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ORIGINAL CONTRIBUTION

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Electron and light microscopical investigation of defect structures in mesophases of pharmaceutical substances

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Abstract Transmission electron microscopy of freeze fractured and replicated samples (TEM) and polarizing light microscopy (PLM) are used to investigate the defect structures of the thermotropic and lyotropic mesophases of the non-steroidal antiinflammatory drug fenoprofen sodium and of the thermotropic mesophase of the nonionic surfactant sucrose oleate (O1570). All mesophases have a layered, smectic structure. The thermotropic liquid crystal of fenoprofen sodium is an interdigitated smectic A phase (smectic Ad) having the highest viscosity of the investigated samples. The thermotropic mesophase of the sugar ester is also of the type smectic A, likely to be of subtype smectic A2 (bilayered smectic structure). The lyotropic mesophase is of lamellar liquid crystalline nature and has a much lower viscosity than the thermotropic mesophases. In the PLM the lyotropic fenoprofen mesophase has a strong tendency to form a pseudoisotropic texture, indicating a strong tendency to form undisturbed layered structures. Other textures exhibited in the PLM are fan-shaped texture and maltese-cross texture. Confocal domains, cylinders, pits and peaks as well as screw dislocations are found in great number in the TEM. However, no greater regions of undisturbed lamellar arrangement in the lyotropic mesophase could be detected. The only texture of the thermotropic fenoprofen mesophase visible in the PLM is the fan-shaped texture, indicating confocal domains as predominant structural elements. However, no confocal domains (tori or Dupin cyclides) are found in the TEM. In the PLM the sugar–ester mesophase exhibited a fan-shaped texture, maltese crosses and oily streaks as dominant textures. In the TEM only a few $+\pi$ and $-\pi$ disclinations and imperfect confocal domains could be detected. The discrepancies in the appearance of defect structures and textures between the mesophases as well as the discrepancies in the findings in the PLM and in the TEM investigations are caused by the different sample preparation and the different viscosities of the mesophases.

Key words Fenoprofen sodium – sugar esters – defect structures – thermotropic mesophase – lyotropic mesophase – transmission electron microscopy – polarizing light microscopy

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Introduction

Defects can be defined as every deviation from the strictly periodic arrangement of ions or molecules in a crystal. If the concentration of defects is low, they have to be regarded as mistakes in the regular formation of the crystalline order. If, however, the defect concentration is high, defects have to be considered as a fundamental part of the structure of the crystalline substance [1]. In mesophases the degree of order is considerably lower than in crystals. Lyotropic lamellar mesophases as well as thermotropic smectic A phases have a layered structure with a random molecular packing within the layer planes. Due to the fact that they form a layered structure they have a one-dimensional positional long-range order in addition to the one-dimensional orientational long-range order of the nematic mesophases [2]. As the mobility of the molecules within the layers is high, these types of mesophases have a liquid character in two dimensions (within the layer plane), and can be regarded as being crystalline with respect to the third dimension. A nonstriking finding, therefore, is that defect structures exist also in mesophases and that their concentration is much higher than in solid crystals [3]. Defects in liquid crystals certainly are essential for the mesomorphic phases. In case of thermotropic and lyotropic smectic mesophases, defect structures must be compatible with the layered structure of the liquid crystal. Point defects, i.e. zero-dimensional defects such as Schottky- or Frenkel-defects, may appear in smectic mesophases in higher concentration than in solid crystals, due to the higher mobility of the molecules [3]. However, in a thermotropic smectic A or a lyotropic lamellar mesophase, it may not be appropriate to discuss the appearance of point defects, as these types of mesophases have a liquid character in two dimensions and also do not show a correlation of the molecules from layer to layer, as it is found in higher-ordered smectic mesophases [2]. Point defects cannot be visualized by TEM and also do not exhibit a texture in the PLM. They will therefore not be discussed in this study.

Linear, i.e. one-dimensional defects, can exist in smectic mesophases as both, translational and rotational dislocations, the latter ones are also called disclinations [3]. Translational dislocations, that are compatible with the layered structure of the smectic mesophase are edge and screw dislocations. Possible disclinations are $+\pi$ and $-\pi$ disclinations as well as a combination of $+\pi$ and $-\pi$ disclination (planar structures), and cylinders (2π disclinations), tori and Dupin cyclides (nonplanar structures) (Fig. 1). The torus is a special case of the Dupin cyclide and both can be summarized as confocal domains. In a well-formed cyclide the disclination line L2, a hyperbola, passes through one of the foci of the disclination line L1, which is an ellipse. One of the apices of the ellipse, on the other hand, coincides with the focus of the hyperbola. In a torus the ellipse is changed into a circle and the hyperbola is changed into a straight line. This geometry has the advantage of preserving the thickness of the layers [4].

