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## The Polymorphism of Liquid Crystals

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# The Polymorphism of Liquid Crystals

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**Abstract**—120 substances with one or more liquid crystalline phases have been studied in 180 binary systems by the combined examination of the relations of miscibility and the observation of the textures by means of a micro heating stage. The examinations enable us to give two systems of liquid crystalline phases. The system based on the observation of the textures corresponds with the system based on the relations of miscibility. All liquid crystalline phases investigated can be divided into four groups, one nematic, and three smectic; the latter being called A, B and C. Some facts point to structural differences between the three smectic groups.

## 1. Introduction

Anisotropic liquid states are formed by about 1700 compounds which are almost exclusively organic in nature. These anisotropic liquid states have been classified into two main groups which are called smectic and nematic states. This classification was originally made on the basis of the characteristic phenomena of the liquid crystalline phases by means of microscopic observation with polarized light. These optical phenomena will be called textures.

Meanwhile we have enough facts available to understand principally these two groups as structural variations of the liquid crystalline state. By interaction of the intermolecular forces and the thermal movement there arise arrangements in layers of the strong formanisotropic molecules. These are the smectic phases. In the nematic phases there is only an orientation of the long axis of the molecules around one main direction.

One may say that our knowledge of details with regard to macroscopic and molecular characterization is still in its initial stage. Today comprehensive experimental researches by different methods are limited to relatively few substances which are easy to prepare. Extensive comparative investigations have only been

done by those who have synthesized substances with liquid crystalline phases: e.g. Vorländer<sup>1</sup> and Weygand<sup>2</sup> and recently Gray.<sup>3</sup> Their results give the basis for a knowledge of the functional connection between chemical constitution and the appearance of liquid crystalline states.

Generally only one physical constant of the substances has been determined, and these constants are the transition points and their trends in homologous series with variation of the number of atoms in the carbon chain. These trends often show a remarkable simplicity<sup>3</sup> and this points to the existence of related groups of liquid crystalline phases.

One can now ask whether there are relationships between the liquid crystalline phases which on the one hand exceed the relationships existing in homologous series and on the other allows us to specify the general division into nematic and smectic phases. This is suggested by the fact that there are substances available which have more than one smectic modification.

TABLE 1 General Scheme of the Polymorphism of Liquid Crystalline States

		clpt	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>
a)	is	n			
b)	is	s			
c)	is	n	s		
d)	is	s <sub>I</sub>	s <sub>II</sub>		
e)	is	n	s <sub>I</sub>	s <sub>II</sub>	
f)	is	s <sub>I</sub>	s <sub>II</sub>	s <sub>III</sub>	
g)	is	n	s <sub>I</sub>	s <sub>II</sub>	s <sub>III</sub>

Table 1 gives the polymorphism of the liquid crystalline phases of the known compounds. The liquid crystalline phases are given from left to right as the phases appear out of the isotropic (is.) phases as the temperature decreases. The temperature at which the transition of the isotropic state into the respective liquid

crystalline state (nematic  $n$  or smectic  $s$  states) or inverse takes place is called the clearing point (clpt). The transition temperatures between the liquid crystalline states are indicated with  $T_1, T_2, T_3$ .

In drawing up Table 1 no attention was paid to whether the liquid crystalline state lies in the supercooled region with respect to the solid state, since this is not relevant to the system of polymorphism. The designation of the smectic phases I, II, III, does not imply agreement in any of the characteristics, but only shows the succession of their appearance when the temperature decreases.

Today seven cases of liquid crystalline (l.c.) polymorphism are known: l.c. monomorphism, (a) nematic only (b) smectic only; l.c. dimorphism, (c) nematic, smectic (d) smectic, smectic; l.c. trimorphism, (e) one nematic and two smectic states (f) three smectic states; l.c. tetramorphism, (g) one nematic and three smectic states.

All the known compounds cannot be arranged into any of the special groups given in Table 1, because in many cases no description is available which would make it possible to arrange them either in the nematic or the smectic type.

The compounds of the type of soaps are not given in Table 1. Some of them show up to five, possibly smectic, modifications. Due to their high transition temperatures no comparative studies have been done so far. Also the optically active compounds which exhibit smectic as well as liquid crystalline phases with special texture, called cholesteric phases, have not been examined in the following experiments.

It is first necessary to examine more closely the physical properties of the known liquid crystalline polymorphic states which are given in Table 1. It was useful to use two methods which allowed us to examine a comprehensive range of materials with small quantities of substances in a relatively short period. The first method utilized a systematic study of the textures of the microscopic preparations under similar conditions. The second method utilized the examination of phase diagrams such as temperature-concentration diagrams of binary systems in order to find out the miscibility relationships between the liquid crystalline phases. Both these methods were used in conjunction with one another.

## 2. The textures of Liquid Crystalline Phases

The situation in the field of examination of textures of liquid crystalline phases has great similarity with that of the microscopic examination of solid metallic products. At a glance both show a large number of varieties. But a close examination of the microscopic pictures of metallic products shows relatively few major phenomena which can be differentiated from each other. We are a long way away from a well-founded knowledge of the texture phenomena of liquid crystalline phases.

