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Sanidics: A new class of mesophases, displayed by highly substituted rigid-rod polyesters and polyamides

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The structure of rigid-chain polyesters and polyamides which possess flexible side chains consisting of methylene or 1,4,7-trioxaoctyl oxide units have been investigated by means of X-ray scattering. The X-ray studies were performed on fibres and monodomains. Additional information was gained from calorimetric, dilatometric and microscopic studies. The investigations revealed that these polymers display mesophases and that the structures of the mesophases differ from those observed for discotic and calamitic phases. They are characterized by the fact that in the ordered and disordered phases board-like molecules are stacked parallel on top of each other and that these stacks of molecules are oriented parallel to each other. In the least ordered phase the molecules are only oriented parallel to each other. The various modifications of the mesophases observed so far differ with respect to each other in terms of the order within the stacks as well as in terms of the spatial arrangements of the stacks. A characteristic feature is the frequent absence of any correlation between the long range order which exists along different principal axes of the structure. We have coined the term sanidic for this new type of mesophase.

1. Introduction

Dating back to the early work of Onsager [1], Ishihara [2] and to later theoretical investigations by Flory *et al.* [3-6] it has been recognized that the anisotropy of the repulsive forces and thus the geometric shape of molecules is a key factor in controlling their spatial arrangement both in solutions and in the condensed fluid state. It is in accord with these concepts that rod-like molecules have been found to display the so-called calamitic phases (from the Greek, *calamis* = reed) where the characteristic feature is the presence of long range orientational order of the long molecular axes [7-9]. Disc-like molecules, on the other hand, are known to display discotic phases [10-13] (from Greek, *discos* = disc), the simplest case being the nematic discotic phase (abbreviation N_D). It is now the normal of the disc-like molecule which displays long range orientational order.

This paper presents results on the structures formed by molecules with an approximately board-like shape. Their chemical structure is, in all cases, characterized by the fact that the chain is composed of an essentially rigid chain backbone which by itself would induce a calamitic phase. The second structural feature is, however, the presence of side chains which are flexible and sufficiently long to cause the geometry of the chain molecule to become board-like, provided that the concentration of side chains along the chain backbone is sufficiently large [14-23]. Here we show that

the polymers considered display a new type of mesophase, which differ from those known and which we have called sanidic mesophases [18–22]. This term originates (as calamitic and discotic) from the Greek and it describes a board-like shape.

2. Experimental

2.1. Samples

We consider a set of polymer species which differ with respect to each other first of all in the chemical nature of the chain backbone. Polyesters and polyamides are taken into account (see figure 1); they differ with respect to the chemical nature of the side chains (methylene units and 1,4,7-trioxaoctyl units), in the length of the side chains and in the number of side chains per repeat unit. The parameters which are influenced by these variations of the chemical structure are predominantly the flexibility of the main and side chains, and the torsion angle between the different aromatic rings (hydroquinone/phenylenediamine and terephthalic acid respectively). In fully aromatic polyamides the torsion angle between the aromatic rings is substituent dependent but generally smaller than the torsion angle between different phenyl rings in fully aromatic esters, which is normally about 60° in the crystalline state [24]. For fully aromatic polyesters and polyamides these facts may lead to distinct differences in the packing behaviour of these two types of polymers [25]. In this paper we consider the case when the number of side chains per repeat unit amounts to four (the hydroquinone or the phenylenediamine is fully substituted only) and six (in addition application of disubstituted terephthalic acid derivatives) (see figure 1). Similar compounds have recently been synthesized consisting of rigid main chain polyamides and polyesters with one or two flexible alkyl side chains per repeat unit [15–17, 26].

The general finding is that the polyesters and polyamides exhibit one or even two fluid-like mesophases in addition to the isotropic melt and the crystalline state. The transition enthalpies and transition entropies are of the same order of magnitude as found both for low molar mass and polymeric liquid crystals, i.e. of the order of $1\text{--}10\text{ kJ mol}^{-1}$ and $2\text{--}20\text{ J K}^{-1}\text{ mol}^{-1}$, respectively.

2.2. Sample orientation

We were able to obtain monodomains of the liquid-crystalline materials, in which the principal axes of the structure were macroscopically oriented along different directions. The method used to achieve this essential step and the set-up used to this end are illustrated in figure 2. We induced a one-directional flow within a heated cell along direction 2 by applying pressure along direction 3. The geometry of the sample was kept constant along direction 1 so that the sample could only flow along direction 2.

2.3. Experimental methods employed

The textures displayed by the polymers were investigated with a polarizing microscope (Leitz, Wetzlar) equipped with a Mettler hot stage FP 82. The textures characteristic of these mesophases could not be assigned to any known type with the exception of the schlieren textures shown by the polyamides containing 1,4,7-trioxaoctyl side groups, as we describe in more detail later.

The scattering properties of oriented samples were determined with a flat film camera which was equipped with a heating chamber. The size of the sample was