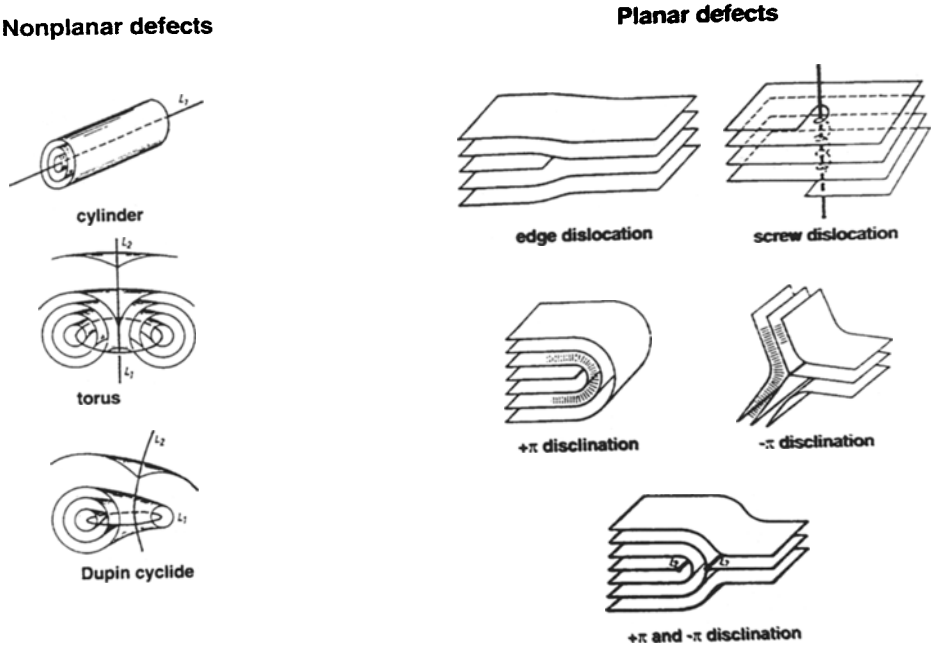


Fig. 1 Planar and nonplanar defects, compatible with a layered structure (after [3] and [4])

In principle, all one-dimensional defects in layered mesophases can be visualized by TEM. However, due to the small Burgers vectors of the translational dislocations, these may be difficult to detect, if the spacing of the smectic mesophase is small, i.e. if it is near to the maximum of resolution of the electron microscope. The disclinations are defect structures with a much bigger size and therefore can easily be detected in the TEM. The disclinations also cause characteristic textures (optical appearances of the mesophase) in the PLM, which will be discussed in connection with the findings in this study.

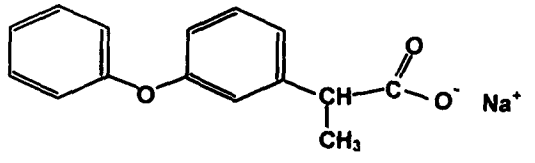
The aim of the present study is to investigate, if different thermotropic and lyotropic smectic mesophases of pharmaceutical substances exhibit the same defect structures and if for the same mesophase, textures in the PLM can be related to structures in the TEM.

Materials and methods

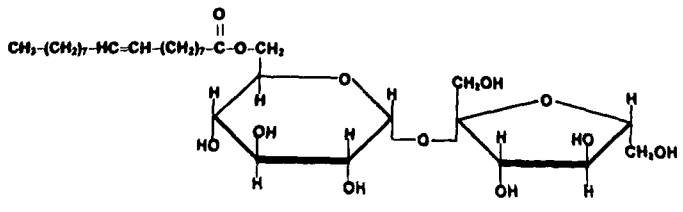
Materials

The structural formulae of the used mesogens are shown in Fig. 2. *Fenoprofen sodium* and *fenoprofen acid* are prepared from fenoprofen calcium (Eli Lilly, Gießen, Germany). The calcium salt is dispersed in an aqueous HCl-solution (10% w/v). To extract the free acid, the dispersion is shaken several times with dichloromethane. After evaporation of the dichloromethane, fenoprofen acid is obtained as a clear, yellow liquid of which the refractive index is 1.569.

Fig. 2 Structural formulae of (a) fenoprofen sodium and (b) sucrose monooleate (main component in O1570)



a) structural formula of FNa



b) structural formula of a sugar ester

According to the Merck Index the refractive index is 1.574 [5]. To prepare the sodium salt, the acid is dissolved in an equimolar amount of 1 N NaOH. The solvent is evaporated until fenoprofen sodium crystallizes as a dihydrate with a water content of 12%, determined by thermogravimetry (TGA 2/TADS 3600, Perkin-Elmer, Überlingen, Germany) and by Karl–Fischer titration (701 KF Titrino/703 Ti, Metrohm, Herisau, Switzerland). The melting point of the sodium salt in a closed system, determined by DSC is 79 °C (DSC2-C/TADS 3600, Perkin-Elmer, Überlingen, Germany).

Sucrose oleate (O1570, Ryoto Sugar Esters, Mitsubishi-Kasay Foods Corporation, Tokyo, Japan) is used without further purification (HLB 15; purity of fatty acids: ~70% oleic acid; ester composition: ~70% mono ester, ~30% di, tri and poly esters, melting range: 27–43 °C, decomposition temperature: 227 °C [6]; water content at room temperature: 2.2%, determined by Karl–Fischer titration).