Nevertheless the examination of texture has so far allowed us to differentiate between nematic and smectic states. Friedel<sup>4</sup> has put forward an explanation of these characteristic phenomena which are based on the structural specialities of both main groups of the liquid crystalline phases. The characteristics which enable a further specification of the textures of the polymorphic smectic states have not yet been worked out.

A present analysis in this respect combined with the previous results is now available. It has been necessary to limit observation to phenomena which are visible under similar conditions. For observation those products were used which were enclosed between a glass slide and a cover slip. Examination without a cover slip would allow textural alterations to occur which would render the picture less clear. Under these conditions we get first the following classification (especially 5. commun.<sup>5</sup>):

### A. Unspecific textures

- (a) Paramorphoses
- (b) Pseudoisotropy

### B. Specific textures

- (a) Nematic textures

The extreme variations are the "marbled textures" (marmorierte Texturen) and the nematic "schlieren textures" (Schlierentexturen).

## (b) Smectic textures

- ( $\alpha$ ) Focal conic textures  
(fan-shaped and polygon textures)
- ( $\beta$ ) Smectic schlieren textures
- ( $\gamma$ ) Mosaic textures

A. Unspecific textures do not allow the identification of liquid crystalline states.

(a) In case of transition the texture of the original phase can still remain unaltered to a great extent even after the complete transition. Such a case is called paramorphosis.

(b) In the case of pseudoisotropy the optical axis of a large range of liquid crystalline phases lies vertical to the boundary surface and thereby lies in the direction of view. There is no more double refraction to be observed. In many cases the pseudoisotropic layers are produced spontaneously or can be produced through shifting of the cover slip. Nematic pseudoisotropic preparations sometimes show flashes on different parts of the preparation. The use of pressure on the cover slips produces flashing of the whole surface and for a short period a specific texture can appear.

B. Specific textures allow us to identify the liquid crystalline states.

(a) The nematic textures were observed in different varieties. Extreme cases of this are the marbled textures (marmorierte Texturen) as shown in Fig. 1 and the schlieren textures (Schlieren-texturen) which are also called threaded textures (Fadentexturen). They are given in Fig. 2. The marbled texture leaves an unchanged impression for a long period, whereas the threaded texture shows a continuous movement of the optical discontinuities.

(b) ( $\alpha$ ) Very often the smectic texture appears in the form of a fan shaped texture (Fächertextur). This smectic texture does not require any special measures for preparation. It is so called because the lines of discontinuity are arranged in fan shape as shown in Fig. 3. Fan shaped textures are very often observed in the smectic state. The fan shaped textures change to the so-called polygon textures in case of thick layers or by adding certain products

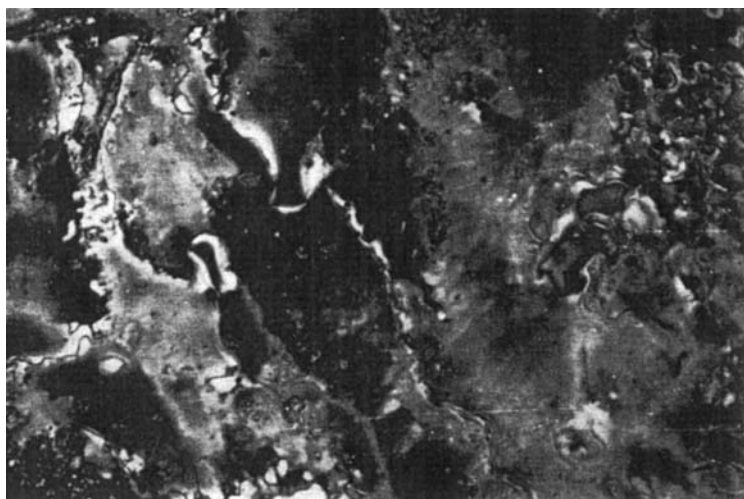


Figure 1. Nematic marbled texture.

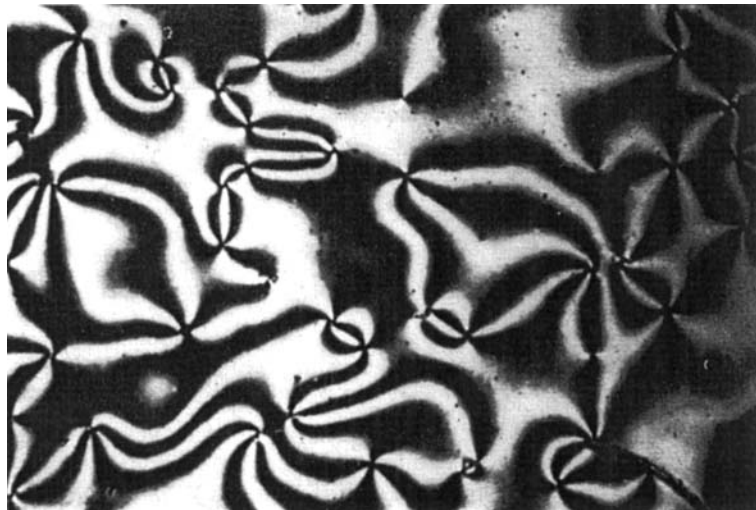


Figure 2. Nematic schlieren texture.