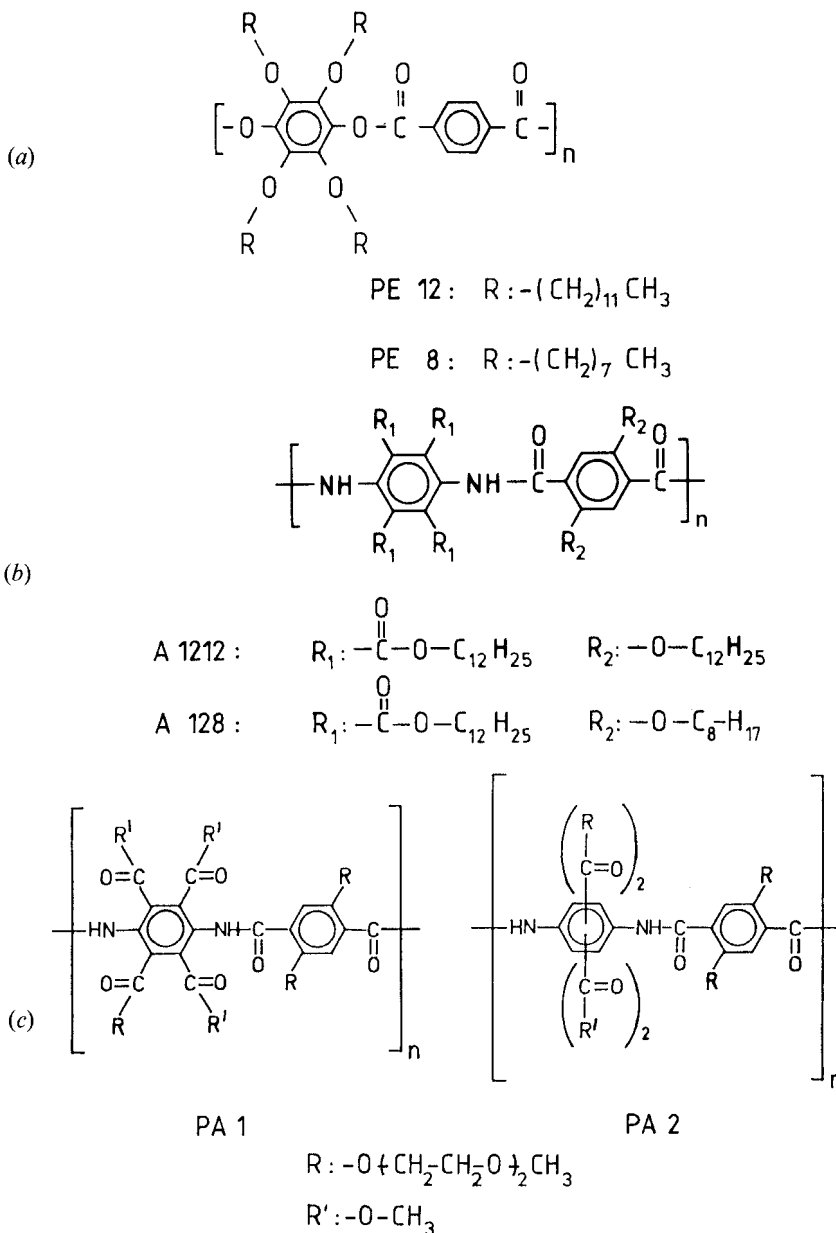


Figure 1. (a) Repeat units of the polyesters PE 12 and PE 8. (b) Repeat units of the polyamides A 1212 and A 128. (c) Repeat units of the polyamides with 1,4,7-trioxaocetyl side chains PA 1 and PA 2.

selected in such a way that the primary beam was able to travel along all three macroscopic axes 1, 2, 3 of the monodomain. In order to check the results and to obtain accurate data on the lattice dimensions we also performed wide angle and small angle X-ray scattering experiments on unoriented samples, employing a Siemens wide angle X-ray goniometer (D500) as well as a Kratky small angle camera. A heating chamber allowed us to obtain the scattering pattern for temperatures up to

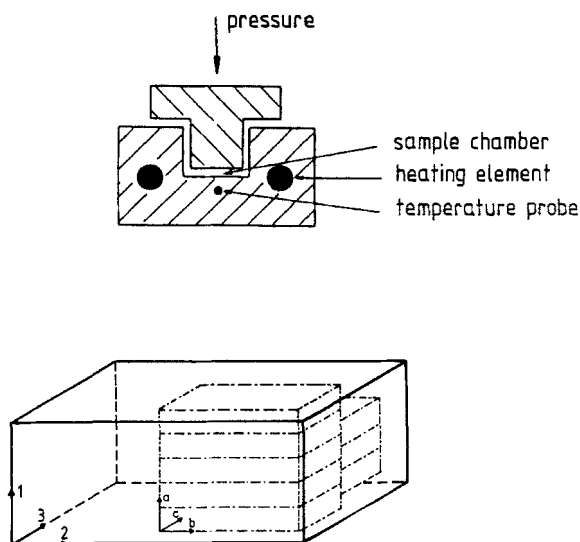


Figure 2. Experimental set-up used to obtain monodomains and geometry of the oriented sample (2, direction of flow; 3, direction of pressure).

about 250°C. The density of the samples was determined as a function of temperature with a glass dilatometer filled with mercury.

3. Results and discussion

3.1. The polyesters PE 12 and PE 8

The polyester PE 12 (see figure 1 (a)) has two first order transitions, one at about 15°C and the other at 195°C. The corresponding transition enthalpies are 35 J/g and 8 J/g, respectively. The microscopy studies reveal the presence of an isotropic fluid state above 195°C and of an anisotropic, apparently viscous phase below this temperature. The texture observed using the polarizing microscope cannot be assigned to any known type of mesophases. The transition taking place at 15°C is crystallization. This particular polymer displays therefore a liquid-crystalline phase in the temperature range between 15°C and 195°C. The polyester PE 8 (see figure 1 (a)) was also found to exhibit a mesophase. The transition into the isotropic state happens at 245°C and this particular mesophase is frozen into a glassy state at about 150°C. The transition enthalpy of the liquid crystal–isotropic transition is 9 J/g.

The rather ordered structure of the mesophase for polymer PE 12 is evident from figures 3(a)–(c) which show the X-ray flat camera diagrams when the primary beam was oriented

- (a) parallel to direction 1 (perpendicular to pressure and flow);
- (b) along the flow direction (2); and
- (c) along the pressure direction (3).

In each case we obtain a totally different scattering pattern. The features of these diagrams will now be considered. The diagrams contain three different sets of highly oriented and sharp reflections denoted by *B*, *C* and *E*. It is a characteristic feature of the scattering pattern that they do not always display all of the reflections. The reflections *B* are, for instance, the only ones found in figures 3 (a) and (b) and they are