Water is used in double-distilled quality.

Methods

Sample preparation

No special sample preparation is necessary in case of the investigation of the thermotropic mesophases, as these are formed from one-component systems. The lyotropic mesophases are formed at room temperature by mixing different amounts of fenoprofen sodium, fenoprofen acid and water. The components are either mixed at room temperature to form the liquid crystal or are mixed and subsequently heated to 70 °C, to form an isotropic solution. In this case, the lyotropic mesophase forms during the cooling of the isotropic solution to room temperature. A mixture of fenoprofen sodium 40% (w/w), fenoprofen acid 25% (w/w) and water 35% (w/w) resulted in a monophasic liquid-crystalline system. Details of the ternary phase diagram of fenoprofen sodium, fenoprofen acid and water are reported in refs. [7, 8].

Polarizing light microscopy

A Photomikroskop III (Zeiss, Oberkochen, Germany) is equipped with crossed polarizers and a λ-sheet (phase difference 550 nm). For hot-stage investigations, a heating and cooling device (FP 5/FP 52, Mettler AG, Gießen, Germany) is inserted into the optical bench. Thermotropic samples of fenoprofen are investigated at 125 °C and 145 °C, the thermotropic mesophase of the sugar ester O1570 is heated to 180 °C. The thermotropic samples of

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fenoprofen sodium are investigated on an object slide without cover glass, in order to allow rapid and complete evaporation of the hydrate water. The evaporation of the water is a prerequisite for the formation of the thermotropic mesophase [9]. The thermotropic mesophase of O1570 as well as the lyotropic mesophase of fenoprofen are investigated on an object slide with cover glass. Lyotropic samples are observed at room temperature.

Transmission electron microscopy

The thermotropic samples are heated directly on the lower part of a copper sample holder to the same temperatures as in the PLM investigations (Kofler-Mikroheiztisch, C. Reichert, Wien, Austria). The upper part of the sample holder is heated to the same temperature and is placed on the sample just prior to the cryofixation of the sample with liquid propane, using a maximal preheated jet-freeze device (JFD 030, Balzers Wiebaden, Germany). The frozen samples are freeze fractured at $-100\,^{\circ}C$ at a pressure of 5×10^{-6} bar (BAF 400, Balzers, Wiesbaden, Germany). Shadowing of the samples is performed with platinum/carbon (layer thickness 2 nm) at 45° and with carbon (layer thickness 20 nm) at 90°. The replica are cleaned with chloroform/methanol (1:1 (v/v)) and water. Replica on uncoated grits are viewed with a transmission electron microscope at 80 kV (EM-300, Philips, Kassel, Germany) at various magnifications.

Fig. 3 PLM photograph of the lyotropic lamellar mesophase of fenoprofen: (a) mesophase formed by cooling a heated, isotropic solution: homoeotropic texture and fan-shaped texture, (b) mesophase formed by mixing the components at room temperature: spherulitic texture, birefringent stripes and pseudoisotropic texture

X-ray diffraction

Small- and wide-angle X-ray diffraction are performed using a Mueller Micro 111 generator (45 kV, 20 mA), with a tube PW 2253/11 (wavelength 0.154 nm, copper as anode material, Ni filter; Philips, Kassel, Germany). For the wide-angle measurements a goniometer PW 1050/25 (Philips, Kassel, Germany) equipped with a scintillation counter Type A (Siemens, Karlsruhe, Germany) as detector are used. The small-angle measurements are performed with a Kiessig camera (of our own construction) equipped with a Braun 50 PSD (Braun, München, Germany) as detector. The sugar-ester samples are preheated to 180 °C in the sample-holder and immediately investigated.

Results and discussion

Lyotropic mesophase of fenoprofen

The lyotropic mesophase of fenoprofen has a lamellar structure with a spacing of 2.8 nm, determined by small-angle X-ray diffraction [8]. The molecules are oriented in bilayers (the length of a single fenoprofen molecule is about 1.1 nm [8]) perpendicular to the layer plane. This can be concluded from the strong tendency of the mesophase to appear in pseudoisotropic or homoeotropic texture. This texture emerges, when the initial birefringence of the mesomorphous sample disappears with time. If the sample is sheared, the birefringence returns but vanishes again, at least partially, after some minutes. The reason for this behavior is that the layers of the lamellar mesophase orientate themselves parallel to the layer plane. If the molecules are arranged perpendicular to the layer plane, the optical axis of the liquid crystal is oriented parallel to the propagating light and subsequently no birefringence can be developed. Like a few other mesogens, e.g. certain cinnamates [3], lyotropic mesophases of fenoprofen strongly tend to form such homoeotropic textures (see Fig. 3). As the pseudoisotropic texture corresponds to undisturbed lamellar structures, those structures could be expected to be found in the TEM investigations in great areas of the sample. Figure 4 shows a TEM photograph of

