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The Problems of Polymorphism in Liquid Crystals†

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Abstract—We deal with the actual position of the system of liquid crystalline modifications. This system is based on the relations of miscibility of the liquid crystalline modifications and on their textures. We describe the method of classification and the main textures of thermotropic liquid crystals. The connection between the structures and the system of modifications is discussed.

1. Introduction

This paper is a review and summary of the problems of polymorphism in liquid crystals. The main subject is the system of different types of liquid crystalline modifications.

The first part (Section 2) deals with the actual position and the base of the system of liquid crystalline modifications derived from miscibility investigations. In the second part (Section 3) we describe the optical phenomena (textures) observable during microscopic investigation of liquid crystals. The textures are summarized according to common optical phenomena and the different groups of textures are compared with the system derived from miscibility investigations. The third part of the paper (Section 4) presents a short description of the structures (especially found by X-ray measurements) of the different types of liquid crystals. The paper ends with a short discussion about the system derived from miscibility investigations in connection with the structural classification of liquid crystals (Section 5).

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2. The System of Polymorphism by Miscibility Relations

2.1 The Rule of Selective Miscibility

Comprehensive studies of the miscibility relations of liquid crystalline modifications in binary systems (isobaric temperature-concentration diagrams) yielded a system of different types of liquid crystals.(2–8,10,11,13,15–17,22,43,46) This system is based on the following rule of selective miscibility:

All liquid crystalline modifications which exhibit an uninterrupted series of mixed crystals in binary systems without contradiction can be marked with the same symbol. "Without contradiction" means that those liquid crystalline modifications which have the same symbol in no case exhibit an uninterrupted series of mixed crystals with the liquid crystalline states of another symbol.

2.2 The System of Liquid Crystalline States

Table 1 shows the variants of polymorphism in the liquid crystalline state based on the application of the rule of selective miscibility. The liquid crystalline modifications are given from left to right as they appear from the isotropic state and as their transitions occur with decreasing temperature. It is to be seen that, besides the nematic (N) and cholesteric (CH) modifications, there are so far 7 types of smectic modifications with the symbols *A* to *G*.

From the standpoint of the rule of selective miscibility there is no difference between the modifications N and CH; until now in all cases uninterrupted series of mixed liquid crystals have been found between these two types. But because of the well-known differences in their structures and their properties, it seemed suitable to list them in different variants of polymorphism.

Besides the numerous occurrence of N and CH modifications smectic *A*, *B* and *C* modifications are also favoured. So far we know more than 250 substances with smectic *A*, more than 150 substances with smectic *C* and nearly 80 substances with smectic *B* modifications. Only a few cases with other modifications have so far been observed: 2 with *D*, nearly 10 with *E*, 3 with *F* and 4 with *G*.

The existence of the variant Te_1 (Table 1) of polymorphism

TABLE 1 System of Liquid Crystalline Modifications

Degree of polymorphism	Variants of polymorphism					References
Monomorphism (M)	M_1	N				1
	M_2	CH				1
	M_3	*A*				2, 3
	M_4	*C*				2, 3, 5
Dimorphism (D)	D_1	N	*A*			2, 4
	D_2	CH	*A*			6
	D_3	N	*B*			7
	D_4	N	*C*			2, 3
	D_5	CH	*C*			9, 27, 42, 94
	D_6	*A*	*B*			2, 4
	D_7	*A*	*C*			10, 16
	D_8	*A*	*E*			11, 12
	D_9	*C*	*B*			13, 14
	D_{10}	*D*	*C*			10
Trimorphism (T)	T_1	N	*A*	*B*		2, 5, 6, 15
	T_2	N	*A*	*C*		43
	T_3	CH	*A*	*C*		27
	T_4	N	*C*	*B*		13
	T_5	*A*	*B*	*E*		31
	T_6	*A*	*C*	*B*		17–20
	T_7	*A*	*D*	*C*		10
	T_8	*A*	*C*	*G*		21
Tetramorphism (Te)	Te_1	N	*A*	*C*	*B*	17–20
	Te_2	*A*	*C*	*F*	*G*	21, 22

which possesses 4 modifications in the same substance is of special importance. All variants with one or more of these modifications can be derived from variant Te_1 by deficit of one or more of these modifications. In no case has a change in the sequence of the existence ranges of these modifications in the temperature scale been found. Except for the variant of monomorphism B, all variants which are possible on the basis of this rule are known (see Table 1).

The variants D_8 and T_5 allow the supposition that in general the *E* modifications are low temperature forms with respect to *A* and *B* modifications. The variant D_5 in the original publication(9) is designated as CH_{II}, CH_{I}, but now the low temperature modification has been recognized as smectic *C*.†(94)

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† Because of its occurrence in an optically active substance this modification has a twisted structure.

In the last few years a number of new substances with smectic modifications have been described. In some cases, on the basis of texture observations alone the classification of the smectic modifications has been tried,(19,20,30,32–35) and a number of *A*, *B* and *C* modifications have been determined. In some cases it seems that other types of modifications exist.(20,30,32–34) Of special interest are some substances with a great number of smectic modifications: some bis-(4-*n*-alkoxybenzylidene)-phenylenediamines possess up to four,(23–25) some 4-*n*-alkoxybenzylidene-4′-*n*-alkylanilines(33) and bis-(4-*n*-alkanoyloxybenzylidene)-*p*-phenylendiamines(91) up to five smectic modifications. There is a good chance of finding new types of smectic modifications in these polymorphic substances.

2.3 The Practice of Classification of Liquid Crystalline Modifications by Miscibility Investigations

The miscibility investigations of liquid crystalline modifications generally yield information on two possibilities: either a complete series of mixed liquid crystals exists or it does not exist.

If there is a complete series of mixed liquid crystals between two modifications in the diagram of state of a binary system, the said modifications belong to the same type (rule of selective miscibility).

If there is not a complete series of mixed liquid crystals, it is necessary to decide whether the two liquid crystalline modifications are of the same type or whether they belong to different types.

In the practical classification of liquid crystalline modifications based on miscibility investigations, we use arguments described in the following Sections (a)–(d).

a) *The existence of polymorphism variants with a great number of modifications*

If there exist several liquid crystalline modifications in one substance, these modifications certainly have to be attached to different types. A system of liquid crystalline modifications based on miscibility criteria must have at least as many different types as the substances with the highest degree of polymorphism have liquid crystalline modifications.

In this sense the variant Te_1 is very important. At the beginning of our miscibility investigations we only found *A*, *B* or *C* modifications. So far most of the smectic modifications belong to one of these types (see Table 1).

For the classification of the other smectic types, the existence of variants with a high degree of polymorphism is also of special importance.

The variant T_5 shows that the *E* modifications cannot be *A* or *B* modifications. The variant T_7 excludes *D* modifications being identical with *A* or *C* modifications. Furthermore, it follows from variant Te_2 that *F* and *G* are different to *A* and *C*.

So on the basis of miscibility investigations and consideration of the higher degrees of polymorphism, it is possible to reduce the great number of modifications to a few types.

But the question remains open, as to whether smectic *E* is different from *C*, *D*, *F*, *G*; whether smectic *D* is different to *B*, *E*, *F*, *G* and whether smectic *F* and *G* are different to *B*, *D*, *E*.

b) *The rule of the sequence of the modifications*

In no case has a change in the sequence of the existence ranges of the types of the liquid crystalline modifications in the temperature scale been found. This rule can be used as a second argument for the classification.

In a great number of cases this rule has been proved for the sequence of the modifications *N*, *A*, *C*, *B*. With respect to variant T_5 (*A*, *B*, *E*), smectic *E* is then different from *C* and with respect to variant T_7 (*A*, *D*, *C*), *D* is different from *B*. The modifications *E* and *D* cannot belong to the types *A*, *B* or *C*.