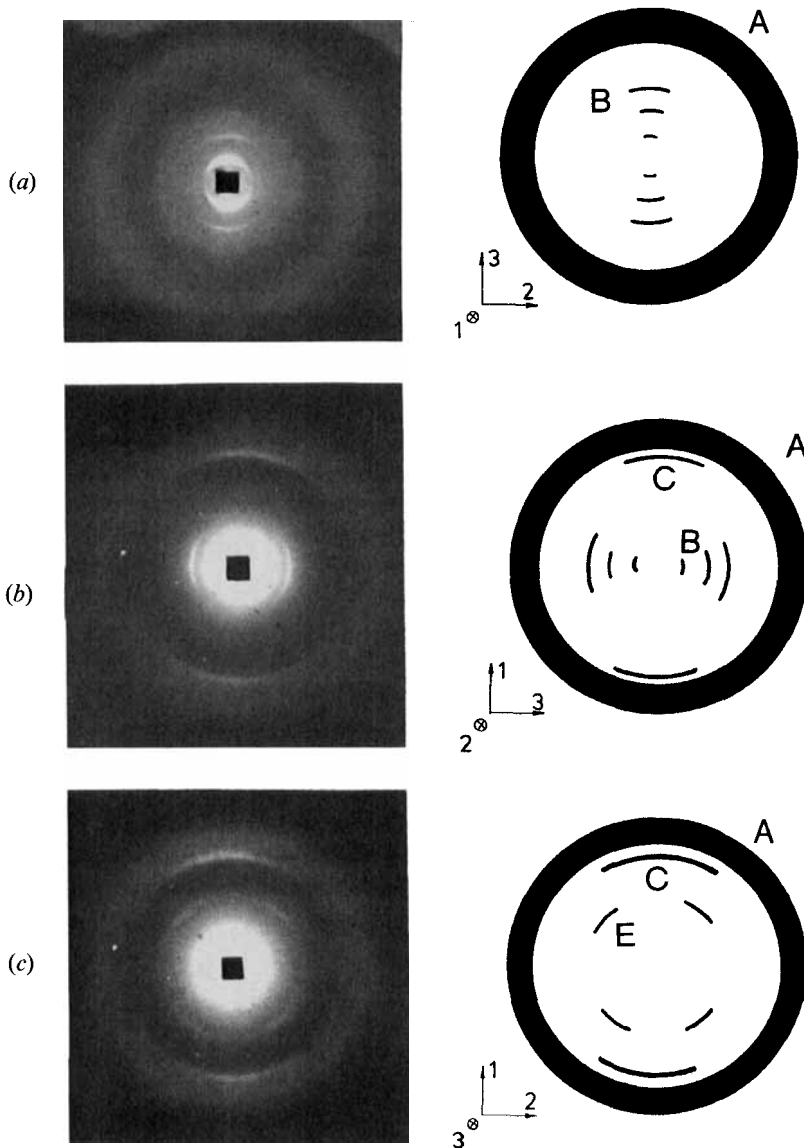


Figure 3. X-ray diffraction pattern of the oriented polyester PE 12. (a) Primary beam parallel to direction (1). (b) Primary beam parallel to direction of flow (2). (c) Primary beam parallel to pressure direction (3).

absent in figure 3(c). The reflections *C* can be observed in both figures 3(b) and (c), whereas the reflections *E* can only be detected in the scattering geometry used to obtain figure 3(c). It is a further feature that the sets of reflections *B* and *C* occur just along the equator or meridian whereas the set denoted by *E* is located off the meridian and the equator.

These experimental findings show therefore that the structural features are different along all three macroscopic and consequently also along all three molecular axes. It is also evident that all of the diagrams show an unoriented amorphous halo *A* despite the fact that the other reflections are all oriented. The X-ray patterns

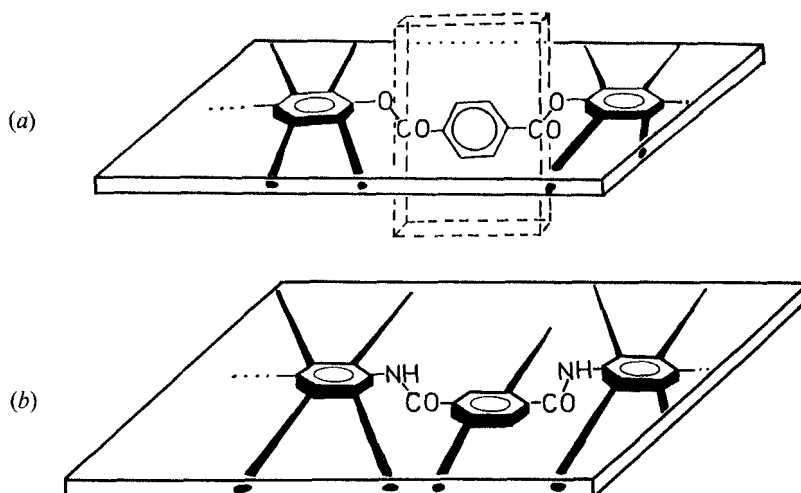


Figure 4. Shapes of the chains of the polyester and polyamides. (a) The polyesters are characterized by undulations of the board-like shape because of the torsion between aromatic rings. (b) The polyamides are essentially flat.

reported so far are not unique for the polymer PE 12; similar patterns are obtained for the polymer PE 8.

Figure 4 shows a structural model which is able to account for the X-ray results reported so far. It suggests that the chain molecules have essentially a flat shape (a more detailed discussion on this shape will follow), that the molecules pack one on top of the other in a regular manner to form stacks and that the stacks are arranged parallel to each other again in a regular fashion. An additional structural feature is the occurrence of a registry of the chain backbone within the stacks. The following discussion will reveal that the chain backbones (the *b* axis) are oriented in the monodomains along the flow direction (2) and that the stack normal (*a*) is oriented along direction (1) which is perpendicular to the flow and pressure direction within the monodomain film.

The unoriented amorphous halo is attributed to the flexible side chains which display, as for discotic systems, just short range positional order [10–13]. The parallel packing of the stacks of chain molecules is responsible for the occurrence of reflections *B* with Miller indices (001) (see figures 3(a) and (b)). The magnitude of the corresponding lattice distance amounts to about 2.39 nm for polymer PE 12 and to about 1.78 nm for polymer PE 8. Assuming a linear relation between this distance and the length of the side chains we obtain the result that this distance should be about 0.56 nm when no flexible side chains are present. This corresponds quite well to the width of the chain backbone.

