discussion of the water absorption

4.1. *From a saturated atmosphere*

A water filled petri dish was put in a dessicator for several days to obtain a completely water saturated atmosphere. Samples of the different three chain diols, freeze dried from benzene solution, were placed in DSC pans under an argon atmosphere, weighed and quickly put in the dessicator. After various times, the samples were taken out and the increase in weight was determined. As an example for all [25], several samples of the compound with $n = 12$, exhibiting a different water content, was



(*a*)

(*c*)

(*b*)

(*d*)

Figure 7. Optical textures of the water saturated three chain diol with $n=10$, between crossed polarizers; after cooling from the isotropic melt, (*a*) at 80°C; (*b*) at 60°C; (*c*) at 40°C; (*d*) streak-like defects after heating to 60°C.

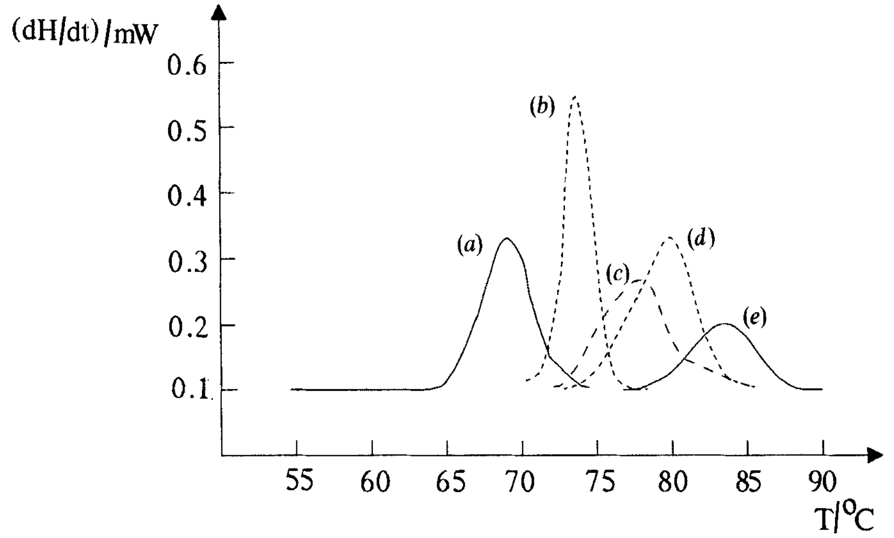


Figure 8. The dependence of the shift of the clearing temperatures of the three chain diol with $n = 12$ on the water content; (*a*) 0 mole, (*b*) 0·15 mole, (*c*) 0·44 mole, (*d*) 0·62 mole, (*e*) 1 mole of water per mole of three chain diol.

studied using DSC. According to the amount of water absorbed the appearance of a new crystalline phase and the shift of the clearing temperature to higher values can be observed. Figure 8 shows the dependence of the peaks of the clearing temperature on the water content of the samples. The transition temperatures of all other three diols were determined only in the saturated state.

The limit of water absorption of all *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates was determined to be one mole of water per mole of three chain diol. This value was reached in a period of 24 hours for the compound with $n = 12$. It has to be checked whether the length of the alkoxy side chains influence the rate of water absorption. Therefore, three chain diols with different lengths of the side chains ($n = 6$, 9 and 14) were investigated in the manner just described. Due to the lower hydrophoby, the compound with only six carbon atoms in the side chain reaches the limit of water absorption within 20 hours, while the compound with fourteen carbon atoms needs 48 hours. The three chain diol with $n = 9$ absorbed one mole of water within 24 hours. The results of these investigations are shown in figure 9. To verify the threshold value of one mole of water per mole of three chain diol all samples were left in the saturated atmosphere for more than one month. None of the three chain diols exhibit a further water absorption.

Moreover it was a point of interest to check whether the kind of absorbing phase has any influence on the rate of water absorption. Therefore, exemplary for the three chain diol with $n = 9$, the water absorption of crystalline samples (freeze dried from a benzene solution) as well as samples in the mesophase (freeze dried, heated above the clearing point and cooled down to room temperature under a dry argon atmosphere) were investigated [25]. Though the crystalline sample has a much greater surface, the water absorption is slower than for a sample being in the mesophase. This result is illustrated in figure 10.