By comparison of the variants T_5 (*A*, *B*, *E*), T_7 (*A*, *D*, *C*) and Te_1 (*N*, *A*, *C*, *B*), we conclude that smectic *D* is not identical with *E*.

With respect to the sequence in the variants T_8 (*A*, *C*, *G*) and Te_2 (*A*, *C*, *F*, *G*) and comparison with T_7 (*A*, *D*, *C*) it follows that smectic *F* and *G* are not identical to *D*.

It is only the differentiation of the modifications *F* and *G* from *B* and *E* which has not yet been determined on the basis of miscibility investigations alone. Here further arguments (see 3 and 4) have been used.

c) *The shape of the diagrams of state*

If there are two regions of mixed liquid crystals starting from the modifications of the pure substances which do not form a complete

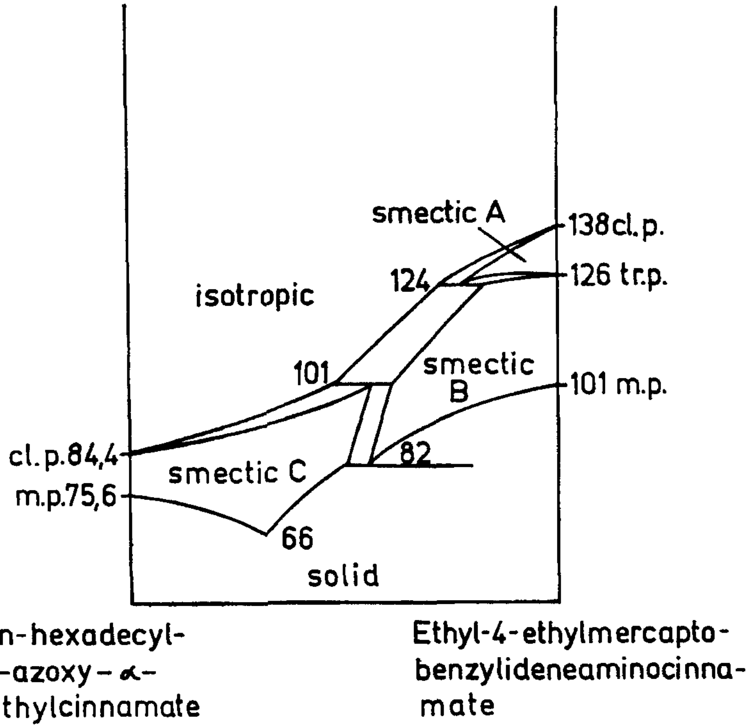

Figure 1. Diagram of state of a binary system with heterogeneous regions between the existence regions of different liquid crystalline modifications.

series of mixed liquid crystals, a great number of special shapes of the diagram of state are possible.

One type of diagram of state is of special importance for the classification of the modifications: two regions of mixed liquid crystals starting from the pure substances are connected by a heterogeneous region in which the mixed liquid crystals are in equilibrium (see for instance smectic *C* and *B* in Fig. 1). This heterogeneous region is a further argument for the differing nature of these two modifications. Until now we have observed in only one case a heterogeneous region between 2 modifications of the same type.(48) But in over 100 cases we found heterogeneous regions between modifications of different types.

The diagrams of state can be very complicated, especially if the components exhibit a high degree of liquid crystalline polymorphism.

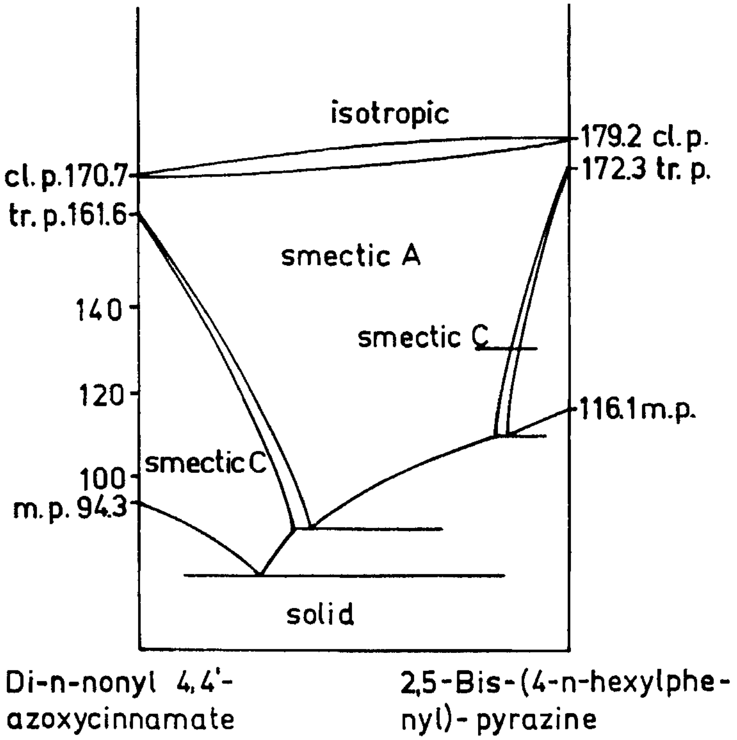

Figure 2. Diagram of state of a binary system with the existence region of another type between two regions of modifications of the same type.

Sometimes the existence ranges, starting from the liquid crystalline modification of each of the components, do not touch by means of a simple heterogenous region, but there is the existence region of a third phase (isotropic, liquid crystalline, solid; for instance smectic *A* between two regions of smectic *C* in Fig. 2) between them. In this case a decision about the types of liquid crystalline modifications is not possible. Then it can be useful to exchange one component for a related compound (another member of a homologous series, a similarly substituted compound): in most cases it is possible to get a diagram of state with an uninterrupted series of mixed crystals between modifications of the same type (see for instance Fig. 3 with another homologue of the right component of Fig. 2) or a heterogeneous region between modifications of different kind.

The range of the existence region of a liquid crystalline phase can

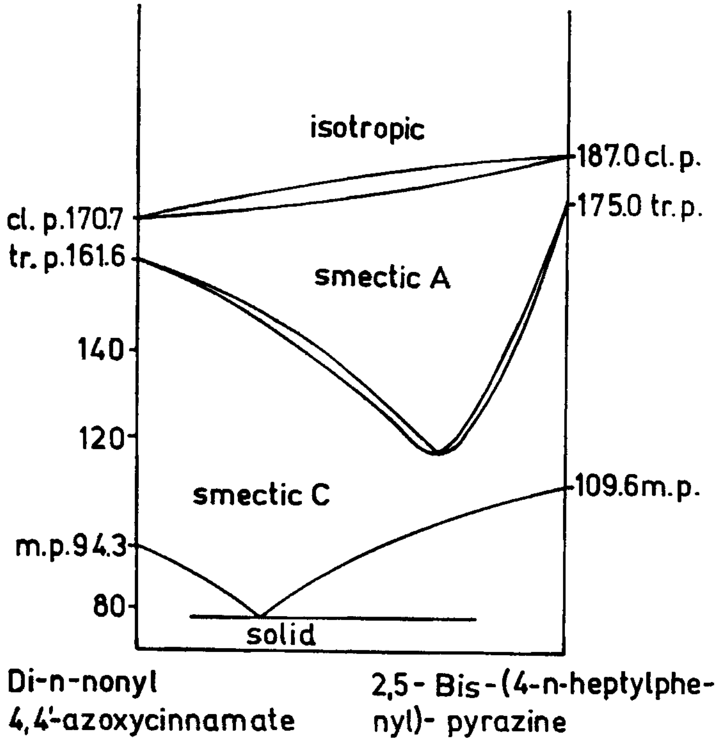

Figure 3. Diagram of state of a binary system with complete miscibility relations between the liquid crystalline modifications of the components.

also be an argument for the classification. If this region only persists in a very little range of concentration, it is probable that the second component of the binary system will not exhibit a modification of the same type (Fig. 4).

d) *Polymorphism in homologous series*

The connections between molecular structure and polymorphism are very complicated. Even slight changes in molecular structure may cause surprising effects on the liquid crystalline properties of the substances. So far it has not been possible to predict with any certainty whether a given compound would be nematic or smectic.