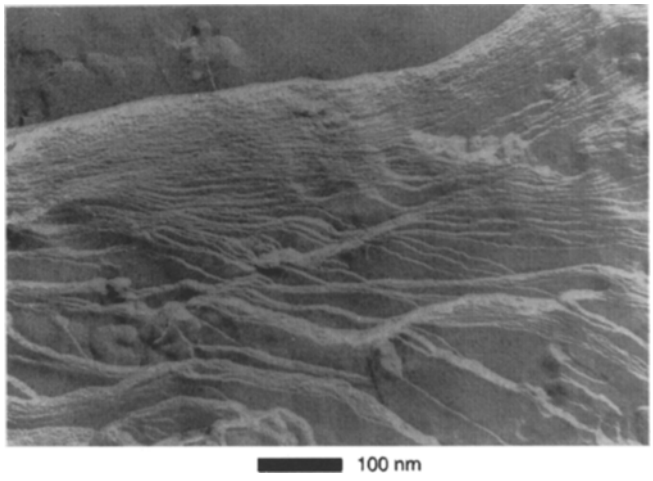

Fig. 4 TEM photograph of the lyotropic lamellar mesophase of fenoprofen: undisturbed lamellar structures

such a rather undisturbed lamellar arrangement of the mesophase. However, no greater regions, free of disclinations could be detected in the TEM investigations, so that the structural appearance of the liquid crystal in Fig. 4 has to be regarded as rather exceptional.

By careful investigation of the layers of the lamellar mesophase at a higher magnification, it can be observed that some layers suddenly seem to disappear, if the fracture is nearly parallel to the layer plane (Fig. 5). These findings can be interpreted as a visualization of a screw dislocation, penetrating the layer and leaving a step in the surface. Screw dislocations are defects of small Burgers vector. They were first observed in mesophases in the lamellar liquid crystal of phospholipids by Kléman and Williams [4] and can be found in the undisturbed parts of the samples investigated. On the other hand, no edge dislocations can be detected in the lamellar mesophase of fenoprofen. This too is in agreement with the investigations of the phospholipid liquid crystal and the reason for the absence of edge dislocations could be the same as discussed in ref. [4]: A screw dislocation does not change the spacing of the layers, while an edge dislocation does. Changes in the layer spacing would lead to a much higher impact of energy into the system, which subsequently would lead to a transformation of the edge dislocation into other defect structures [3]. However, one has to keep in mind that the thickness of the layers in case of the lamellar fenoprofen mesophase is only about 2.8 nm, being near to the maximum resolution of the TEM used in this investigation. In the PLM neither screw nor edge dislocations would exhibit a special texture, i.e. both are compatible with the pseudoisotropic texture.

The defect structures most frequently found in the freeze-fractured samples of the lamellar liquid crystal are

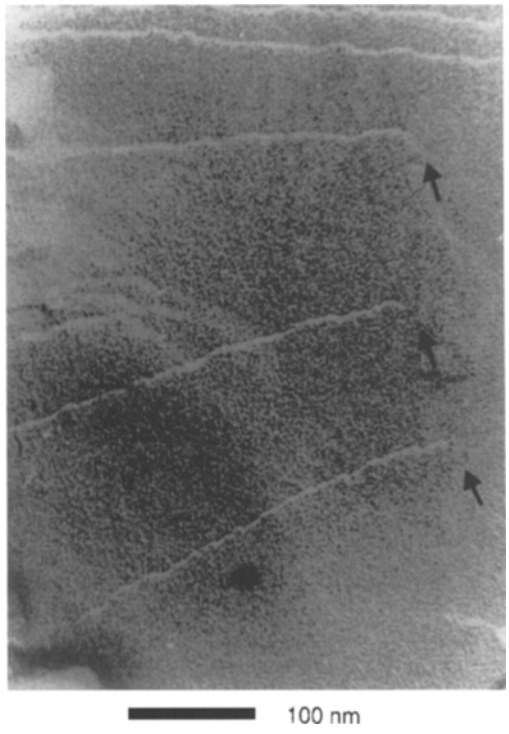

Fig. 5 TEM photograph of the lyotropic lamellar mesophase of fenoprofen: arrows indicate screw dislocations

confocal domains. In Fig. 6, two examples of freeze fractures are shown, exhibiting a great number of confocal domains, may it be tori or Dupin cyclides. These defects all nearly have the same orientation in the sample. The fracture plane is perpendicular to either the elliptical or circular disclination line of the confocal domain (L1 in Fig. 1) and is parallel to the other disclination line (L2 in Fig. 1), but is in most cases far away from the fracture plane. The arrows in Fig. 6 indicate parts of the sample, in which the fracture plane is nearer to the disclination line L2. It is important to notice that the confocal domains are often not perfect and that they do not fill the space iteratively.