The regular stacking of the chain molecules along the stack normal and the regular registry of the chains within the stacks gives rise to a two dimensional face centred orthorhombic lattice. It seems that this registry of neighbouring chains results from the undulation of the board-shaped molecules, as shown schematically in figure 4(a). The torsion angle between different phenyl rings in fully aromatic esters is normally about 60° in the crystalline state [24]. Space filling requires a matching of the undulations, thus giving rise to the two dimensional face centred orthorhombic lattice shown in figure 5. This lattice causes the occurrence of the reflections *E* with the Miller

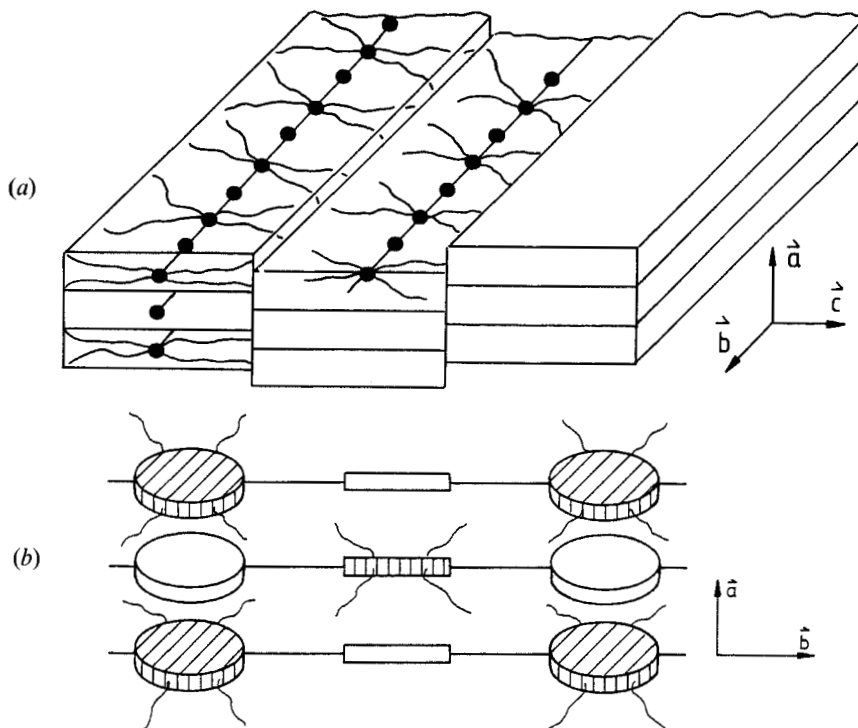


Figure 5. Structural model proposed for the mesophase of the polyester PE 12. (a) Stacking. (b) Chain registration.

indices (110) and of the reflections C with the Miller indices (200) (see figures 3(c)). The a dimension amounting to 1.06 nm corresponds to the actual repeat distance along the stack normale and the b dimension amounting to 1.2 nm to the repeat distance along the chain backbone. It is a particular feature of the diffraction pattern that the (020) reflection is missing. It is possible to account for this observation on the basis of structure factor calculations (18). The result is that the ratio of the intensities should be

$$I_{200} : I_{110} : I_{020} = 1 : 0.04 : 0.0004,$$

which agrees well with the experimental results. So we are able to account for all of the features of the scattering pattern obtained for the polyesters on the basis of the structural model shown in figure 5. In addition the model is able to account for the observed density given by:

$$\rho = 2M/abcN_A,$$

where M is the molecular weight of a repeat unit. The value calculated from the structural model amounts to 1.07 g/cm³ for PE 12 and to 1.11 g/cm³ for PE 8 whereas the experimentally determined densities are 1.04 g/cm³ and 1.09 g/cm³, respectively.

3.2. The polyamide A 128

The polyamide A 128 (see figure 1(b)) exhibits an isotropic phase above a temperature of 122°C, and as is apparent from calorimetric and optical studies an

anisotropic, viscous state below this temperature. The transition from the viscous state to the isotropic state is quite broad (about 60 K) and its enthalpy change amounts to 10 J/g. The observed texture could not be attributed to any known type. It agrees with those observed for polyamide A 1212 to be discussed later.

The scattering pattern obtained for the monodomain are given in figures 6(a)–(c) when

- (a) the primary beam travels along a direction perpendicular both to the flow (2) and pressure (3);
- (b) along the flow direction (2); and
- (c) along the pressure direction (3).

We observe an unoriented halo *A* and three sets of sharp reflections *B*, *C* and *D* which are located either along the meridian or along the equator. The surprising finding is that no off-equatorial or off-meridional reflections are apparent, as observed for the polymers PE 12 and PE 8, and that the amorphous halo is unoriented despite the fact that the reflections denoted by *B*, *C* and *D* are highly oriented. These scattering features were independent of the temperature range (up to 122°C).

Figure 7 shows a structural model which is able to account for the X-ray results obtained for the polyamide. It suggests that the chain molecules have a flat shape, that the molecules pack one on top of the other in a regular manner to form stacks and that the stacks are arranged parallel to each other again in a regular fashion. The absence of a chain registry within the stacks is the only feature which distinguishes this structure from that observed for the polyesters. It will be demonstrated in the following that the chain axis (*b*) is parallel to the flow direction (2) within the monodomain and that the stack normal (*a*) is perpendicular both to the flow (2) and pressure direction (3), i.e. parallel to direction (1) in the monodomain films.

The disordered aliphatic side chains cause the unoriented amorphous halo *A*. The regular parallel arrangement of the stacks of the board-like molecules gives rise to the occurrence of a one dimensional lattice leading to the set of three (001) reflections *B* (see figures 6(a) and (b)). The lattice distance is 2.10 nm, as expected on the basis of geometric considerations. The regular sequence of repeat units along the chain backbone is responsible for the intrachain reflections *D* with a lattice distance of 1.26 nm (see figures 6(a) and (c)) and the regular arrangement of the board-like molecules within the stacks causes the reflections *C* with a lattice distance of 0.78 nm (see figures 6(b) and (c)). The absolute values of the lattice distances characteristic of the packing within the stacks and of the sequence of repeat units along the chain backbone agree with those found from space filling models.

The obvious difference between the structures adopted by the polyesters and the polyamide A 128 is the absence of mixed reflections (*hk0*) in the latter case. The reason is that the two one dimensional lattices defined by the chain backbone and by the packing within the stacks are no longer correlated. The polyamide chain molecules are apparently shifted past each other in a more or less statistical way within the stacks in contrast to the polyester chain molecules. It is conceivable that the alternating sequence of aromatic units along the backbone with and without side chains and the undulation of the board cause a registry of neighbouring chains for the polyesters whereas the absence of such an effect is responsible for the missing registry for the polyamide A 128. Figure 4(b) gives an impression of the essentially flat shape of the polyamide chain.