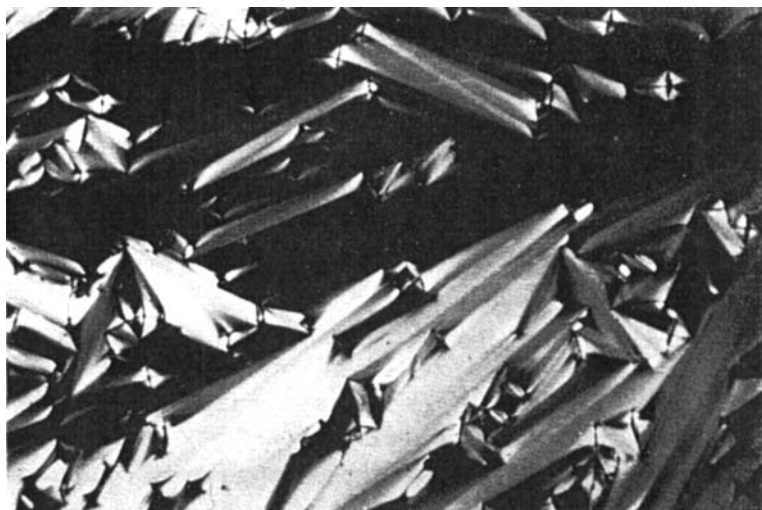


Figure 3. Smectic fan-shaped texture (simple form).

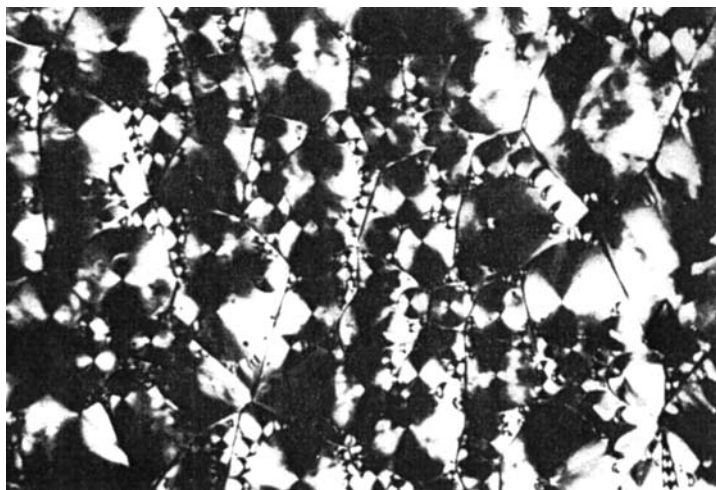


Figure 4. Smectic polygon texture (simple form).



(Fig. 4). In the polygon texture elliptically shaped discontinuities appear and are included in groups of polygons of discontinuity. Friedel<sup>4</sup> described these textures, which he recognized as having to do with focal conics of pairs of one ellipse and one hyperbola each.

( $\beta$ ) In the case of certain substances smectic textures can be obtained, especially by quick cooling of the melts, which are very similar to nematic schlieren textures. For this reason they are called smectic schlieren textures (Fig. 5). Continuous changes in detail can also be observed here.

( $\gamma$ ) A few substances showed textures which are given in Fig. 6 and are called mosaic textures (Mosaiktexturen). Larger almost optical homogeneous areas were observed which did not show any lines of discontinuity in their interior.

It is clear that in the case of unspecific textures a comparative examination can hardly be done. The formation of pseudoisotropy for example is observed very often and is an undesirable phenomenon.

The observation of specific textures, as given above, allows us to characterize the liquid crystalline state corresponding either to nematic or smectic groups. But this situation with regard to the problem has been known for a long time. This division of nematic and smectic textures can also be obtained without keeping to the observation of the substance enclosed between a glass slide and a cover slip, for example by the examination of the so-called stepped drops (Grandjean terraces).<sup>6</sup>

With respect to smectic polymorphism the question arises whether the textures which are given under B (b) are specific to certain types of liquid crystalline phases, so that classification of smectic phases can be done on the basis of their appearance. Especially those substances should be taken, in which more than one smectic state can be detected. The question arises with which texture change in this case the transformation of smectic phases occurs.

A comparison of Fig. 7 and Fig. 8 gives the difference in texture of the smectic high temperature (Fig. 7) and the low temperature

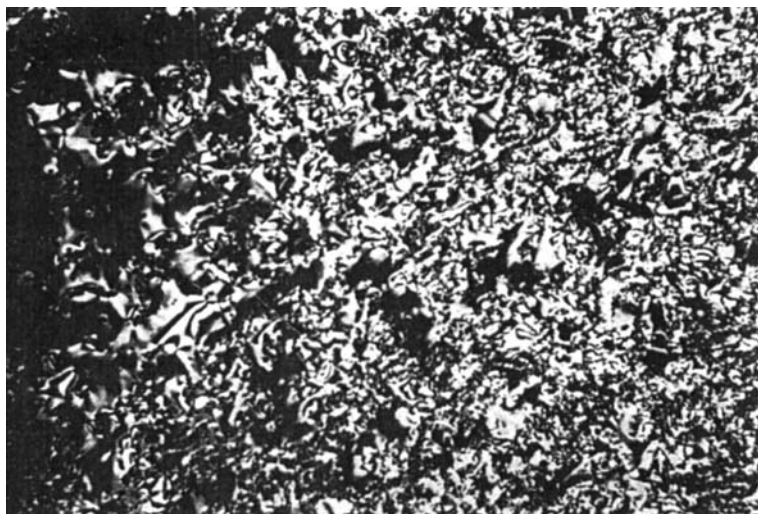


Figure 5. Smectic schlieren texture.

