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Liquid Crystals

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Lytropic liquid crystals of a soluble polydiacetylene

A comparative investigation by means of optical and electron microscopy

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The liquid crystalline properties of a concentrated solution of poly{5,7-dodecadiyne-1,12-diol bis[[(4-butoxycarbonyl)methyl]urethane]} (P-4-BCMU) —a soluble polydiacetylene— in chloroform, beyond the critical concentration, have been investigated. Optical microscopy shows the anisotropic liquid crystal solution of P-4-BCMU in chloroform to be a polymer nematic. Disclinations with strengths of $s = +\frac{1}{2}$ and $-\frac{1}{2}$ are the most frequent type. Some disclinations with $s = +1$ were observed, but rarely disclinations with $s = -1$. Therefore, the liquid crystal texture usually displays a schlieren with two brushes in the vicinity of the singularities. The supramolecular structure observed by transmission electron microscopy shows a lamellar type morphology. As previously shown, the thickness of the lamellae is correlated to the molecular chain length. The chain length distribution leads to segregation with respect to molecular length and can be observed by thickness variations of both individual and subsequent lamellae. A kinetic study of disclination annihilation induced by isothermal relaxation in the liquid crystalline phase is presented. Possible mechanisms of the relation of the lamellar texture and the disclination annihilation are discussed. A stripe texture observed over large regions of the solid film is suggested to be a decoration effect due to internal stress as a result of solvent evaporation when the films are prepared by solution casting.

1. Introduction

Polydiacetylenes (PDAs) are synthetic polymers which can be obtained as large and nearly defect free single crystals by solid-state topochemical polymerization of monomer crystals [1, 2]. The polymerization gives rise to macromolecules with a conjugated backbone consisting of a sequence of double, single and triple bonds, as illustrated in figure 1. Extensive delocalization of the π -electrons along the backbone provides for interesting optical properties [3, 4]. Though most polydiacetylenes are insoluble, some of them form solutions in common organic solvents such as chloroform and tetrahydrofuran. One such soluble polydiacetylene was first synthesized [6, 7] in 1978 from 5,7-dodecadiyne-1,12-diol bis[[(butoxycarbonyl)methyl]urethane] and is commonly called P-4-BCMU. The chemical structure of P-4-BCMU is shown in figure 1. The properties of dilute solutions of P-4-BCMU in common organic solvents, in particular the chromic transitions induced by changes in temperature or solvent, have been extensively discussed in the literature [7-14]. Despite a number of investigations which assumed a rod-like nature of P-4-BCMU

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and similar polydiacetylenes [10, 11], the formation of a liquid crystal phase has, to the best of our knowledge, never been demonstrated until now.

Liquid crystalline polymers (LCPs) attract increasing attention [14–21], because their properties are vastly different from those of low molecular weight liquid crystals (LMWLCs). Depending on the chemical structure three different types of LCPs are differentiated: side chain LCPs, main chain LCPs which contain flexible spacers in the main chain (so-called semi-flexible LCPs), and rod-like main chain LCPs. The liquid crystal properties and textures of rod-like polymers are significantly different from LMWLCs, because of the large form anisotropy of the molecules. The formation of liquid crystals of rod-like macromolecules has been predicted in terms of a generalizing theory [22]. The length distribution normally present in polymers is an additional property which could bring further phenomena to light with respect to LMWLCs. However, experiments were hampered because the previously available rod-like molecules with high aspect ratios, but small cross-sections, are in general insoluble in common organic solvents. They can also not be melted without decomposition. Attaching flexible side chains to the moieties forming the rigid backbone is a means to improve solubility and fusibility, without influencing chain stiffness. This has also become a strategy of synthesis for a variety of rod- and worm-like macromolecules, sometimes denoted as 'hairy rods'. P-4-BCMU although the product of a solid state polymerization belongs to this class