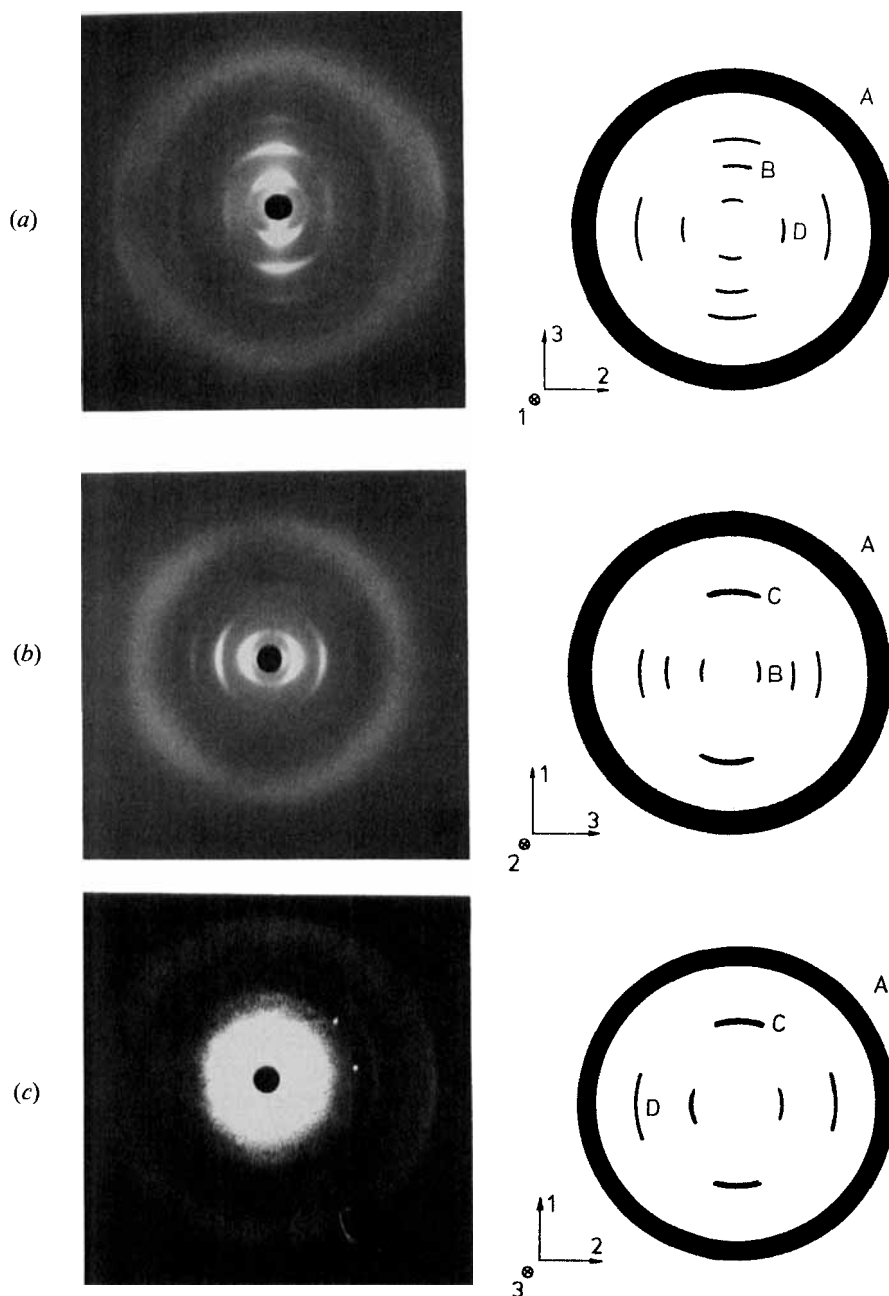


Figure 6. X-ray diffraction pattern of the oriented polyamide A 128. (a) Primary beam parallel to direction (1). (b) Primary beam parallel to direction of flow (2). (c) Primary beam parallel to pressure direction (3).

Structure factor calculations performed on the basis of this model lead to the predictions that the intensity of the second order intramolecular reflection (from the set of reflections *D* which result from the electron density variations along the chain backbone) should be larger than those of the first and third order reflections, in

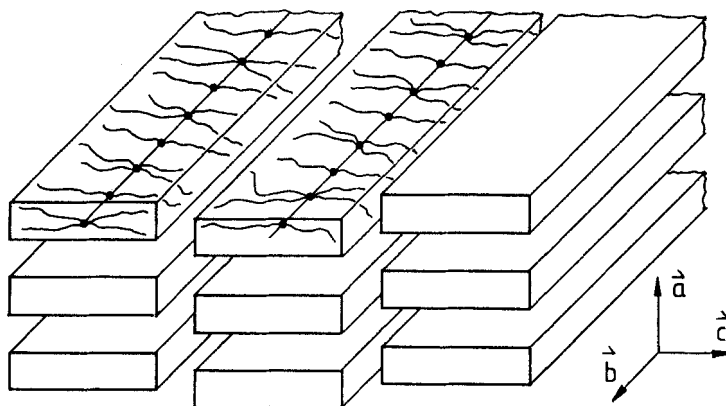


Figure 7. Structural model proposed for the mesophase of the polymer A 128.

agreement with experiment. So again all of the features which are displayed in the scattering diagrams can be explained on the basis of the structural model given in figure 7. The structural model is thus able, as for the polyesters, to account for the experimentally determined density. This value is 1.06 g/cm^3 whereas the calculated one is 1.08 g/cm^3 .

3.3. The polyamide A 1212

The polyamide A 1212 (see figure 1 (b)) exhibits two first order phase transitions. The transition temperatures are 67°C and 127°C and the corresponding transition enthalpies are 2 J/g and 3 J/g , respectively. The transition at 127°C results in the formation of an isotropic melt whereas the two low temperature phases are optically anisotropic and non-solid. This is apparent from polarizing microscopy studies. It is possible to distort the textures in both phases by sliding one of the glass slides parallel to the other along a given direction. These distortions are typical for liquid crystal phases.