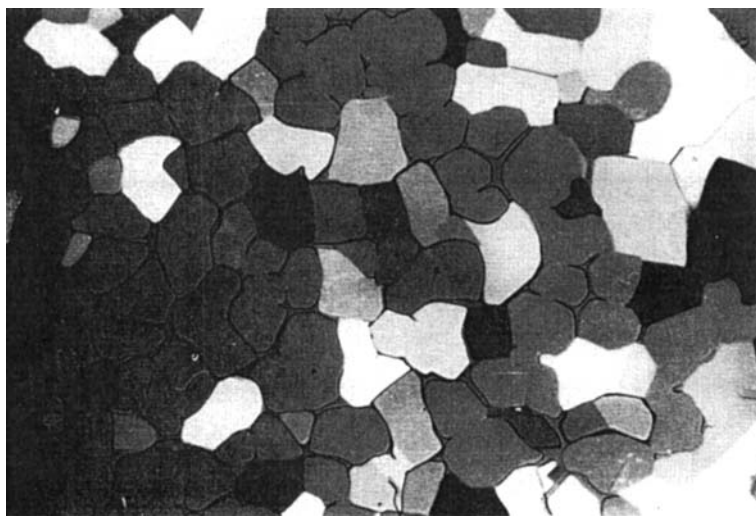


Figure 6. Smectic mosaic texture.

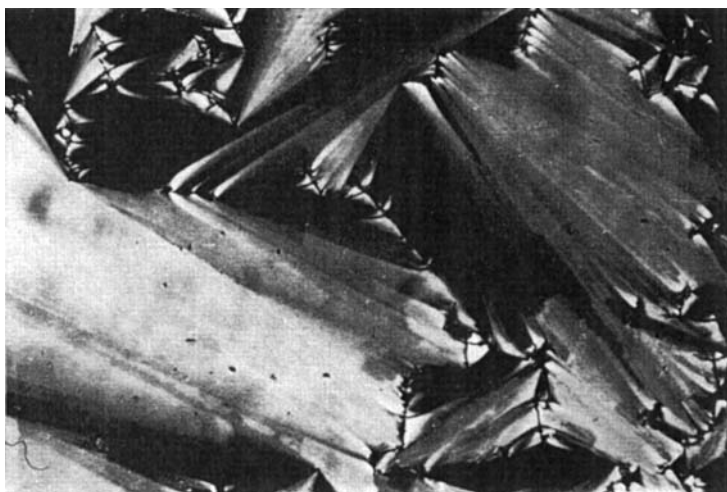


Figure 7. Smectic simple fan-shaped texture.

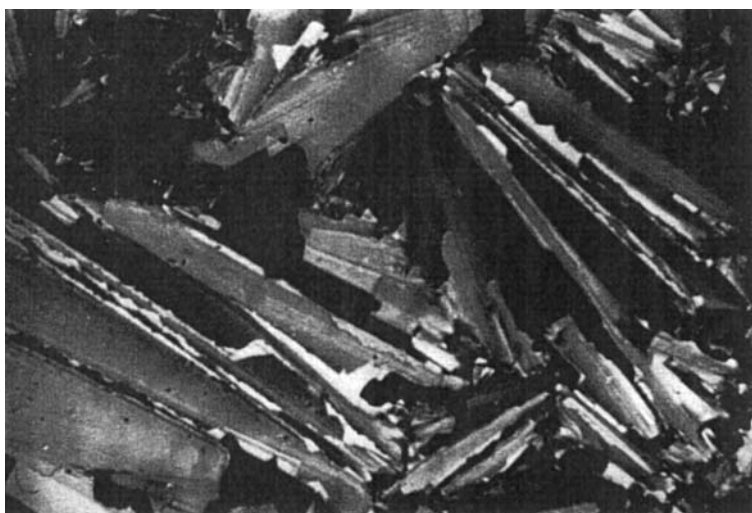


Figure 8. Smectic broken fan-shaped texture.

form (Fig. 8) of hexyl-*p*-azoxycinnamate. One can find more lines of discontinuity in Fig. 8 than in Fig. 7. There occurred a texture which we called the broken fan-shaped texture (durchbrochene Fächertextur). A change of this type was observed in a large number of smectic dimorphous products. The simple fan-shaped textures were always found in cases of smectic high temperature phases. The smectic monomorphous products show only either one or the other form of fan-shaped texture. As far as is known today, this phenomenon can also be observed in the case of polygon textures. In this the polygon variation (Fig. 4) of a simple fan-shaped texture changes into the broken polygon texture which corresponds to the broken fan-shaped texture. The formation of the simple fan-shaped texture and that of the simple polygon texture as well as the broken fan-shaped texture and that of the broken polygon texture can be used to characterize liquid crystalline smectic phases.