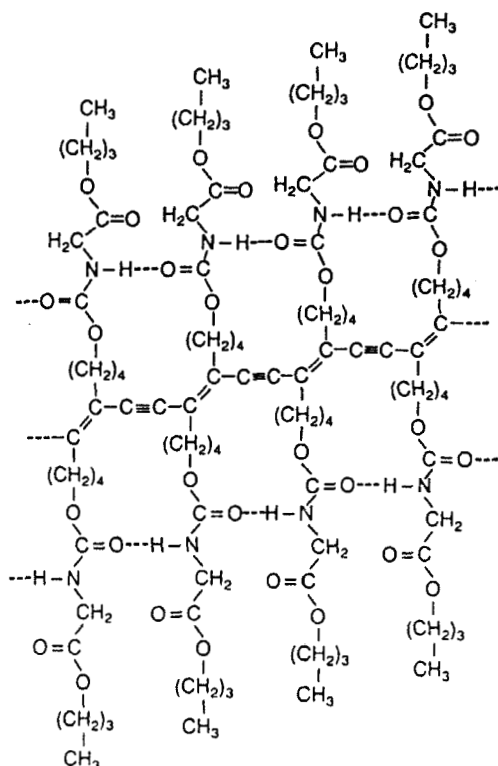


Figure 1. Section of the molecular structure of P-4-BCMU according to Patel *et al.* (1978). All hydrogen bonds are assumed to be intramolecular.

of polymers. Very long molecules are available which is particularly advantageous in view of the necessary resolution for electron microscopic investigation.

The present work shows that the solution of P-4-BCMU in chloroform forms lyotropic liquid crystals when a critical concentration is reached. On this basis, we have investigated the processes by which certain textures and types of disclination are formed using optical microscopy; the supramolecular structure, in particular the formation and annihilation of disclinations, was revealed by transmission electron microscopy. The interplay between a lamellar texture formed by extended macromolecules and the disclinations will be discussed.

2. Experimental

The synthesis of P-4-BCMU has been described by Patel *et al.* [5,6]. The molecular weights and weight distributions of samples were determined by gel permeation chromatography using a tetrahydrofuran (THF) solution. The calibration curve was determined by light scattering measurements on selected samples. A series of P-4-BCMU samples of various molecular weights was prepared by ultrasonic degradation of the high molecular weight sample in dilute chloroform solution. The details of synthesis and molecular weight determination of the P-4-BCMU samples used in the present investigation are described elsewhere [23, 24].

P-4-BCMU gives a dark yellow solution in chloroform at room temperature. Films were cast from such solutions at a concentration of 5 g l^{-1} when thick films for optical microscopy had to be prepared, and at a concentration of 1 g l^{-1} for the preparation of thin films to be investigated by transmission electron microscopy (TEM). All films were obtained by casting the solution on to glass slides. The films were bright red after the solvent had evaporated.

To bring out the textures of P-4-BCMU lyotropic liquid crystals as a function of annealing time at room temperature, the films were put in a closed glass container with a flat bottom and lid. The concentration of the solutions was increased by taking advantage of small leaks in the sample cell by which the solvent evaporated slowly. After formation of the anisotropic solution, its concentration could be kept constant by adding a small quantity of the pure solvent in the sample cell, avoiding direct contact between solution and solvent. The equilibrium between the liquid chloroform and the liquid crystalline solution of the polymer was allowed to be established via the vapour phase. Changes in the phase structure arising through adjusting the concentration of the chloroform in the films were monitored by UV/VIS spectra. P-4-BCMU is known to change colour on going from the solution to the solid state.

The texture of P-4-BCMU liquid crystals in chloroform solution or in the solid after complete evaporation of chloroform was observed at room temperature by optical microscopy (Zeiss Photomikroskop III) with or without polarizers. Microscopical observation of the films under these preparation conditions was restricted by the use of long distance objectives with low resolution.