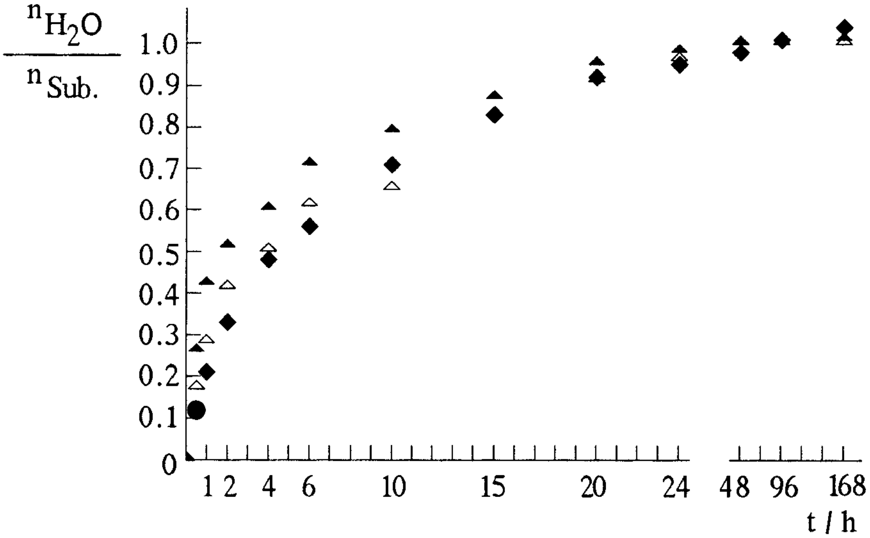


Figure 9. The dependence of the rate of water absorption of three chain diols on the number n of carbon atoms of the alkoxy side chains; (▲) $n=6$; (△) $n=9$; (◆) $n=14$.

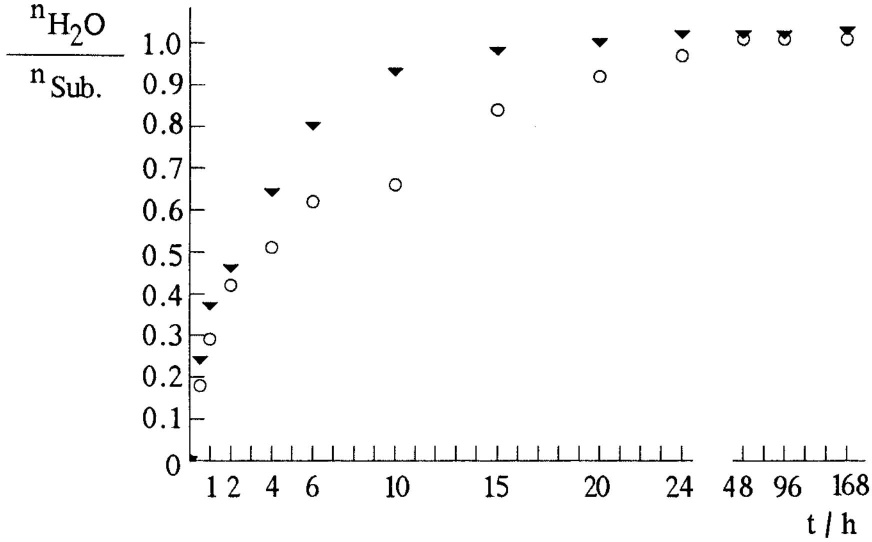


Figure 10. The dependence of the rate of water absorption of the three chain diol with $n=9$ on the absorbing phase; (○) crystalline phase; (▼) mesophase.

4.2. *In direct contact*

The freeze dried samples were weighed in DSC pans under an argon atmosphere and various amounts of water were added. During the subsequent DSC measurements (heating and cooling rate of 5 K min^{-1}) the material was homogenized in the isotropic phase. For every compound, free water could be detected as an ice peak. Figure 11 shows, as an example, the DSC thermogram of the three chain diol with $n=12$. For this particular compound, a complete phase diagram, diol/water, has been established (cf. figure 12). In the corresponding DSC thermograms, onset temperatures were taken as