A further change in the fan-shaped texture by transforming smectic phases is given in Figs. 9 and 10 (ethyl-*p*-[4-ethoxybenzylidene amino]-cinnamate). The number of lines of discontinuity in the low temperature form has decreased.

The polygon texture appears with a decreased number of lines of discontinuity in the smectic low temperature state.

By prolonged heating a mosaic texture can be produced in such substances which generally show a fan-shaped texture with a decreased number of lines of discontinuity.

By changing the working procedure a smectic schlieren texture can be produced in some of the substances which generally show the broken fan-shaped texture or also the fan-shaped texture with decreased number of discontinuities.

Summarizing, one gets the following picture: Fan-shaped textures (f.sh.t.) and polygon textures (p.t.) are in general the texture variations of smectic phases, in which the formation of fan-shaped textures under the given conditions represents the normal case. In their formation as simple fan-shaped textures (simple polygon textures), broken fan-shaped textures (broken polygon textures), fan-shaped textures with decreased number of lines of

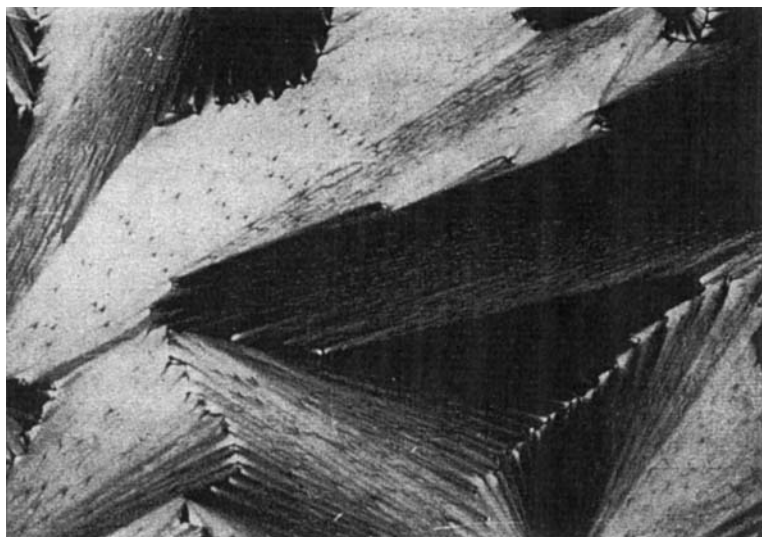


Figure 9. Smectic simple fan-shaped texture.

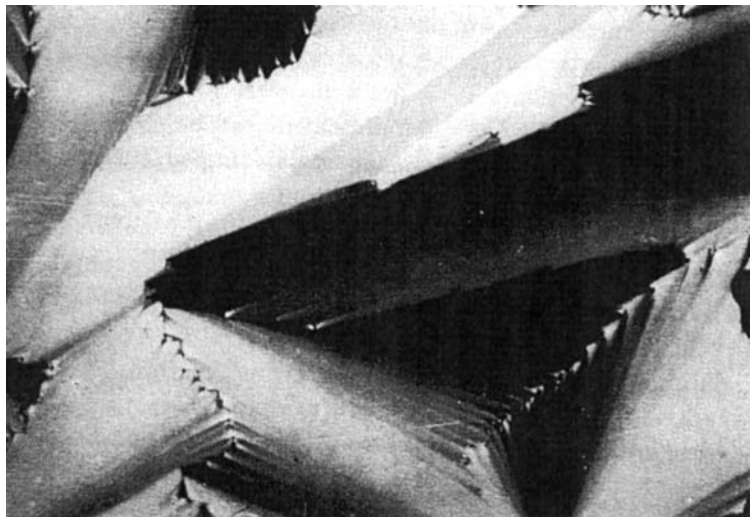


Figure 10. Smectic fan-shaped texture with diminished number of discontinuities.

discontinuity (and the analogous polygon texture), these textures represent typical phenomena of different smectic polymorphous phases. The phases which exhibit fan-shaped textures with a decreased number of lines can also exhibit the mosaic texture and the schlieren texture. The latter can also be observed in phases with the broken fan-shaped texture.

Thus in the liquid crystalline smectic forms which we have investigated we have found three texture groups A, B and C. These are summarized in Table 2. Each liquid crystalline smectic state we have observed appears in one of these texture groups only.

TABLE 2 Scheme of Texture Groups of Smectic Liquid Crystals

A	C	B
simple f. sh. t. simple p. t.	broken f. sh. t. broken p. t.	f. sh. t. } with decreased p. t. } number of lines mosaic t.
		schlieren t.

The description of the textures of systems with several components is important with respect to the following relations of miscibility between liquid crystalline states. The liquid crystalline mixed phases show no texture which is not identical with one of the textures mentioned.