Most of the features of the X-ray diagrams obtained for this polymer agree with those observed for the polymer A 128. The main difference is the absence of the reflections *C* which were attributed to a regular packing of the board-like molecules within the stacks. So apparently there is no long range order along the stack normal; this is shown schematically in figure 8. We observe, on the other hand, again the reflections *B* indicative of the parallel packing of stacks and the reflections *D* originating from the regular sequence of repeat units along the chain backbone. The latter agree exactly with those found for the polyamide A 128.

The polyamide A 1212 shows the interesting feature of a transition from one mesophase to another for which the basic features of the scattering diagrams agree. Figure 9 shows the results of small angle X-ray scattering studies performed at different temperatures above and below the transition between the two mesophases. We observe that the transition is connected with a stepwise decrease of the particular lattice distance which originates from the parallel packing of stacks of board-like molecules. This decrease in the layer distance is evidently accompanied with a corresponding increase of the distance between the molecules lying on top of each other within the stacks, since the density does not change at this transition. This is apparent from dilatometric results [18] (sensitivity 0.1 per cent). Dielectric relaxation studies,

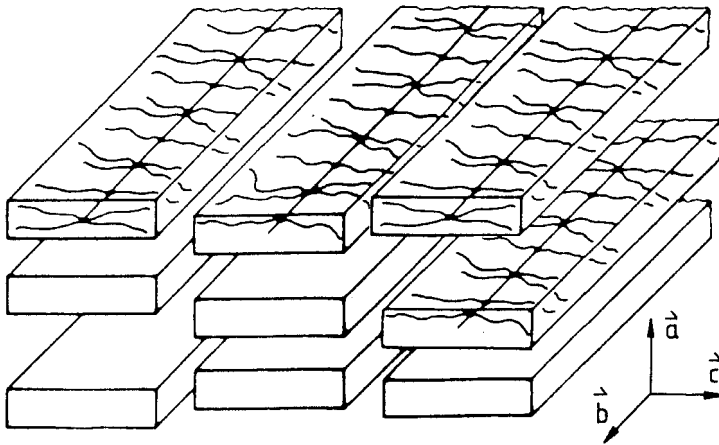


Figure 8. Structural model proposed for the polymer A 1212.

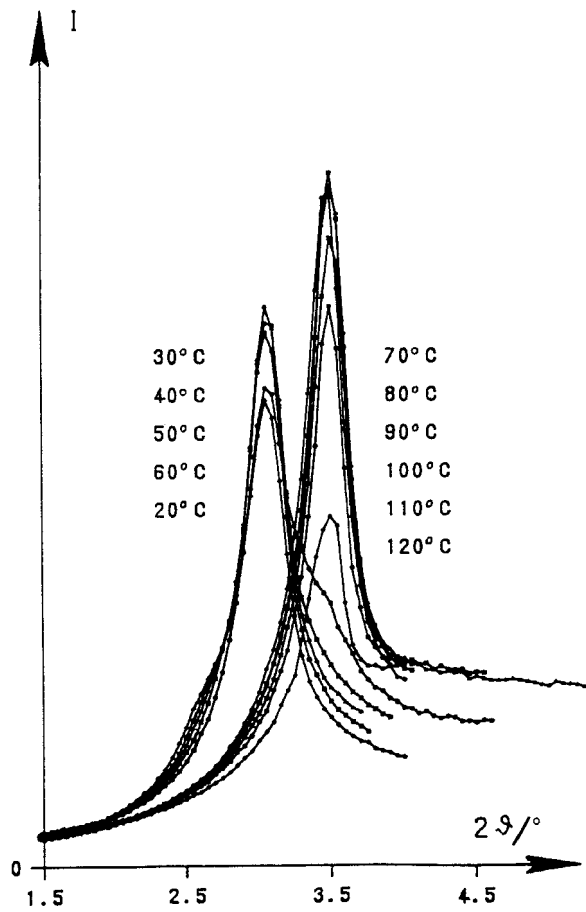


Figure 9. Small angle X-ray scattering results for the polyamide A 1212 at different temperatures.

on the other hand, revealed a stepwise increase of the dielectric constant at this transition, which may be taken as an indication of a discontinuous increase of the molecular mobility at the transition.

It seems therefore that both mesophases formed by the polyamide A 1212 are similar and that the main difference between the two results from structural and dynamical variations which seem to be connected with conformational changes of the side chains.

3.4. Polyamides containing 1,4,7-trioxaoctyl side chains

Next we consider the phases formed by the polyamide containing 1,4,7-trioxaoctyl side chains (see figure 1(c)). The D.S.C. and the polarizing microscopy studies reveal for both species the existence of an isotropic melt above 262°C and 216°C, respectively. They also exhibit an anisotropic viscous phase below this temperature. The transition enthalpies are 0.4 J/g for both polymers. These polyamides display well-defined schlieren textures in the mesophase indicative of a nematic phase [22]. Crystallization occurs at lower temperatures.

Figure 10 shows the X-ray results obtained on unoriented samples within the mesophase. Two halos are observed for both polymers having 1,4,7-trioxaoctyl side chains, one in the small angle regime and the other in the wide angle regime. So we have to conclude that no long range translational order exists in the mesophases. This is a characteristic feature of the nematic state and the occurrence of a schlieren texture reported here is in agreement with this interpretation.

It was not possible to produce a monodomain for the polyamide containing 1,4,7-trioxaoctyl side chains because of crystallization on cooling into the solid state. We were however able to induce a fibre texture in the nematic phase, by the interaction with a magnetic field of about 1 T. The patterns obtained on oriented fibres