But in homologous series some regularities exist which have been proved in many cases.(74) Connections of this kind between molecular structure and polymorphism may yield some arguments for the

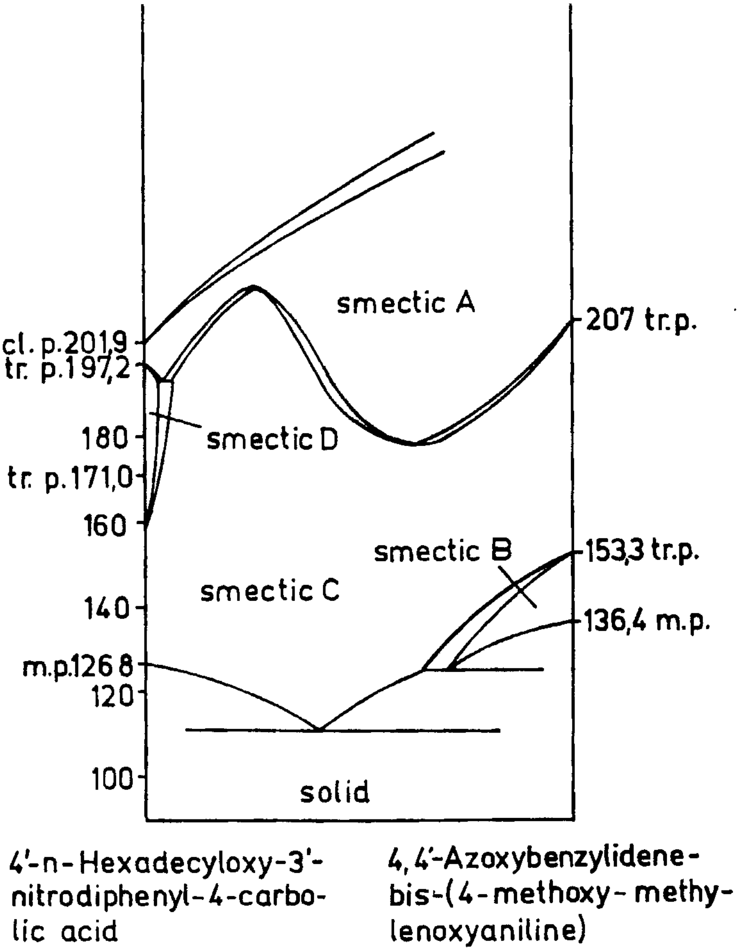

Figure 4 Diagram of state of a binary system with homogeneous regions in a very little range of concentration.

classification of the liquid crystalline modifications of the members of the homologous series.

The following regularities should be mentioned:

1) Usually the clearing and transition temperatures within a homologous series show a regular trend. It should be emphasized that the alternation of the temperatures from odd to even members may be considered as part of this trend. The existence of such regular trends points to the transition of modifications of the same type.

2) The degree of polymorphism usually shows a regular trend within a homologous series. Often the lowest members exhibit only nematic modifications, the middle members additional smectic ones and the highest members only one or more smectic modifications.

3) Usually by going from lower to higher members additional modifications appear as low temperature modifications. Thus modification, which is missing at the next higher member, is usually the high temperature modification at the lower member. Often neighbouring members exhibit the same degree of polymorphism or differ only by one liquid crystalline modification, either one missing or one more.

Two exceptions of this rule are to be mentioned:

In the series of the 4′-*n*-alkoxy-3′-nitrodiphenyl-4-carboxylic acids(10) and the bis-(4-*n*-alkoxyphenyl)-pyrazines,(13) one additional modification does not exist at a lower temperature, but intermediately between two modifications already existing at the lower member.

4) If one member of a series lacks a special type of modification which exists in the lower members, all higher members also lack this type.

There are only exceptions in the case of some substituted benzylideneaminocinnamates(32,90) In these series the neighbouring members do not differ by one terminal CH_2-group, but by one inner CH_2-group. The ends of the molecules consist of phenyl or isopropyl. The members exhibit and lack a nematic modification alternatively.

To summarize, these regularities often allow the classification of the liquid crystalline modifications of one compound if the types of modifications of one neighbouring member of the homologous series are known. In some cases it is possible to classify the polymorphism of the whole homologous series if the modifications of one member are known.

2.4 REMARKS ON THE CLASSIFICATION OF LIQUID CRYSTALS BY MEANS OF MISCIBILITY INVESTIGATIONS

It should be emphasized that the classification of liquid crystals by means of miscibility investigations is quite empirical. The relevance of the system based on miscibility investigations is to be seen in the fact that it is possible to reduce the great number of liquid crystalline modifications of substances with partially very different molecular structures to only a small number of different types. This system offers the possibility of reasonable selection of substances for further physical investigations which may prove the physical relevance of this system.

With respect to the known connection between miscibility properties and structure in solid crystalline materials, similar connections are also to be expected in liquid crystals. In fact such connections have been found (Secs. 3 and 4).

3. Texture and Polymorphism of Liquid Crystals

3.1 GENERAL REMARKS

The microscopic observation of liquid crystals in linearly polarized light is the simplest and most often applied method for a preliminary characterization. The textures obtained by this method are a strong support for the system of liquid crystals based on miscibility investigations. Furthermore, the textures offer the possibility of introducing some ideas on the structure of the liquid crystalline modifications.

In this paper we are only dealing with the occurrence of different textures, without discussion of many details. It is our purpose to emphasize the connection of the textures with the said system of liquid crystals.

With respect to the relatively large number of possible texture variants it is a necessary supposition for the occurrence of typical textures to work under special conditions.

Usually the textures of liquid crystals are observed in preparations which are enclosed between glass slides and cover slips in polarized light with crossed polarizers. In this paper we are only dealing with textures observed under these circumstances (except stepped droplets). Examinations without cover slips allow some additional textural alterations.

The following pictures have been taken in carefully manufactured and specially selected preparations. This was done for the purpose of yielding preparations with easily observable texture characteristics. During the practical examination of substances, more or less marked texture variants are often to be observed. These variants depend upon the special properties of the substances and the production of the preparations. Often textures occur whose characteristics are somewhat obscure because of the existence of mechanical impurities, paramorphoses on influences of the walls. In these cases the characteristics are observable only with difficulty, even at large microscopic magnification. Also in preparations with only weak birefringence (e.g., cholesteryl esters) observation of specific textures may be difficult.

3.2 PARAMORPHOSES

The melting of a solid substance commonly yields paramorphoses, (except for the low viscous nematic liquids), but not specific textures. In the case of the paramorphosis, the picture of the solid crystals is only slightly altered after the transition to a liquid crystal (see for instance Fig. 1b in Ref. 53). The characteristic discontinuities of the liquid crystalline textures are usually not visible at the paramorphoses.