### 3. The Relations of Miscibility Between Liquid Crystalline Phases

#### (a) THE EXPERIMENTAL METHODS

Thermal analysis is usually the favoured method for the examination of isobaric phase diagrams. The system of textures given in Section 2 can be used for the examination of phase diagrams. For this reason the microscopic examination of the preparations in polarized light on a micro heating stage was exclusively used. This allowed us to work with small quantities of substances and the use

of Kofler's contact method.<sup>7</sup> By the application of the latter it was possible to work out a comprehensive mass of material in a relatively short time.

These combined methods allowed the observation of the textures of the phases and of all their transition occurrences. They also enabled us to determine repeatedly the temperatures of the transitions occurring in the direction of increasing and decreasing temperature. The textures of the phases, which are in equilibrium, are different from each other. Due to this fact the displacement of the equilibrium is directly visible with regard to the changing relative quantities or the occurrence of three-phase reactions.

The favourable possibility of the observation of specific textures allows the use of the contact method in a comprehensive manner in ternary systems also. By this method it is possible to determine the basic shape of phase diagrams in only one procedure. For this purpose two substances in the isotropic or nematic state are put between a glass slide and a cover slip in such a manner that by diffusion a contact zone is produced. The preparation contains the complete possible concentration range which begins at the first substance and ends with the second substance. By changing the temperature one can determine the temperature of each transition which occurs in the contact zone between the two pure substances.† The contact method is limited because the concentration gradient in the contact zone is unknown. Consequently one can determine by this method only the temperatures, but not the concentration of the position of the transitions, which occur in the contact zone. One can complete the phase diagram and fix the concentration position of the transitions by the study of preparations which have singular concentrations.

† The microscopic method which was used for the investigation of the diagrams has been demonstrated by means of the colour film "The transition occurrences in a binary system with liquid crystalline phases" from H Arnold and H. Sackmann, Halle (Saale) 1958, film archive (Hochschulbildstelle) of the University of Halle. There are to be seen the transitions in the binary system of 4,4'-di-n-dodecyloxyazoxybenzene and 4,4'-di-n-octyloxyazoxybenzene (2. commun.<sup>5</sup>).

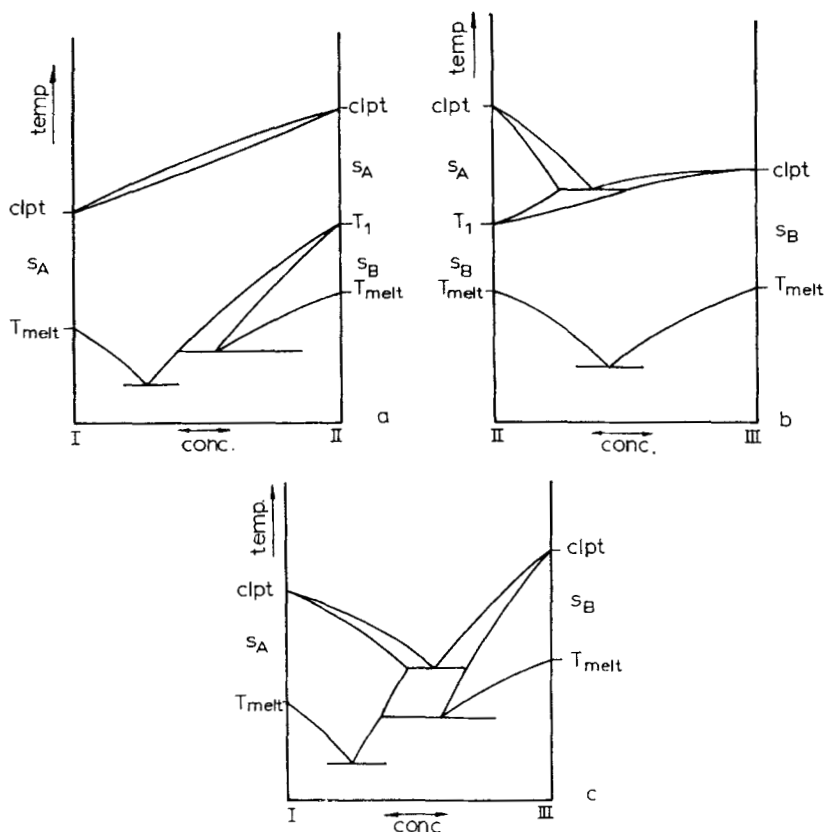


Figure 11. Demonstration of the method of marking liquid crystalline phases.

(b) THE METHOD OF PHASE CHARACTERIZATION BASED ON THE EXISTENCE OF UNINTERRUPTED SERIES OF MIXED LIQUID CRYSTALS

The attempt was made to mark with the same symbol all liquid crystalline phases between which an uninterrupted series of mixed crystals exists. This may be demonstrated by the three diagrams, which are schematically given in Fig. 11: substance I exhibits a smectic modification, which is arbitrarily marked with the symbol  $s_A$ . Substance II exhibits two smectic phases. The binary phase



diagram of the substances I and II is given in Fig. 11 under (a). The liquid crystalline phase region of substance I exhibits an uninterrupted series of mixed liquid crystals with the high temperature phase region of substance II. By virtue of this fact alone the liquid crystalline phase of substance II is marked also with the symbol  $s_A$ . Each phase of other substances which exhibits with one of the marked phases an uninterrupted series of mixed crystals is also marked with the symbol  $s_A$  and can transfer it in the same manner to other phases.