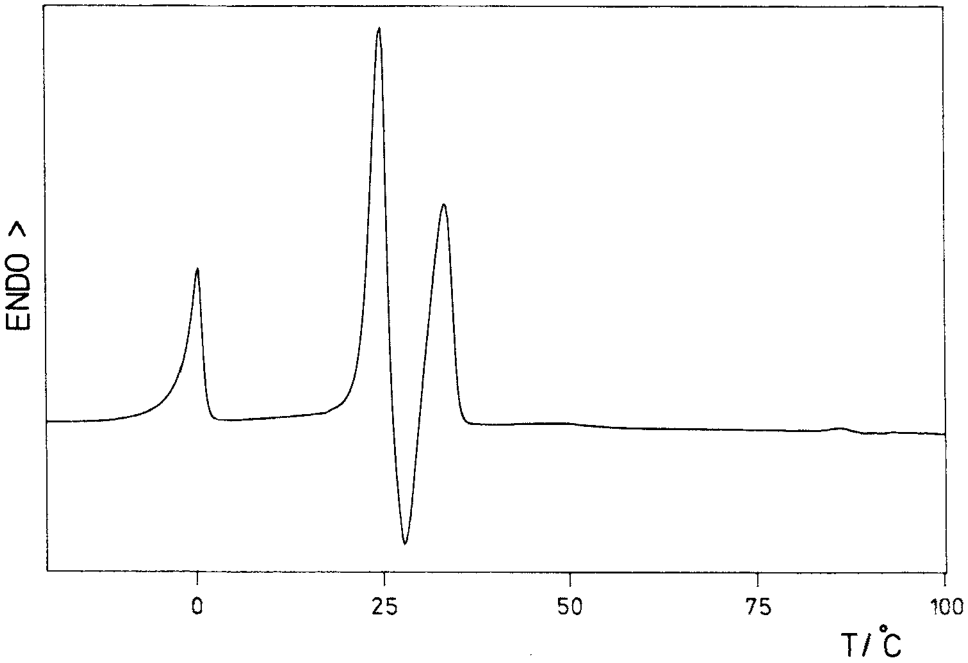


Figure 11. DSC thermogram of the three chain diol with $n=12$ in direct contact with water.

the point of intersection between the tangent to the ascending branch of the endotherm or exotherm and the approximately extrapolated baseline. The completion temperature was likewise established at the descending branch. As can be seen in figure 12, the clearing temperature increases with increasing water content, until a maximum value is reached at the absorption of one mole of water per mole of diol, i.e. at the formation of a monohydrate. After a very slight decrease, until an apparently formed dihydrate, the clearing temperature remains constant. The melting process is more complex. In the concentration region between the dry sample and the monohydrate, inhomogeneous transition peaks are observed. The onset of the first peak is not affected by a change in water content. With an increasing amount of water, the second peak shifts towards higher temperatures. Simultaneously, the relative areas of the two peaks vary. This indicate a coexistence of the water-free crystalline phase C_1 and the crystalline phase C_M of the monohydrate. The melting behaviour of C_M, being indicated by a sharp single peak, is regarded to be incongruent, as assumed from the existence of two crystalline modifications after water absorption from a saturated atmosphere. In the concentration range between the mono and the dihydrate, two endotherms and one exotherm appear. The onset of the first endotherm remains constant. Despite the inaccuracy because of the superposition with the exothermic process, we found a slight decrease in the completion temperature of the first endotherm and a constant onset of the second. This behaviour is interpreted as the coexistence of C_M with either a metastable crystalline phase C_{D_1} of the dihydrate or its more stable modification C_{D_2}. Above two moles of water per mole of three chain diol, beside the melting of free water, only C_{D_1} can be observed, which melts and recrystallizes to C_{D_2} on heating (cf. figure 11).