Paramorphoses have also been observed after transitions of one liquid crystalline modification to another. The texture of the initial modification is only slightly altered. Paramorphoses of this kind often occur in the smectic state, for instance smectic *B* often appears in the form of a fan-shaped texture which is characteristic for smectic *A* (see for instance Fig. 10 in Ref. 46). Occasionally it is possible to get nematic textures bearing strong similarity to the fan-shaped texture of smectic *A*.

3.3 SCHLIEREN TEXTURES

a) *Nematic schlieren textures*

Schlieren textures are often observable in liquid crystals. They are found in nematics, mainly in somewhat thicker layers(25,46,49–51,52) (Fig. 5). This texture is caused by a nonhomogeneous orientation of the structure. The optical characteristics of this texture are dark brushes which start from point singularities. These point singularities are characterized by

$$|s| = \text{number of brushes}/4$$

There are points with 4 or 2 dark brushes. The sign of the point is positive when the brushes turn in the same direction as the rotated

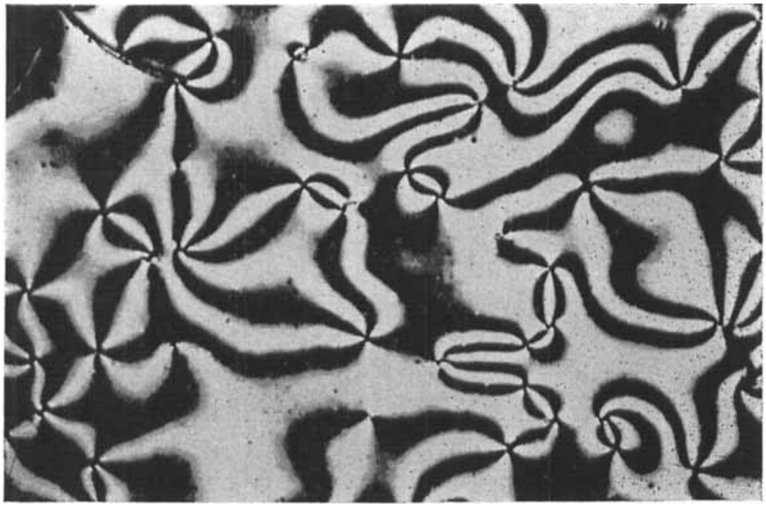

Figure 5. Nematic schlieren texture, crossed polarizers, × 120.

polarizers, and negative when they turn in the opposite direction. In nematics the existence of point singularities with $s = +\frac{1}{2}, -\frac{1}{2}, +1, -1$ has so far been established. The point singularities are the projections of threadlike discontinuities which are oriented perpendicularly to the layer. In thicker nematic samples (*ca.* 100 μm) the threads are not perpendicular to the layer. They are attached at their ends to the walls but otherwise float freely. They are visible as straight or bent lines in the threaded texture (see, for instance, Ref. 49).

In nematic schlieren textures with molecular alignment nearly parallel to the slides occur continuous changes of the molecular alignment by 180° within certain regions. These alignment changes are called " inversion walls of the first kind ".(49) In the case of a very thin inversion wall, it is called an " inversion line of the first kind ". There are also inversion walls (or lines) of the second kind,(49) which arise along a boundary between homogeneous regions with different inclination with respect to the layer.

A great number of smectic *C* modifications also show schlieren textures.(25,46,49,50,53) They look very similar to those in nematics, but usually they are disturbed (Fig. 6). The point singularities are

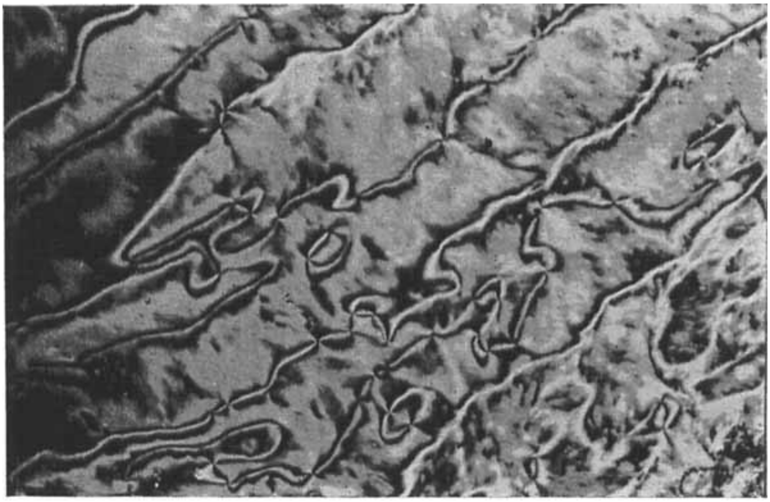

Figure 6. Schlieren texture of smectic C, crossed polarizers, × 120.

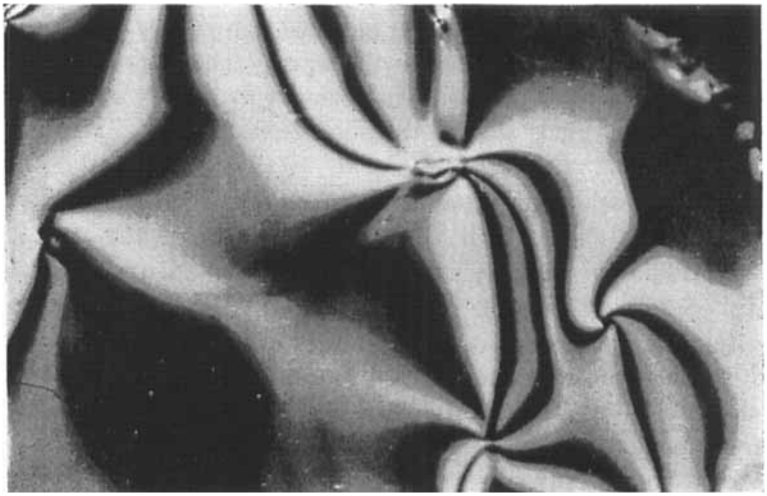

Figure 7. Schlieren texture of smectic B, crossed polarizers, × 120.

of types $s = +1$ or -1; in no case has $s = \pm \frac{1}{2}$ been observed.(49) Inversion walls (or lines) of the first(49) and the second kind(54) occur.

The smectic B modifications of some substances show very clearly schlieren textures (Fig. 7). They are similar to those in nematics, but have only point singularities with $s = +1$ or -1. Inversion lines of the first kind have been observed.(55) The smectic F modifications, which have so far been found in 3 substances can occur in schlieren textures. These schlieren textures are very similar to those of smectic C (see Figs. 3 and 5 in Ref. 22) but their details have not yet been investigated.

3.4 Focal Conic Textures

a) *Simple focal conic textures*

The most important variants of the focal conic textures(46,51,53) are the fan-shaped texture (Fig. 8) and the polygon texture (Fig. 9), the latter existing usually in somewhat thicker preparations.

Characteristic for these textures is the occurrence of ellipses and hyperbolae in confocal arrangement. In the fan-shaped textures the hyperbolae and in the polygon textures the ellipses are easily observable. Their occurrence is caused by the existence of a layer structure with equidistant parallel but not plane layers. The simple focal conic textures are characteristic for smectic A.

Also cholesteric liquid crystals(51,56) and the neat modifications of aliphatic(57) and aromatic(58) salts often appear in simple focal conic textures. Because of their somewhat disturbed appearance and less birefringence, the characteristic discontinuities are usually not as clearly visible as in the case of A modifications.