Because of the marking of the high temperature phase of substance II with the symbol  $s_A$ , the low temperature phase must have another symbol, here arbitrarily  $s_B$ .

The relations of miscibility of substance II with substance III are given in diagram (b). The liquid crystalline low temperature phase of substance II exhibits a complete series of mixed crystals with the liquid crystalline phase of substance III and for that reason the latter phase gets the same symbol.

It is necessary for the consistent use of this method that in the binary phase diagram of the substances I and III both phase regions  $s_A$  and  $s_B$  do not exhibit an uninterrupted series of mixed crystals. Therefore they must show a behaviour as given for example in diagram (c) in Fig. 11.

#### 4. The Results

So far 120 substances have been studied in 180 binary systems by the combined examination of the relations of miscibility and the observations of the textures.<sup>5</sup> The results may be summarized as follows:

(1) In the binary systems studied, all isotropic phases show complete miscibility.

(2) The liquid crystalline states show mutually selective relations of miscibility.

(3) The selective relations of miscibility in the liquid crystalline states may be specified in the following rule of selective miscibility: All liquid crystalline states 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 states which have the same symbol, in no case exhibit an uninterrupted series of mixed crystals with liquid crystalline states to another symbol.

(4) All liquid crystalline states whose characterization is based on the rule of selective miscibility, can be divided into two groups, the smectic and the nematic phases. The smectic phases require a further division into three groups, which have been marked with the symbol A, B and C.

(5) A division based on specific textures exists which corresponds with the group division of the liquid crystalline states based on the rule of selective miscibility. These textures are to be divided in the following manner (see also Table 2):

	nematic textures
	smectic textures
group A	ordinary fan-shaped texture (gewöhnliche Fächertextur) or ordinary polygon texture
group B	fan-shaped or polygon texture with diminished discontinuities mosaic texture smectic schlieren texture
group C	broken fan-shaped or broken polygon texture smectic schlieren texture

(6) If one substance exhibits both nematic and smectic states, then the nematic are the high temperature forms and the smectic are the low temperature forms.

(7) Most of the smectic states are marked with A on the basis of the criteria 3, 4, 5. They appear with decreasing temperature always from the isotropic or nematic melt, never from a smectic state which has another symbol.

(8) The smectic states which are marked with B were always found in the substances which exhibit also an A-phase.

(9) The smectic states which are marked with C were to be found

alone or also together with a nematic or a smectic A-phase. They are always low temperature forms.

(10). The substances which are smectic trimorphous, exhibit liquid crystalline phases with decreasing temperature in the following succession:

isotropic—nematic—smectic A—smectic C—smectic B.

The relations of polymorphism so far found and given in Table 1 can now be characterized in detail. Table 3 shows the progress with respect of our knowledge of the polymorphism of the liquid crystalline states, based on the experimental results which are briefly given in the points 1 to 10. Only case (f) has not been investigated so far.

TABLE 3 Detailed Scheme of the Polymorphism of Liquid Crystalline States

		clpt	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	
a)	is	n				
b <sub>1</sub> )	is	s <sub>A</sub>				
b <sub>2</sub> )	is	s <sub>C</sub>				
c <sub>1</sub> )	is	n	s <sub>A</sub>			
c <sub>2</sub> )	is	n	s <sub>C</sub>			
d <sub>1</sub> )	is	s <sub>A</sub>	s <sub>B</sub>			
d <sub>2</sub> )	is	s <sub>A</sub>	s <sub>C</sub>			
e <sub>1</sub> )	is	n	s <sub>A</sub>	s <sub>B</sub>		
e <sub>2</sub> )	is	n	s <sub>A</sub>	s <sub>C</sub>		
f)	is	s <sub>I</sub>	s <sub>II</sub>	s <sub>III</sub>	so far not investigated	
g)	is	n	s <sub>A</sub>	s <sub>C</sub>	s <sub>B</sub>	

This gives not only a specification of the separate groups from Table 1, for instance in group d by means of  $d_1$  and  $d_2$ . The marking of the smectic phases with A, B and C summarizes all identically marked phases on the basis of the given criteria—in contrast to the marking I, II and III in Table 1.

## 5. Discussion

If one tries to explain the results obtained one does best to begin with experience of the relations of miscibility in the solid state. An

uninterrupted series of mixed crystals is to be most readily expected, when the components of the system have molecules with the same or similar shape, similar chemical structure and, consequently, intermolecular interaction of the same quality. In the case of not very different sizes of molecules one can generally find the same lattice types (isotypic). As is known, even small differences in the size of the molecules prevent the occurrence of complete miscibility.