Besides the confocal domains, other defect structures can frequently be found in the samples. In Fig. 7 one can see wave-like layers, which could also be detected in the lamellar mesophase of phospholipids in regions between neighboring confocal domains [4]. In Fig. 7 no confocal domain structures like in Fig. 6 can be detected. However, little depressions and also little peaks are visible (small arrows in Fig. 7). These structures can be interpreted as a visualization of the L2 singularity of the confocal domains. In this case, the domains are oriented perpendicular to the ones in Fig. 6, i.e. the fracture plane is perpendicular to the disclination line L2 of the confocal domain. Also, in

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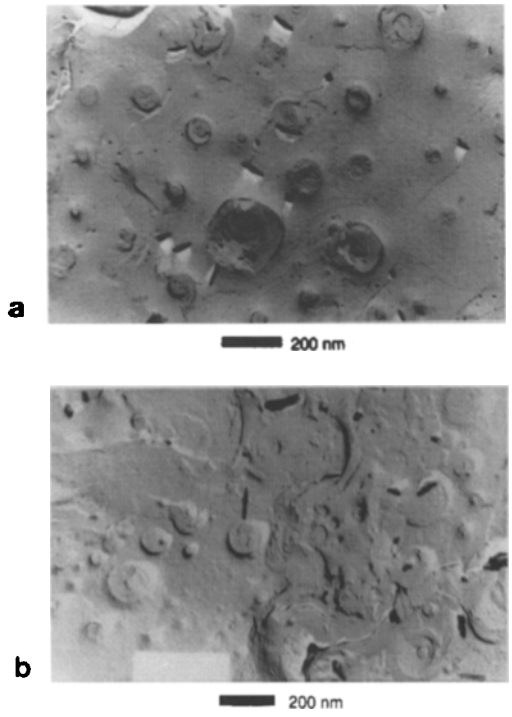

Fig. 6 TEM photograph of the lyotropic lamellar mesophase of fenoprofen: (a) confocal domains, (b) confocal domain, arrow indicates confocal domain with disclination line L2 close to the fracture plane. The photograph (b) is taken from the mesomorphous part of an aqueous liquid crystalline dispersion

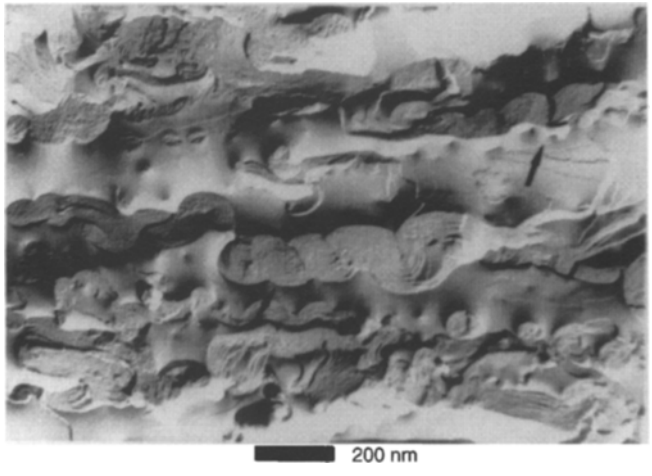

Fig. 7 TEM photograph of the lyotropic lamellar mesophase of fenoprofen: big arrow indicates wave-like layers, small arrows indicate little depressions and peaks, which may represent the disclination line L2

this appearance most of the confocal domains are oriented in the same direction.

The appearance of the confocal domains as a texture in the PLM depends on orientation of the domains with respect to the plane of preparation. If the disclination lines L2, are lying in the plane of the cover glass and object slide, the so-called fan-shaped texture appears. This is usually the case in thin preparations of mesophases of smectic arrangement [3]. Figure 3a shows a PLM photograph of the lyotropic lamellar mesophase of fenoprofen generated by cooling the isotropic sample from higher temperature to below the upper transition temperature or clearing point of the mesophase. Due to the low viscosity of the sample in the isotropic state, this type of sample preparation leads to thin mesophase preparation, resulting in a fan-shaped texture besides the homoeotropic texture, mentioned above. The optical appearance of the mesophase is different if it is produced at room temperature by mixing the components without preheating them to temperatures above the clearing point. Instead of a fan-like texture, usually a spherulitic texture together with birefringent stripes in a pseudoisotropic texture becomes visible (Fig. 3b).

The so-called polygonal texture, which appears in the PLM, if the confocal domains are oriented with the disclination lines L1 lying parallel to the object slide, and which tends to appear in thicker preparations [2, 3], is never observed in samples of fenoprofen lamellar mesophases.

In Fig. 8 another defect structure is shown that can be found in TEM investigations of the lamellar liquid mesophase. The arrows in the photographs of Fig. 8 show rows of the so-called pits and peaks. These small defects can be adjacent to confocal domains as in Fig. 8a, but also appear without being directly related to confocal domains (Fig. 8b). It is not clear, whether these pits and peaks are structures that originally exist in the mesophase, for example to relax stresses between neighboring defects, or if they are artefacts that appear during the freezing process of the sample [4]. They, however, appear frequently in samples that show no other signs of having developed artefacteous structures. They are also frequently found adjacent to cylindrical defects (2π-disclinations with a single, straight disclination line) in accordance with the observations of Williams and Kléman in phospholipid mesophases [4]. However, cylinders are not found in monophasic fenoprofen lamellar liquid crystals, but only in aqueous dispersions of this mesophase (not shown here, see ref. [8]). These defects are commonly attributed to the batonnet texture [3] usually appearing close to the clearing point of a smectic mesophase, but could be detected in TEM samples of aqueous mesophase dispersions that exhibited no batonnet textures in the PLM [9].