It should be mentioned that the focal conic textures are also characteristic for the lyotropic lamellar phases.(58,59)

b) *Broken focal conic textures of smectic C*

The C modifications, in particular those with high viscosity often occur in focal conic textures.(46,53) Thin preparations show broken, fan-shaped textures (Fig. 10), while thicker preparations show broken polygon textures (see for instance in Ref. 46). Besides the usual discontinuities as ellipses and hyperbolae in confocal arrangement

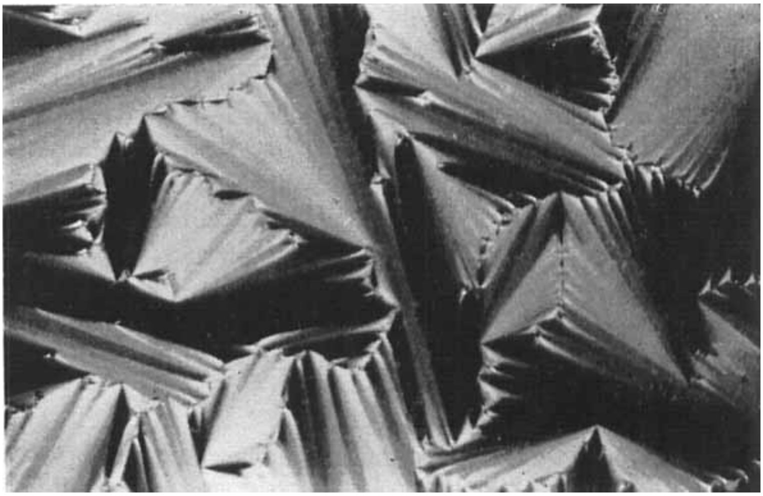

Figure 8. Simple fan-shaped texture of smectic *A*, crossed polarizers, × 120.

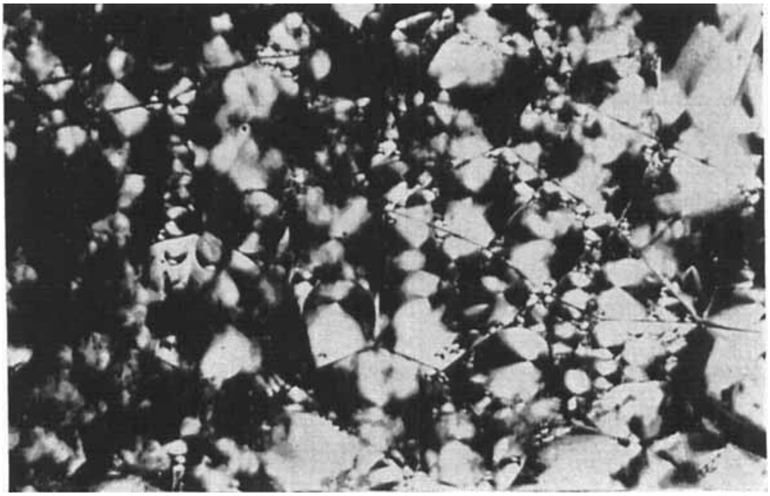

Figure 9. Simple polygon texture of smectic *A*, crossed polarizers, × 120.

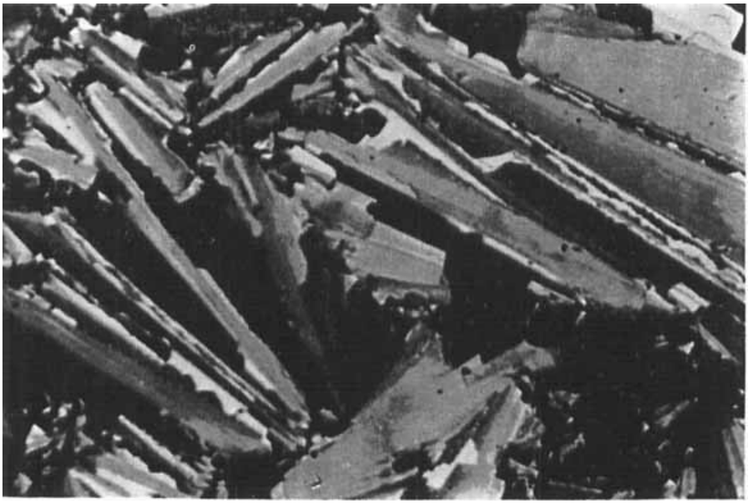

Figure 10. Broken fan-shaped texture of smectic C, crossed polarizers, × 120.

within the focal domains, a number of irregularly shaped, different-coloured regions are visible.

Without a doubt the occurrence of focal conic textures in smectic C is based on the existence of non-planar equidistant layers, as in the case of smectic A. The formation of different regions within the focal domains points to a different alignment of the molecules. It is known that in smectic C the molecules have a tilted arrangement with respect to the layers.(60–65)

Assuming that the tilt angle with respect to the layer is constant but that the direction of the molecules changes discontinuously from one region to another along a surface nearly perpendicular to the layer, this surface should be visible as an " inversion line of the second kind ". With this explanation, the additional discontinuities and the different-coloured regions in the broken focal conic textures seem to be understandable.

c) *Striped broken fan-shaped textures of smectic F*

F-modifications(21,22) can occur in broken fan-shaped textures with additional well-defined concentric arcs (Fig. 11). The details

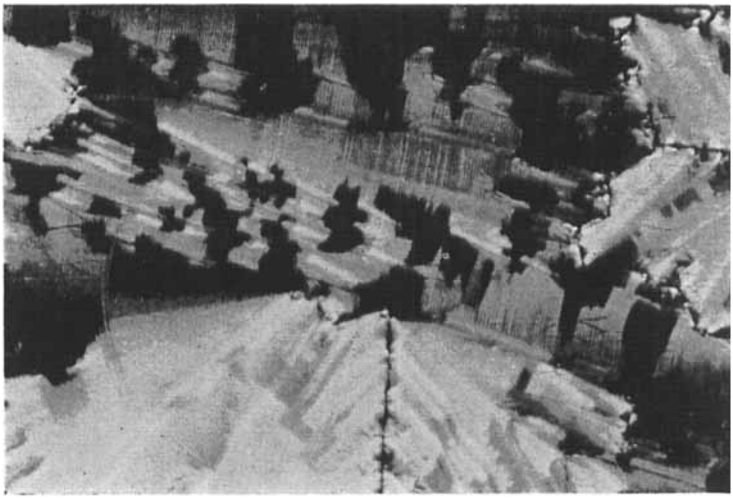

Figure 11. Fan-shaped texture of smectic F, crossed polarizers, × 180.

of this texture are still unknown. So far we cannot exclude certainly that this texture might be a paramorphosis (see (d) which follows).

d) *Paramorphic focal conic textures*

After the transition of smectic A to smectic B, the focal conic texture may be preserved without great changes as a paramorphosis.(46,53,66) Only the number of discontinuities is decreased (focal conic texture with a decreased number of lines of discontinuity). If this texture is heated for some hours at the temperature of the existence range of smectic B, it is altered to a mosaic texture.

E modifications(11) can appear from smectic A in the form of a fan-shaped texture with concentric arcs (Fig. 12). This texture is also a paramorphosis: if it is heated for some hours at the temperature of the existence range of the E modification it is changed to a mosaic texture (Fig. 13).

Occasionally nematic liquid crystals form from A modifications into paramorphic fan-shaped textures. Obviously their occurrence is due to boundary effects: the flowing of the nematic liquid keeps the fan-shaped texture nearly unchanged. After crystallization and a second melting of the sample, the typical nematic textures may be observed.