In the isotropic liquid state the limits for the existence of complete miscibility are generally to be drawn much wider. The fact of the existence of complete miscibility alone will permit few systematic conclusions. Working on a large scale one could obtain the well-known division into metal melts, electrolytic melts and non-electrolytic melts. The limitation of the molecular order to small regions (close range order) obviously enlarges to a great extent the possibility of the existence of homogeneous mixed phases between structurally differentiated components. Further in the isotropic liquid state the phenomenon of polymorphism is unknown, except for the liquid helium with its special peculiarities.

Looked at in this way, the conditions in the solid state are too narrow and in the isotropic liquid state too wide with respect to the occurrence of relations of complete miscibility. Examination of the latter will not produce any remarkable general systematic characterization. The state of order of the liquid crystalline phases lies midway between the "border states" solid and isotropic liquid.

In this way for instance the relations of miscibility of the members of the homologous series of the 4,4'-di-n-alkoxyazoxybenzenes (especially 2. and 7. commun.<sup>5</sup>), schematically given in Table 4 can be understood. This table gives under (a) the investigated binary combinations characterized by the number of carbon atoms of the alkyl-chains, under (b) the relationships of miscibility in the isotropic, liquid crystalline and solid (sd) states. The uninterrupted series of miscibility found between the phases of the components are indicated by lines. There are always complete series of miscibility between the isotropic liquid states and complete series of mixed liquid crystals, if the two components exhibit either smectic or nematic or both liquid crystalline phases. An uninterrupted series

of mixed liquid crystals has in no case been found between smectic and nematic phases. This is in accordance with the rule of selective miscibility no. 3 in Section 4. All smectic phases in this homologous series have the symbol C. But in the solid state an uninterrupted series of mixed crystals is only to be found between numbers with a ratio of the sizes of the molecules near 1 as in the combinations  $C_8$ - $C_9$ ,  $C_8$ - $C_{10}$  and  $C_{11}$ - $C_{12}$ .

TABLE 4 Relations of Miscibility in the Homologous Series of the 4,4'-di-n-Alkoxyazoxybenzenes

a	2 3	2 8	4 8	4 10	7 12	8 9	8 10	8 12	11 12
b	is - is	is - is	is - is	is - is	is - is	is - is	is - is	is - is	is - is
	n - n	n - n	n - n	n	n	n - n	n - n	n	n
	s	s	s	s	s - s	s - s	s - s	s - s	s - s
	sd sd	sd sd	sd sd	sd sd	sd sd	sd - sd	sd - sd	sd sd	sd - sd

The existence of liquid crystalline states is connected with a more special molecular structure. It is still impossible to lay down definitive relations between the occurrence of liquid crystalline states and chemical structure, but in the main these are substances with strong formanisotropic molecules with strong hindrance of intramolecular mobility. These products are predominantly non electrolytic in character. Except for the higher melting soaps, molecular shape and energy parameters of the interaction are so similar that in the isotropic liquid state complete miscibility is always to be found.

Apart from one exception an uninterrupted series of liquid crystals also exists between nematic phases and is to be understood from its structure. The incorporation of molecules of different length into states which are only characterized by one main direction of the orientation of their long-shaped molecules, should be possible within the wide scope found in the variations of the molecules which exhibit liquid crystalline phases.

One can expect a limitation of the conditions for the occurrence of uninterrupted series of mixed crystals by changing to the smectic states with a layer arrangement of the molecules.

It seems to be a useful working hypothesis to assume a connection between the classification of the smectic states which we found and the existence of different molecular arrangements in the smectic layers.

In this connection it is noteworthy that the A-phases in the case of smectic polymorphism are the high temperature forms. This seems to be important with respect to the given gradual decrease of order with increasing temperatures. Probably the A-phases are identical with those smectic states which Friedel supposed to be the only ones. Friedel<sup>4</sup> based his texture observations on substances having A-phases according to our present classification.

Only a few A-phases have been examined by X-ray diffraction.<sup>8, 9</sup> The molecules are arranged parallel in layers, their distribution with respect to lateral direction is statistical. The other smectic states then account for more special arrangements of a higher order within the layers. With this the A-phases have a certain exceptional position, for it is to be supposed that the statistical distribution within the layers is produced by the higher thermal mobility of the molecules. So the appearance of the A-phases as smectic high temperature phases is understandable.

The general condition for the occurrence of uninterrupted series of liquid mixed crystals, then, would be the existence of smectic structures of the same kind. The parameters of energy and size can vary extensively according to the lower state of order compared with the solid state, without preventing the uninterrupted series of miscibility. There are only very few cases without the existence of an uninterrupted series of mixed liquid crystals between identically marked smectic phases.

Because of the general connection between double refraction and structure of matter our present texture system points to a structural connection between phases with the same characteristics of texture, especially because there is a coincidence (see no. 5 in Section 4) of texture characteristics of the liquid crystalline phases with their miscibility characteristics. But an explanation of the given texture characteristics on structural backgrounds is needed urgently. To-day no explanation between texture and structure of phases is

known beyond that of Friedel. Nor has any connection between the varieties of textures in the groups (Table 2) been established.

The system given here of the polymorphous liquid crystalline states indicates the present position of our researches. It is neither complete nor definitive. The occurrence of further smectic forms is doubtless to be expected.

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