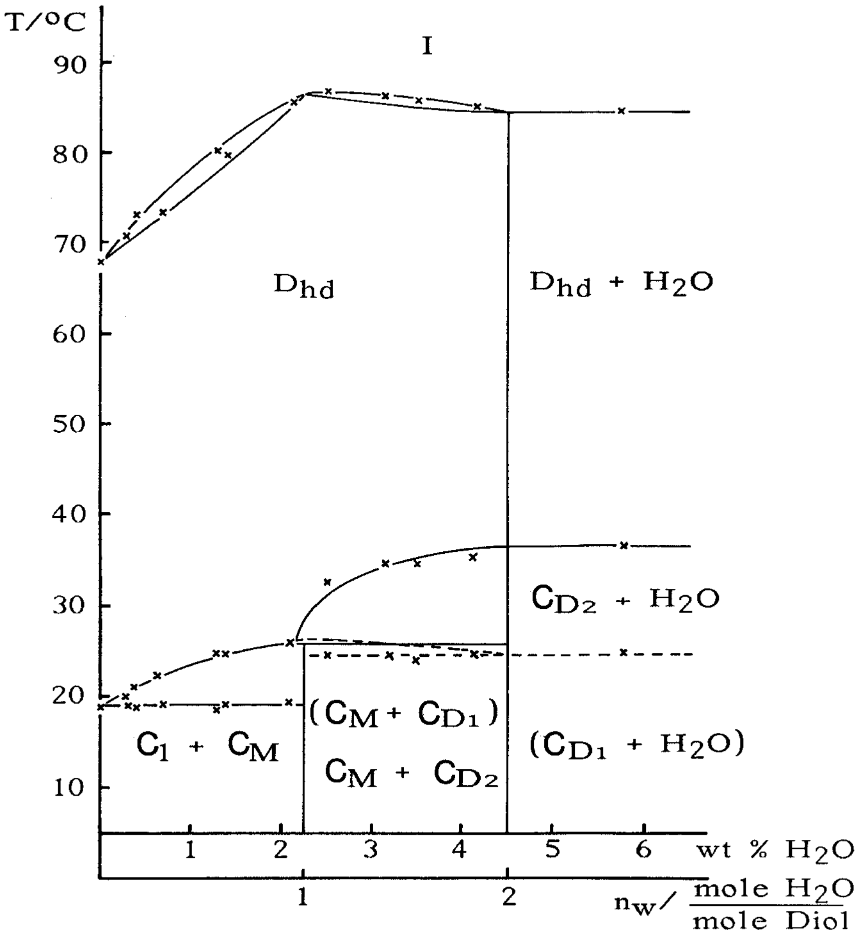


Figure 12. The phase diagram of the three chain diol with $n=12$ with water; C_1 = crystalline phase of the freeze dried sample; C_M = crystalline phase of the monohydrate; C_{D_1} = crystalline phase 1 of the dihydrate; C_{D_2} = crystalline phase 2 of the dihydrate; D_{hd} = hexagonal columnar mesophase; I = isotropic phase.

To summarize, it can be emphasized that, contrary to the absorption of water from a saturated atmosphere, exactly two moles of water per mole of three chain diol were incorporated in direct contact. By comparison, some one chain diols are known to take up water to a degree somewhat above two moles per mole of diol in the liquid crystalline state [17]. In our case, the water is bound in the crystalline state as well. The mesophases of the water-free sample, of the monohydrate and the dihydrate are completely miscible. Therefore, the mesophase structure must be identical in all three cases.

5. Conclusion

The *cis,cis*-(3,5-dihydroxycyclohexyl)-3,4,5-tris(alkoxy)benzoates (three chain diols) aggregate via hydrogen bonding to form supramolecular mesogens. Compared with the phasmids, another class of liquid crystals, forming supramolecular mesogens, the presented diol compounds can be classified still closer to midway between thermotropic and lyotropic liquid-crystallinity. The mesogenic behaviour of the dry diol compounds may be ruled by the same phenomenon being responsible of the mesomorphism of phasmids: the segregation of different parts of appropriate molecules, leading via curved interfaces to stacks of disc-like molecular aggregates [26]. Whereas the interface in phasmidic mesophases is formed by the semi-rigid aromatic part on the one side and the paraffinic part on the other side, the interface in the diol compound systems, however, should be due to the segregation between the hydrophobic alkyl chains and the hydrophilic head group. Whereas in phasmids no lyotropic mesomorphism has been observed, the thermal behaviour of the three chain diols is influenced by water absorption. In view of the stoichiometric amounts of the water absorbed, which do not lead to real solutions of the diol compounds but to a monohydrate and a dihydrate, we prefer to speak not of a lyotropic mesomorphism of those compounds, but of a thermotropic behaviour of supramolecular mesogens having incorporated liquid crystal water, in analogy to the thermal behaviour of crystalline compounds, having incorporated crystal water (water of crystallization).

Further investigations will pay attention to the question as to why there are two different steps in water absorption and why only one i.e. the monohydrate formation, has a strong influence on the clearing behaviour of the three chain diols.

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