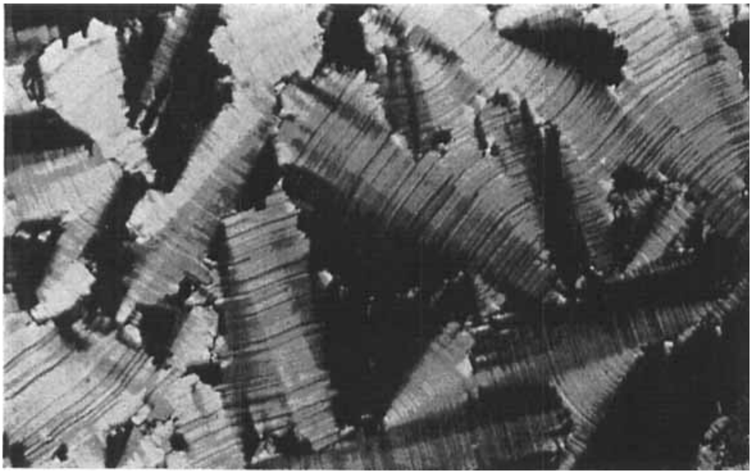

Figure 12. Transient fan-shaped texture of smectic *E*, crossed polarizers, × 120.

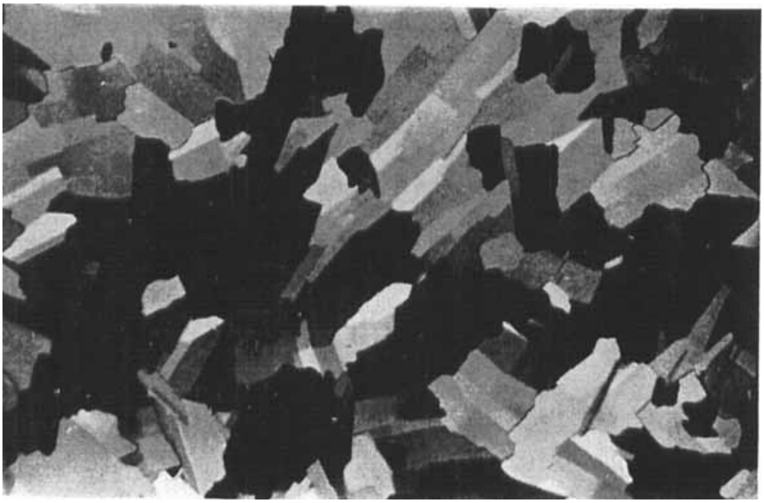

Figure 13. Mosaic texture of smectic *E*, crossed polarizers, × 120.

3.5 MOSAIC TEXTURES

a) *Mosaic textures of smectic B, E and G* (Fig. 13)

Under suitable conditions all *B* modifications can occur in mosaic textures as a stable form of the textures.(15,66) Mosaic textures (see for instance in Refs. 46, 66) consist of different-coloured, optical homogeneous regions with nonregular boundaries. In each of these regions the molecular alignment is uniform (" liquid single crystals "). The optical axes of different regions have different orientations. The optical homogeneity of the regions indicates that the layers of the smectic *B* structure are planar.

The smectic *E*(11) and *G*(21,22) modifications also occur in stable mosaic textures. The properties of these textures are similar to those of the *B* modification.

b) *Mosaic textures of smectic D*

With decreasing temperature, the *A* modification of the 4′-hexadecyloxy-3′nitrodiphenyl-4-carboxylic acid alters to the mosaic texture of the *D* modification.(10) This mosaic texture exists only for a short time and changes spontaneously to an isotropic texture. These texture changes indicate that a structure with plane layers arises which changes spontaneously to a cubic structure (see Sec. 4).

3.6 HOMOGENEOUS TEXTURES

The existence of homogeneous textures indicates a homogeneous alignment of the whole preparation or at least of large parts of it (" liquid single crystals "). With regard to the orientation of the optical axis with respect to the plane of the slide different cases can be observed.

a) *Pseudoisotropic (homoeotropic or uniaxially erected) textures*

In the pseudoisotropic textures,(46,53) the optical axis is oriented perpendicularly with respect to the plane of the slide. The homogeneity of the structure is due to the boundary effects. The boundary effects are furthered by rubbing the slides with special substances, e.g., lecithin.

So far pseudoisotropic textures have been observed at nematic and smectic *A*, *B* and *E* modifications.(31,46,52)

Also the " Grandjean plane structure " of the cholesteric liquid crystals,(51) which possesses the long-known, highly optical activity and selective reflection of circularly polarized light, appears out of the region of total reflection as pseudoisotropic texture, as long as the polarizers are suitably oriented.

It seems that pseudoisotropic textures are also obtainable in the case of the twisted smectic C structure.(9,27,94) The twisted structure forms in optically active substances or by doping inactive substances with small amounts of optically active materials. The optical properties of the texture of the twisted smectic C are similar to those of the nematic liquids.

b) *Stepped droplets*

Stepped droplets are obtained by melting the crystals without a cover slip in smectic A, B, C and E modifications. A necessary presupposition for their occurrence is the existence of a layered structure; therefore they are not obtainable in nematic liquids.

In the case of the A, B and E modifications(31,53) the stepped droplets appear dark between crossed polarizers. For the C modifications this darkness is not observed(53) which is comprehensible with respect to the tilted structure of smectic C.

c) *Homogeneous layers between rubbed slides*

By rubbing the slides in a given direction with paper, silk or other materials the surfaces of the slides become homogeneous.(67–69) This homogeneity of the slides leads to homogeneous layers of the liquid crystals which are enclosed between them.

In nematic liquids the optical axis lies in the plane of the layer and parallel to the rubbing direction. If the slides are not fully homogeneous, schlieren, point singularities and threads can be observed.

In a few cases it was possible to align smectic A modifications between rubbed slides.(54)

Some substances with smectic C modifications yield homogeneous preparations.(50,52,60,65) The smectic layers are parallel to the surfaces of the slides. Sometimes homogeneous regions with 2 different alignments are observable. They are separated by inversion walls of the second kind. Often one alignment changes to the other with the disappearance of the inversion wall. It is to be assumed that the difference in the alignments is due to different orientations of the optical axis with respect to the plane perpendicular to the slide.

d) *Homogeneous textures in electric fields*

Due to their dielectric anisotropy, nematic liquid crystals with low electric conductivity can be aligned homogeneously in strong electric fields. If the nematic layer is aligned homogeneously by boundary effects, its orientation can be changed by electric fields.(70) Such arrangements are of great technical interest as electro-optical devices.(71,72,73,84)

3.7 NEMATIC MARBLED TEXTURES

The nematic marbled textures(46,53) (Fig. 14) consist substantially of a great number of nearly homogeneous regions with different orientations of the optical axis. The homogeneity of the individual regions is due to boundary effects. As the result of a preceding crystallization of the substance, the slide has become homogeneous within the area of each crystal. Because of the different orientation of the crystals the boundary effects after the melting of the solid

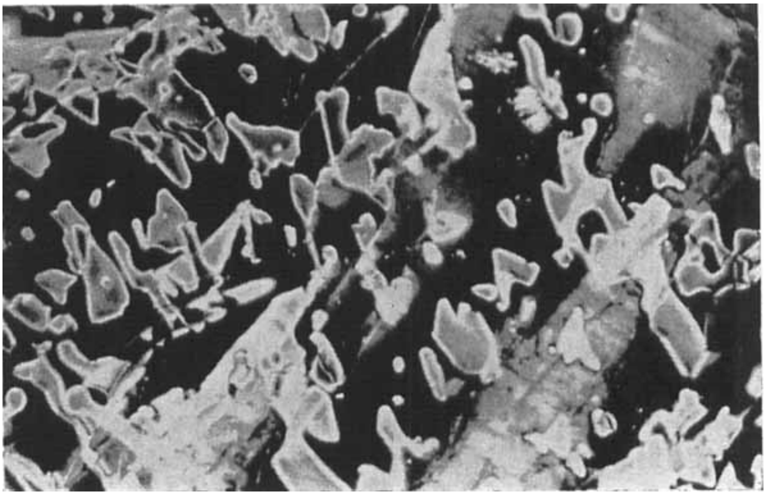

Figure 14. Nematic marbled texture, crossed polarizers, × 120.

crystals are different and the orientation of the optical axis of the nematic liquid changes from one region to another.