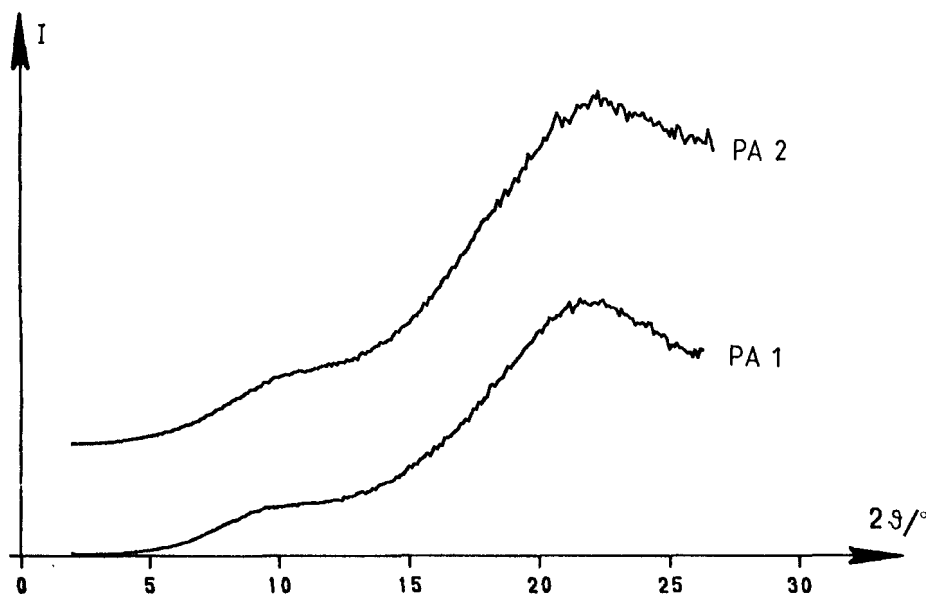


Figure 10. X-ray scattering from unoriented samples of the polyamides containing 1,4,7-trioxaoctyl side chains.

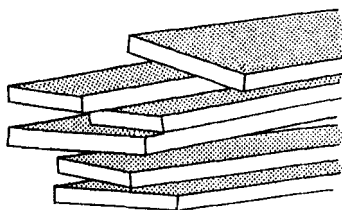


Figure 11. Schematic representation of the biaxial nematic mesophase.

revealed that the two halos, the one located in the small angle X-ray regime and the other in the wide angle regime, occur both on the equator. This is different from that for calamitic nematic phases where the small angle halo is oriented along the director (i.e. along the meridian in the fibre pattern) and the wide angle halo perpendicular to it (i.e. along the equator in the fibre pattern). This indicates first that the nematic director is defined by the chain long axis and that a biaxial short range order exists which is related to the shape of the cross section of the molecules and the corresponding packing perpendicular to the chain backbone orientation.

This polymer evidently displays a mesophase structure which is similar to that of a biaxial nematic phase at least on a local scale. This structure is shown schematically in figure 11. Conoscopic studies [22] have revealed that the polymer actually displays a biaxial nematic phase.

3.5. *The isotropic phase*

The scattering patterns obtained for the isotropic phases of all the polymers considered here have two halos, one in the wide angle range and the other in the small angle range, as for the nematic structure found for the polyamide containing 1,4,7-trioxaoctyl side chains. This finding is indicative of the fact that the side chains cannot be randomly oriented about the chain backbone since this would lead to a cylindrical shape of the chain molecules.

Two important topics will have to be treated briefly next: (i) the actual shape of the molecules and (ii) whether the mesophases described here correspond to ones previously known.

4. Chemical structure: geometric shape

The polymers studied belong to the group of fully aromatic polyesters and polyamides and they carry side chains composed of methylene units or 1,4,7-trioxaoctyl units (see figure 1). The repeat units are approximately disc-shaped because the aromatic cores are surrounded by up to six long aliphatic side chains. The incorporation of such building units into a chain backbone changes the geometry, however, completely. We have to envisage, in principle, two limiting cases for the configuration of the individual chain molecules. One corresponds to the case that the side chains are projected more or less randomly in all directions perpendicular to the chain axis. The molecule would thus assume a cylindrical shape, the diameter being determined by the length of the side chains and the diameter of the chain backbone. The second limiting case corresponds to the situation that the chain backbone and the side chains are located in the same plane, i.e. the molecule adopts a board-like shape. The ratio of the two axes perpendicular to the long axis of the molecule is of the order

of 7 to 10 in the cases considered here. It depends on the length of the side chain and on their flexibility.

The X-ray data reveal that the molecules assume, to a first approximation, a board-like shape both in the isotropic and anisotropic condensed states. The board is almost flat for the polyamides where the torsion angle between the aromatic rings is smaller than for the polyesters where the board will show undulations as depicted schematically in figure 4. This is in agreement with computer simulations using molecular modeling programs. The simulations suggest actually a torsion angle of about 60° for the polyester. However the simulations also reveal that the flexible side chains have a strong tendency to remain within the planes defined by the chain backbone and to explore just the space on this plane. This is in good agreement with the experimental results.

4.2. Type of mesophases

We have shown that space filling requirements give rise to a stacking of such board-like molecules one on top of the other, and that the order within the stacks may vary, as shown in figure 12. Space filling requirements again are responsible for a packing of the stacks one parallel to the other to build up a three dimensional structure. The flexible side chains are assumed to have just a short range positional order. The basic features of our model agree partially with those of the ordered discotic systems where the disc-like molecules form columns which assemble in space in terms of a two dimensional lattice. Other features are reminiscent of calamitic phases such as the layer structures formed by the parallel packing of elongated stacks of the board-like molecules.

The question which has to be discussed next is if the mesophases described here correspond to known ones, as judged on the basis of their structure. The characteristic scattering behaviour found for the monodomains precludes discotic systems as well as nematic (with one exception namely the nematic phase which is, however, biaxial), cholesteric and disordered smectic phases. So we have to compare the observed

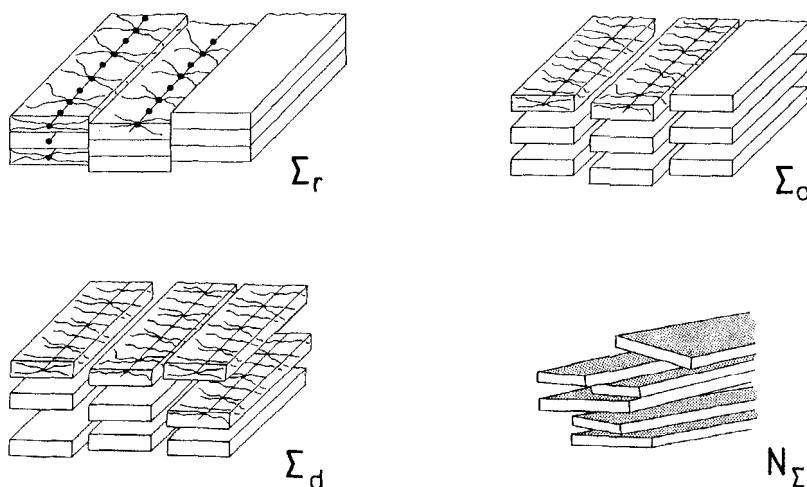


Figure 12. Structural models for the various smectic phases exhibited by the highly substituted aromatic polyamides and by the polyesters.