To summarize the findings in TEM and PLM investigations of the lyotropic mesophase of fenoprofen, one can say that screw dislocations, confocal domains, and pits and peaks can be found in the TEM samples. Neither edge

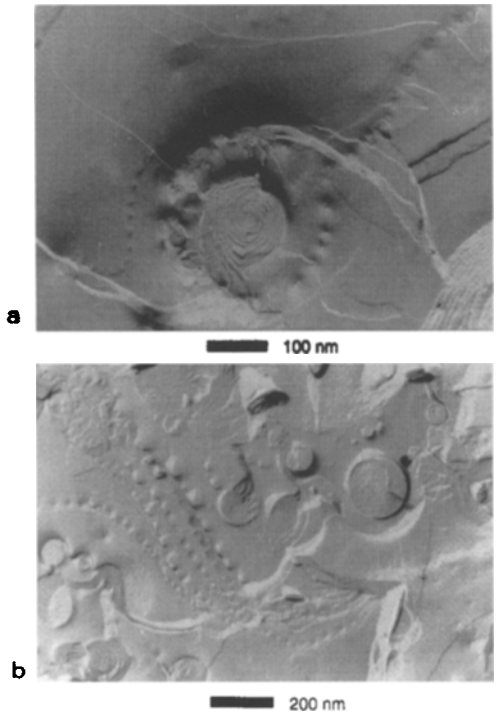

Fig. 8 TEM photograph of the lyotropic lamellar mesophase of fenoprofen: (a) pits and peaks adjacent to confocal domain, (b) pits and peaks not related to confocal domains

dislocations nor other disclinations could be detected. The defects found in the TEM can, in principle, be related to the textures found in the PLM investigations, although undisturbed lamellar areas are found less frequently as it is expected from PLM investigations.

Thermotropic mesophases

Fenoprofen sodium develops a smectic mesophase when heated to temperatures higher than 105 °C. The mesophase only appears if the drug is heated in an open system, allowing the initially crystalline-bound water to evaporate from the dihydrate. The smectic mesophase is of the unusual subtype smectic Ad, which means that the molecules are oriented perpendicular to the layer plane and that they have an antiparallel arrangement in an interdigitated bilayer. In this special case of a bilayer formation, the spacing of the bilayer is approximately 1.4 times the length of the single molecule [2]. The spacing of the thermotropic mesophase of fenoprofen sodium is 1.5 nm, as could be shown earlier with X-ray diffraction [8]. The mesophase develops from an isotropic, nonliquid-crystalline phase that first appears after melting of the crystalline sodium salt. It is present until about 180 °C and

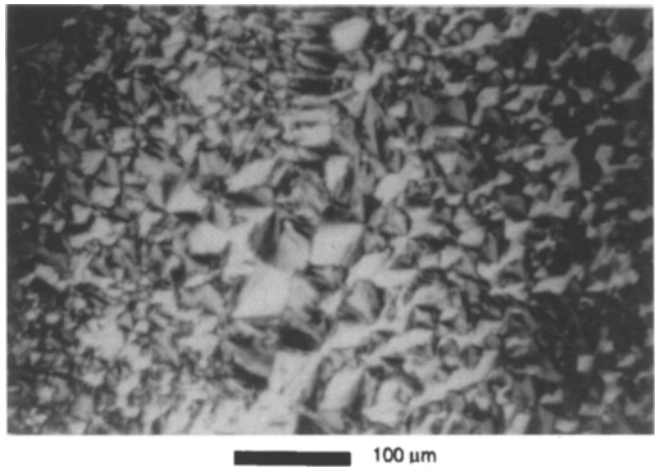

Fig. 9 PLM photograph of the thermotropic smectic Ad phase of fenoprofen sodium: fan-shaped texture

subsequently transforms into a second isotropic melt (for details of the thermal-phase behavior of fenoprofen salts see ref. [9]).

In Fig. 9 a PLM photograph of the smectic Ad phase is shown. It almost completely appears in the fan-shaped texture. Between 105 °C and 180 °C the appearance of the mesophase in the PLM does not change.

In the TEM investigation of the thermotropic mesophase no confocal domains or other defect structures could be detected although the curved layers that can be found point to a liquid-crystalline character of the samples (Fig. 10 shows four different photographs of the thermotropic liquid crystal of fenoprofen sodium). Due to the small layer thickness of the mesophase, the existence of screw or edge dislocations cannot be observed.

The second thermotropic mesophase investigated in this study is the sugar ester O1570. From small- and wide-angle X-ray diffraction it can be concluded that the mesophase has a layer thickness of 4.0 nm. This spacing, the interference pattern in the small-angle region of the diffractogram ($1:\frac{1}{2}:\frac{1}{3}:\frac{1}{4}$) and the absence of interferences in the wide-angle range of the diffractogram (only a halo is detectable), point to a smectic A2 mesophase. Smectic A2 means that the axes of the molecules are in a head-to-head arrangement, perpendicular to the layer plane [2]. However, due to the fact that the preheated samples could not be kept at a constant temperature during the X-ray diffraction investigation, these findings have to be confirmed using a diffractometer equipped with a temperature camera.