3.8 Isotropic Textures

In the liquid crystalline state, cubic structures are known which are optically isotropic and therefore yield isotropic textures. Isotropic textures which are homogeneous in the whole extension of the preparation occur in the *D* modifications as stable textures.(10,28) In the case of cholesteric liquids, they can appear after the transition of the isotropic liquid to the cholesteric liquid as transient textures.(74,95) With certain substances, e.g. cholesteryl nonylphenylcarbonate, this texture is stable for any period of time.(50)

3.9 Transition Phenomena

Transitions with the participation of liquid crystals sometimes show interesting and characteristic phenomena.

These phenomena are of special interest if the texture of a liquid crystal is altered only very slightly by the transition. If a smectic *C* modification turns to a nematic one, transient stripes in form of a " myelin texture " are often visible.(25,36,96) This " myelin texture " is probably due to a heterogeneous region. Transition phenomena, mostly stripes which broaden into larger areas (" transition bars ", Ref. 33), are visible at the transition smectic *A* to *B*.(53,66) They are due to impurities and do not appear in very pure substances.

Sometimes the transition phenomena point to the symmetry of the new modification. For instance, nematic liquids come from the isotropic ones in the form of the well-known droplets,(51) while smectic *A* form " batonnets " which grow into a focal conic texture.(51) Sometimes smectic *A* also appears as droplets which are pseudoisotropic and coalesce to the pseudoisotropic texture. Smectic *B* may grow out of the nematic modification in the form of star-like aggregates with 4 or more sharp points.(7,66) Smectic *D* appears in the *C* modification as regular quadrangles or hexagons which coalesce to the isotropic texture.(10)

3.10 Textures and the System Based on Miscibility Relations

We wish to emphasize that the textures of mixtures are in most cases scarcely altered with regard to the pure components. The

TABLE 2 Characteristics of the Types of Liquid Crystals

Type of modification	Optical properties	Textures	Structure	Examples
nematic	uniaxially positive	schlieren t. threaded t. marbled t. pseudoisotropic t. homogeneous t.	parallelism of long molecular axes	azoxyanisole, MBBA
cholesteric	uniaxially negative or isotropic, optically active	focal conic t. t. with Grandjean steps homogeneous t. isotropic t.	twisted nematic structure	cholesteryl butyrate
smectic *A*	uniaxially positive	focal conic t. (fan-shaped or polygon t.) stepped drops homogeneous t. pseudoisotropic t.	layer structure, molecular axes orthogonal to the layers, random arrangement within the layers	diethyl azoxybenzoate
smectic *B*	uniaxially or biaxially positive	mosaic t. stepped drops pseudoisotropic t. homogeneous t. schlieren t.	layer structure, molecular axes orthogonal or tilted to the layers, hexagonal arrangement within the layers	ethyl ethoxybenzylideneaminocinnamate, terephtalal bis butylaniline

smectic *C*	biaxially	broken focal conic t. schlieren t. homogeneous t.	layer structure, molecular axes tilted to the layers, random arrangement within the layers	dodecyloxy-azoxybenzene
smectic *D*	isotropic or anisotropic	isotropic t. mosaic t.	cubic structure	4′-Octadecyloxy-3′-nitrodiphenyl-4-carboxylic acid
smectic *E*	uniaxially positive(99)	mosaic t. pseudoisotropic t.	layer structure, molecular axes orthogonal to the layers, non random arrangement within the layers(99)	di-*n*-propyl-terphenyl-dicarboxylate
smectic *F*		schlieren t. broken focal conic t. with concentric axes	layer structure	2-(4-*n*-pentylphenyl)-5-(4-*n*-pentyloxyphenyl)-pyrimidine
smectic *G*		mosaic t.	layer structure with non random arrangement within the layers	2-(4-*n*-pentylphenyl)-5-(4-*n*-pentyloxyphenyl)-pyrimidine

liquid crystalline mixed phases in particular show no texture which is not known from a single substance.

Fortunately in many cases different phases also show different textures. Therefore, it is possible to determine phase transitions by texture analysis. Furthermore, it is possible during the investigation of a diagram of state of a binary system to establish the different phase regions purely by microscopic observation.

Sometimes the texture is only very slightly altered by the phase transition, but the transition is recognizable by means of temporary transition phenomena.

Especially in the case of very pure substances it may be very difficult to find all transitions in the smectic state by microscopic observations alone. Then it is advisable to use additional methods e.g. thermal analysis, density measurement etc.

Table 2 gives a survey of the different liquid crystalline modifications and their respective textures. In spite of the fact that nearly all modifications may occur in several different textures, there are some connections between the system of liquid crystals based on miscibility relations and the texture properties.

In optically inactive substances the simple focal conic textures (fan-shaped texture, polygon texture) are typically for smectic *A* modifications. Broken focal conic textures, and schlieren textures, which can be converted into broken focal conic textures, are typically for *C* modifications.

If the schlieren textures or marbled textures occur in modifications which exist at higher temperatures than *A* modifications, they indicate nematic modifications. These examples show how it is often possible to classify the liquid crystalline modifications by texture observation in connection with the variant of polymorphism, despite the several possible textures for one type of modification.

Attempts have been made to classify liquid crystalline modifications exclusively by means of texture observations (see for instance, Refs. 19, 30, 32, 33, 34). This procedure is often not without danger. Even the recognition of a nematic modification by observation of its schlieren texture, which at first seems to present no problem, may become doubtful, if we think of the schlieren textures of smectic *B*, *C* and *F*. For the classification of the liquid crystalline modifications texture observation alone in many cases is not sufficient.

4. Structure and Polymorphism of Liquid Crystals

4.1 GENERAL

As has already been mentioned, connections are to be expected between miscibility relations and structures on the one hand and connections between optical properties (textures, refraction indices) and structures on the other. In fact such connections have been discovered in liquid crystals. In the following we give a short description of the liquid crystalline structures and some remarks concerning these connections.

Most of the knowledge about these structures is based on X-ray diffraction studies. In addition to this, optical NMR and ESR investigations have yielded some information.

4.2 NEMATIC MODIFICATIONS

Nematic liquid crystals differ structurally from isotropic liquids only in the parallel orientation of the long axes of their molecules.(74)

Near the transition point to a smectic liquid crystal, there may be an additional ordering phenomenon. Pretransition effects, such as unusually high values of the molar heats(40) and the elasticity coefficients,(36,97) support the idea of the existence of cybotactic groups.(39) These cybotactic groups may be considered as arrangements of a certain number of molecules in a " smectic-like " way, but different from the true smectic structures these groups have narrowly limited dimensions.

4.3 CHOLESTERIC MODIFICATION

Cholesteric liquid crystals may be considered as a special variant of nematic liquids (twisted nematic liquid), which occur in optical active substances.(41,75) This statement has been proved by changing the nematic liquid into a cholesteric one by doping it with small amounts of optically active materials(51,77,78,83) or artificial twisting imposed by boundary effects.(51,79,80) Reverse, cholesteric liquids can be altered to nematics by strong magnetic or electric fields.(41) Mixtures of dextro and laevo substances usually yield cholesteric liquids, but in special cases as " compensated mixtures "(41,76) or racemates(9,81,82,94,98) also nematic liquids.