scattering behaviour with that found for ordered smectic phases. Some characteristic features are:

- (a) Ordered smectic phases show in all cases a two dimensionally correlated lattice in addition to the one dimensional one resulting from the layer structure [27, 28]. This is in contrast to most of the structures reported earlier, i.e. for the structures displayed by the different polyamides.
- (b) Macroscopically highly oriented smectic phases (smectic A and C) do not display totally unoriented halos, as observed here, resulting from the orientational distribution of aliphatic chain units but rather an inhomogeneous azimuthal intensity distribution, which allows us to obtain information about the orientational order parameter [29, 30]. The features found for the polyesters and polyamides correspond to those characteristic of discotic systems [10–13].
- (c) The director is defined for the polymers studied here by the direction of the chain backbone, as for low molar mass systems or main chain polymers. This is directly apparent from the results on the nematic phases and indirectly from the orientational behaviour described in this paper. The smectic layering occurs, however, perpendicular to this direction in the cases considered here, in contrast to all results reported for smectic systems [27, 28].
- (d) Recent investigations have shown that the stacked phases described here are only stable if the mesogens are polymers and not low molecular weight oligomers. For oligomers only a crystalline phase and the isotropic phase could be detected but no liquid-crystalline phase. Molecular weights of at least 10 000 were necessary to induce liquid crystallinity. For oligomers the characteristic board-like shape apparently vanishes, the molecule is no longer a board. These results were obtained by calorimetric and polarizing microscopy investigations for a polymer with a nematic sanidic (biaxial nematic) phase and for a polymer with the stacked disordered phase. To our knowledge the sanidic phases are the first examples for polymer specific liquid-crystalline phases. Mesophase formation seems to be impossible for any kind of low molecular weight substance but it is conceivable that many highly substituted rigid-rod polymers may form stacked liquid-crystalline phases. Detailed results on the molecular weight dependence of phase formation, transition temperatures and on specific optical textures will be published elsewhere.

The structures of the mesophases displayed by the polyamides and polyesters do not apparently correspond to those of conventional calamitic and discotic phases. They are, in addition, not identical with modifications of the calamitic phases such as for instance with phases showing palisade structures formed by ribbon shaped molecules since the characteristic stacking is absent as apparent from the diffuse reflections in the small and wide angle scattering region [31]. We conclude therefore that polymers consisting of a rigid chain backbone and flexible side chains display a new type of mesophase and we have termed them sanidic from the Greek and we have chosen the symbol Σ for this kind of mesophase. Once these basic features of the sanidic structures have been postulated we are able to discuss all possible sanidic modifications, starting from the most ordered one (see figure 12). The most ordered corresponds to the case that the molecules are arranged within a stack in such a way that a long range order exists along the stack normale as well as along the stack long axis: the chains are stacked regularly one on top of the other and they display a definite

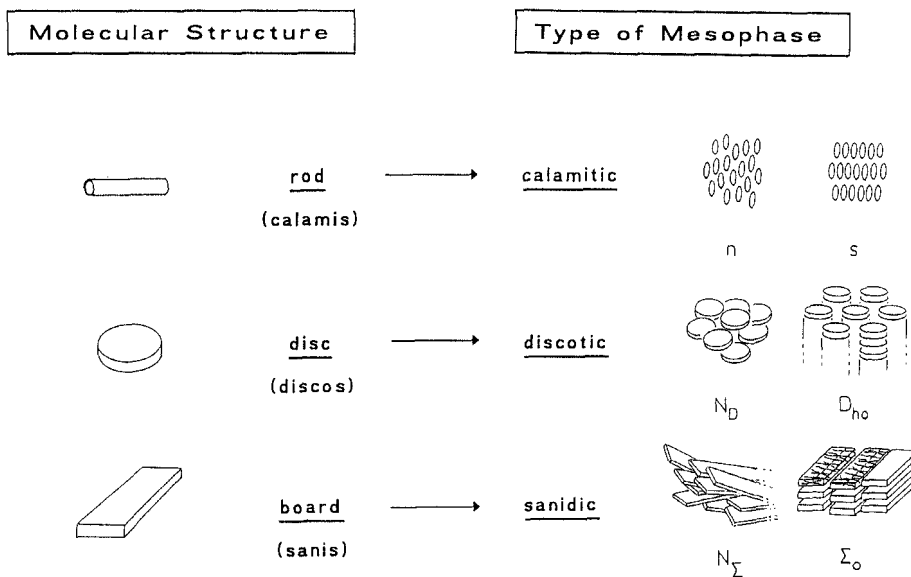


Figure 13. Molecular shape and phase formation.

registry along the chain axis. The stacks are packed regularly side by side (see figure 12). This modification will be called sanidic rectangular Σ_r and it has been shown that this structure is formed by the polyesters PE 12 and PE 8. A less ordered sanidic phase is the one where the board-like molecules are arranged again in stacks, where a one dimensional long range order exists along the stack normal but where there no registry exists along the chain normal. The stacks are again packed regularly side by side. This structure is termed sanidic ordered and the symbol Σ_0 has been chosen (see figure 12). This kind of structure is exhibited by the polyamide A 128. The spatial order is further decreased as we go to an arrangement in which there exists neither a regular registry of chain molecules within the stacks nor a regular packing of the board-like molecules within the stacks along the normal. The only long range order which is present results from the regular packing of stacks side by side. This structure will be called Σ_d , sanidic disordered (see figure 12). It has been shown that the polyamide A 1212 forms this kind of structure. Finally we may envisage the case that the regular packing of stacks of board-like molecules no longer exists. This would correspond, in principle, to the case of a nematic phase, where the chain axis defines the director. However, the structure will have to be biaxial at least locally. It was shown that this is the case for the polyamides containing 1,4,7-trioxaocetyl side chains (see figure 12). Conoscopic investigations even showed that the phase corresponds to a biaxial nematic phase.

In conclusion it thus seems that we may extend the concept that the shape of the molecule is a primary driving force for the formation of liquid-crystalline phases and for the kind of mesophases which is displayed to the case of board-like molecules, as depicted schematically in figure 13.

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