In the PLM investigations the appearance of this thermotropic liquid crystal strongly resembles the appearance of a lyotropic lamellar mesophase (Fig. 11). One can find fan-shaped texture and maltese crosses, indicating

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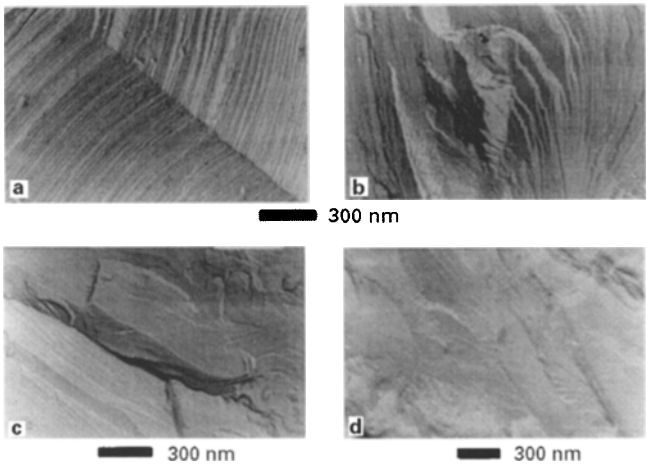


Fig. 10 TEM photographs of the thermotropic smectic Ad phase of fenoprofen sodium

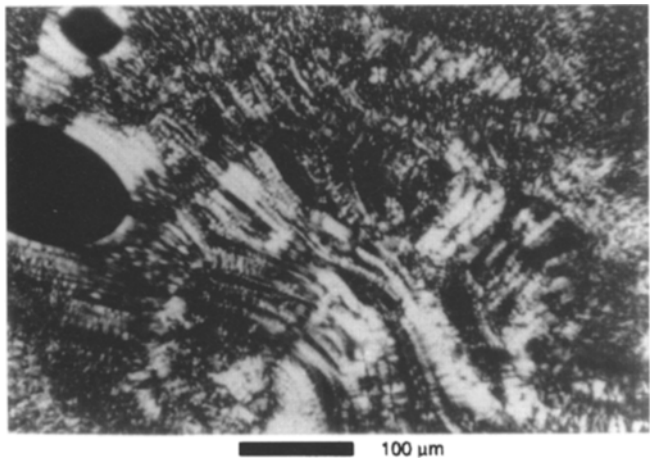
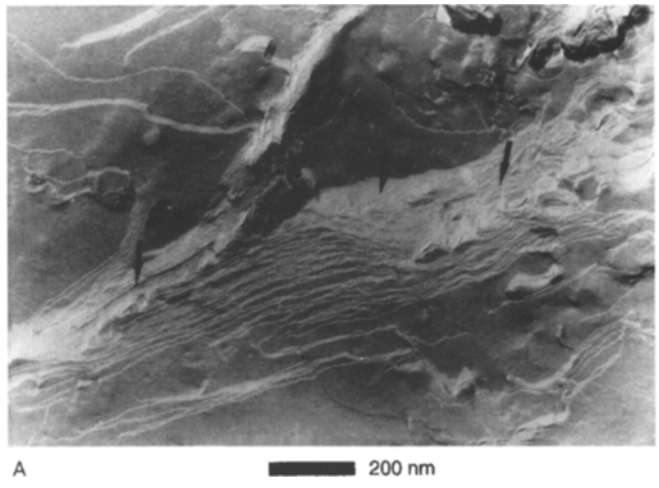


Fig. 11 PLM photograph of the thermotropic smectic A2 phase of O1570: fan-shaped texture, maltese crosses, oily streaks

confocal domains, as well as the so-called oily streaks. These oily streaks are attributed to sets of $+\pi$ and $-\pi$ disclinations [3]. In the TEM investigations (Fig. 12) systems of $+\pi$ and $-\pi$ disclinations can be found (arrow in Fig. 12a). Also, confocal domains (arrows in Fig. 12b) could be detected in the freeze-fractured samples, but the overall appearance of the mesophase is much more disturbed and the confocal domains are far from being perfect, compared to the lyotropic lamellar phase of fenoprofen. Also, the appearance of the sets of $+\pi$ and $-\pi$ disclinations is much less frequent than it could be expected from the PLM investigations.