4.4 SMECTIC *A*

In the smectic *A* modification, the molecules are arranged in layers. The long axes lie parallel to one another, their direction being normal to the plane of the layer. The distribution of the molecules within the layer is irregular.(12,85,88,89)

Smectic *A* modifications behave optically positively uniaxially.(28) Sometimes the layers may be planar (stepped drops, pseudoisotropic or homogeneous texture). Through the influence of weak forces it is possible to obtain the smectic *A* with curved layers (focal conic textures).

4.5 SMECTIC *B*

The molecules are arranged in layers with parallelism of the long axes.(12,85) Within the layers the centres of gravity of the molecules are probably close-packed hexagonal. Two different structures of smectic *B* are known:(19)

1) The long axes lie normal to the planeof the layers. Therefore positive optical uniaxial character has been found.(28)

2) The long axes are tilted with respect to the plane of the layer. Positive optical biaxial character has been observed.(54)

So far very few detailed structure investigations of smectic *B* have been made. Levelut and Lambert(19) examined one substance each with the normal and the tilted *B* modification. In the diagram of state of the binary system these two modifications are connected by an uninterrupted series of mixed liquid crystals.(54) The optical character continuously changes from uniaxial to biaxial.(54) De Vries(26) investigated a substance with a so-called " *H* modification ". The structure of this modification corresponds to the tilted *B* structure; the typical texture is a mosaic texture. Therefore it does not seem improbable that this modification should be a smectic *B* modification. But for a definitive classification miscibility investigations are urgently needed.

4.6 SMECTIC *C*

The structure seems to correspond to smectic *A* with the one difference that the long axes of the molecules are tilted with respect to the planes of the layers.(60–65) The tilt angle may be constant or temperature dependent. There are signs that the tilt angle may also depend on the experimental conditions.(44,45) It has been measured by means of X-ray,(63,64) ESR(61,62) and conoscopic(60) experiments. The optical character of smectic *C* is positively biaxial.(65)

The extremely low transition heats(87) and slight volume changes(7,86) at the *C*/*A* transition point to the closely related structures of these modifications. *C* structures may be twisted by the addition of optically active compounds or by boundary effects. These twisted *C* modifications behave optically in a similar way to cholesteric liquids.(9,27,94)

4.7 SMECTIC *D*

The *D* modifications possess a cubic structure. The lattice points are formed by arrangements with a greater number of molecules and may possess spheric symmetry.(42)

The optical isotropy is compatible to this model.(28) The intermediate occurrence of an anisotropic structure with a typical mosaic texture at the transition smectic *A*/*D*(10) is still a fact which needs further elucidation. (See also Sec. 3.5 (b)).

4.8 SMECTIC *E*

The *E* modifications form layer structures with the long axes of the molecules normal to the layer planes. Within the layers certain ordering parameters must exist, but the exact structure is so far unknown. As opposed to the X-ray diagram of smectic *B*, unoriented samples of smectic *E* show an inner sharp ring with its second order and three sharp rings at larger angles (smectic *B* only one sharp outer ring).(42)

Conoscopic measurements indicate optically positive, uniaxial behaviour, which is a proof of the normal orientation of the long molecular axes with respect to the layer planes. (See " added in proof " in Ref. 99).

4.9 SMECTIC *F*

Smectic *F* has a layered structure which is closely related to smectic *C*. The X-ray diagrams (non-oriented probe : sharp inner ring corresponding to the layer thickness, diffuse outer ring corresponding to the molecular distance within the layers) and the texture phenomena (see Table 2) show only slight differences compared with smectic *C*.(22)

Further investigations are needed for an exact structure description.

4.10 SMECTIC *G*

Smectic *G* forms a layer structure. The X-ray diagrams of non-oriented samples show apart from the sharp inner ring corresponding to the layer thickness, several outer rings.(22) X-ray diagrams of this kind have never been found in other types of liquid crystals. This points to additional order parameters within the layers similar to solid crystals. But there are some arguments for the liquid crystalline character of smectic *G*: the occurrence of the typical mosaic texture; the plastic behaviour; the lack of super-cooling at the transition smectic *F*/*G* and *C*/*G*; the occurrence of a remarkable broad concentration range in mixtures with a chemically different compound.(22)

5. The System of Liquid Crystalline Modifications, Miscibility and Structure

The question of the existence of a system of liquid crystalline modifications is connected with the question of whether there is a system of the structures of the liquid crystalline state. With regard to this, the difficulty arises as to how to define the conception " liquid crystal ", which stems from experimental phenomenology.(93) We shall have to wait for further experimental and theoretical work on the problem of the structures of the " middle order " before it will be possible to give an exact definition of this or, if necessary, a new term.

So far only the structures of nematic, cholesteric, smectic *A* and *C* modifications are known with any certainty. Therefore the difficulties in the use of the concept " liquid crystal " concern the smectic modifications with a somewhat higher state of order and mainly their difference compared with " plastic crystals ".

Coming from the experimental position today we have at our disposal the system of liquid crystals treated above. The thermodynamically established miscibility properties do not allow a direct conclusion on structural facts.

Our general opinion has been explained in Sec. 2.4. In our system we have avoided a nomenclature with structural connotations.

Our knowledge of the structures of the liquid crystalline state as it is shortly described in Sec. 4 allows us to discuss the connections between the system of liquid crystals, based on miscibility properties, and the structure of the different types of modifications.

Two general statements are possible:

1) We have not found the same structures for modifications which belong to different types in our system.

2) The modifications of one type of our system seem to represent the same or closely related structures.

All nematic liquid crystals which represent one type of structure belong to one type of modification. But the cholesteric liquid crystals as a twisted variant of the nematic ones also belong to the same type, as has been proved by their complete miscibility relations. Similar relations exist between the ordinary and the twisted *C* modifications. In the case of *A* modifications only one structural type has so far been found. But the *B* modifications may occur in two structural variants: a layer structure with hexagonal packing of the molecules within the layers; the long axes may be oriented perpendicularly or tilted to the layer planes.

The rule of the sequence of liquid crystalline modifications (Sec. 2.3) may be considered as a rule of the existence of a reduction of order in steps with increasing temperature. The position of the *D* modifications is problematical in this connection.

This at least roughly verified apprehension of the connection between the modification type and the structure allows us to understand the existence of the system itself. As has long been known in the chemistry of solids, complete miscibility is favoured if the components represent the same structure.

As we have already explained,(46) in the liquid crystalline state there exist greater possibilities for variations of quantitative parameters such as molecular size or intermolecular forces, without preventing the existence of complete miscibility. For this reason, in the liquid crystalline state, the complete miscibility of modifications with the same or closely related structures occurs so often, that it can be used for the establishment of a system of liquid crystals.

A few cases, however, indicate that also in the liquid crystalline state, due to great differences of intermolecular forces as expressed by great differences in the melting and clearing points and great differences in molecule lengths, complete miscibility is prevented. With increasing state of order—generally speaking in the sequence: isotropic, nematic, smectic, solid—the possibilities for variations of the components in systems with complete miscibility seem to be more restricted.

Until now all investigated aromatic liquid crystalline substances have shown complete miscibility in the isotropic state. Regions of complete miscibility in the nematic state are very seldom missing but in the smectic state frequently.

Furthermore we found that the substitution of strong polar groups into aliphatic and aromatic compounds, for instance in soaps, prevents complete miscibility with the nonpolar organic compounds(57,58) The neat modifications of the soaps and the *A* modifications of the non-saltlike organic compounds exhibit the same textural peculiarities; structural similarities are also evident. Because they are usually not completely miscible in the isotropic state, it is not surprising that complete miscibility is lacking in every case in the liquid crystalline state.

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