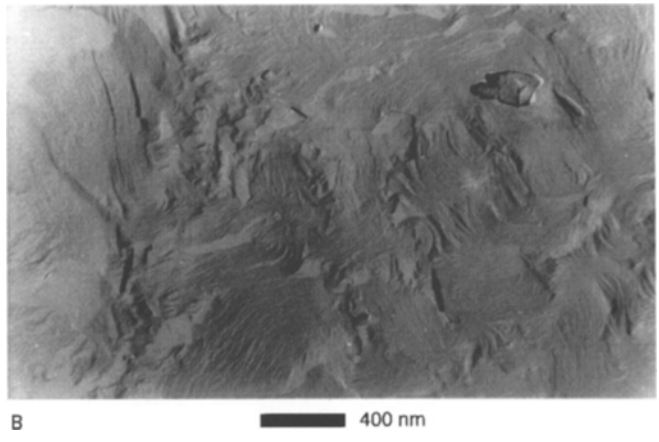


Fig. 12 TEM photograph of the thermotropic smectic A2 phase of O1570: (a) arrows indicate sets of $+\pi$ and $-\pi$ disclinations, (b) arrows indicate confocal domains

Mesophases after shearing

Although, in principle, all smectic mesophases used in this study should exhibit the same textures and structures in PLM and TEM investigations, as they all belong to a smectic A type, some remarkable differences could be detected between the different samples as well as between the results obtained using different microscopical investigation techniques for the same samples. The reasons for the discrepancies found are the differences in the sample preparation in PLM and TEM investigations as well as in the viscosities of the investigated mesophases.

In the PLM investigations the samples are put on an object slide and are optically investigated over a longer period of time in which the samples are not sheared. Therefore, the liquid-crystalline textures have time to develop in the PLM. This can be seen quite clearly in the

formation of the pseudoisotropic texture of the lyotropic mesophase as well as in the formation of the fan-shaped texture of the thermotropic mesophase and the lamellar liquid crystal when cooled from an isotropic solution. Both textures correspond to structures in which the layers or the disclinations have the same orientation in great parts of the liquid-crystalline samples. Also, these structures do not change the layer thickness of the smectic mesophases (at least in case of the confocal domain being a torus rather than a Dupin cyclide) and, subsequently, minimize the free energy of the liquid-crystalline system. If, on the other hand, the samples are investigated using the TEM, immediately prior to the cryofixation, a strong impact of shear forces occurs, due to the sample preparation, when the upper part of the sample holder is placed on the heated sample on the lower part of the sample holder. The time between this impact of shear stress and the cryofixation is between 30 s and 1 min. The appearance of the samples in the PLM, using the usual procedure for PLM investigations, therefore, cannot be compared with the structural appearance in the TEM. Hence, the textural appearance of the sample in the first minute after an input of a shear stress is investigated. In case of the lamellar liquid crystal and the O1570 mesophase this is performed by shifting the cover glass with respect to the object slide and in case of the thermotropic mesophase of fenoprofen by putting a cover glass on the heated sample.

In case of the lamellar mesophase, which has the lowest viscosity of the investigated samples, this procedure destroys most of the undisturbed homoeotropic arrangement of the layers and leads to the appearance of maltese-cross textures. This behavior is similar to that described for the lyotropic mesophase of fenoprofen potassium [10], and explains the absence of great undisturbed lamellar regions in the TEM samples. As an impact of shear stress to the lamellar phase that is formed by cooling the isotropic solution (in this case the dominant textures are homoeotropic and fan-shaped), also leads to a predominantly spherulitic texture, the maltese-cross texture could be regarded as a texture, indicating a less regular orientation of the liquid-crystalline state as the fan-shaped texture. On the other hand, as shown above in the TEM investigations, the confocal domains often show a parallel orientation.

Due to the low viscosity of the lyotropic mesophase, the reorganization of the disturbed system after shearing the sample, to the variety of defect structures visible in the TEM, can also be regarded as the reason for the absence of edge dislocations and sets of $+\pi$ and $-\pi$ disclinations, as it could be shown, that these defects can easily be transformed into confocal domains [3].

In case of the highly viscous thermotropic fenoprofen mesophase, the shearing of the sample causes a destruction of the confocal domains and the comparatively low flexibility of the mesophase does not allow a reorganization of the layers into confocal domains, as will be possible if the thermotropic mesophase formation occurs from the isotropic melt with its low viscosity. The PLM picture of the sheared fenoprofen smectic Ad phase does not show any textural elements that could be related to certain planar or nonplanar defect structures. As in the case of the lyotropic mesophase, the optical appearance of the sheared mesophase corresponds to its electron microscopical appearance.

The viscosity of O1570 is between that of the lyotropic and thermotropic mesophase of fenoprofen. After shearing, the sample still shows some maltese-cross texture as well as oily streaks, although reduced in number, thus confirming the electron microscopical findings.

Summary and conclusions

To summarize the results of this study, one can say that the different smectic liquid-crystalline structures have in common that they all form a fan-shaped or maltese-cross texture, indicating that confocal domains are the predominant structural elements in smectic mesophases. The differences in the textural and structural appearance of the different mesophases can be explained by their different viscosity, and hence different ability to reorganize in structures that minimize the free energy of the liquid-crystalline system after shearing.

In solid crystals the mechanical properties of the crystal strongly depend on the defects present in the crystal. In a mesophase the situation is different: the viscosity of the system, or in other words, the liquid character of this state of matter between liquids and solids, determines the types and quantity of the defect structures.

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