The morphology of thin films of P-4-BCMU was investigated by TEM (Zeiss EM 902) at 50 or 80 kV. The dry films were floated off the glass substrate onto a water surface and transferred to copper grids. No further means of preparation was needed before electron microscopy. Because the films are beam sensitive, platinum-carbon replicas were prepared occasionally in order to check the influence of irradiation damage on the specimens. Electron diffraction patterns were recorded

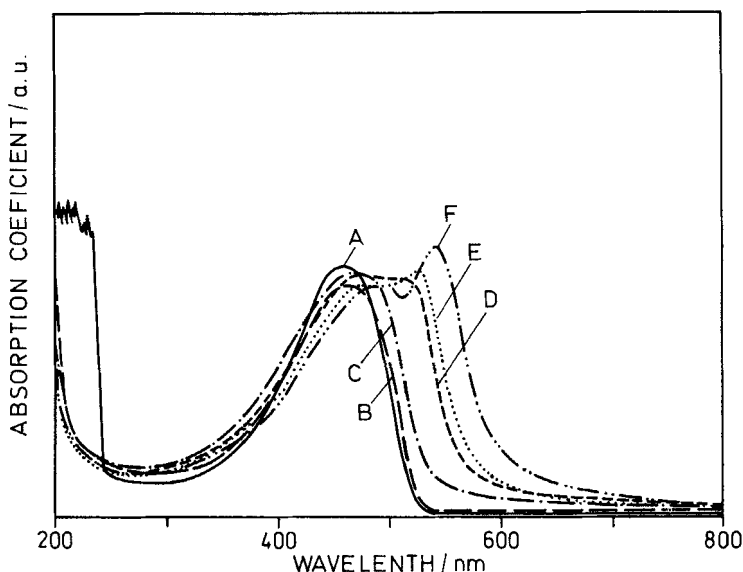


Figure 2. UV/VIS spectra of a thin film of P-4-BCMU swollen by chloroform to various concentrations. A, dilute solution of the polymer as reference; B and C are spectra of the film in the liquid crystal state; D and E are spectra of the same film at lower concentration of solvent when an anisotropic liquid crystal gel is formed; F is obtained from the solidified film.

using a Philips CM12 TEM at a high voltage of 120 kV, and in some cases at a temperature of -130°C .

The transmission UV/VIS spectra of liquid crystalline or solid thin films were obtained using a double beam spectrophotometer (Perkin-Elmer Lambda 3) at room temperature. A bandpass of 2 nm was used; scan speed was 60 nm min.

3. Results

3.1. The two component system P-4-BCMU/chloroform

Chloroform is a good solvent for P-4-BCMU [5-9]. Solutions of the polymer show an intense yellow colour. The conformation of P-4-BCMU chains in dilute chloroform solution is worm-like [9] and the macromolecular chains do not aggregate. A liquid crystalline state can be formed, as will be shown below, when the concentration of P-4-BCMU matches a critical concentration.

Films of high molecular weight P-4-BCMU ($DP_n = 425$) were cast from a 5 g l^{-1} solution. The solvent was allowed to evaporate under the conditions described in the Experimental section. When a polymer concentration of 10-15 per cent (w/w) was reached, the film still showed a bright yellow colour, but a liquid crystalline texture could be observed by polarizing microscopy. The spectra of a dilute solution of P-4-BCMU in chloroform and of the liquid crystalline film are recorded in spectra A-C in figure 2. When the amount of chloroform in the vessel containing the film was decreased, substantial changes in the optical spectra were observed. This is indicated by spectra D and E in figure 2. A shift of the initial absorption to higher wavelength and the occurrence of a second peak at much higher wavelength is seen. The spectral changes are equivalent to a change in the appearance of the films from

dark yellow to orange and finally orange-red. Finally, a bright red colour corresponding to spectrum F in figure 2 was observed on complete evaporation of the solvent, in agreement with literature [26].

The critical concentration, c^* , at which the liquid crystal phase appears and the width of the concentration region, Δc , in which the liquid crystal phase is stable depend not unexpectedly on the degree of polymerization. Two samples of $DP_n = 425$ and 110 were investigated with regard to this effect. The parameters c^* and Δc are summarized in the table. The two samples differing in DP_n by a factor of approximately 4 differ significantly in the critical concentration at which the lyotropic LC phase can be observed. This appears at *c.* 10–12 per cent (w/w) in the case of the sample of higher DP_n , compared to a concentration as high as 25 per cent (w/w) in the case of lower DP_n . In both cases, a solid phase in equilibrium with the LC phase is formed when the polymer concentration is increased to 22.5 per cent (w/w) (higher DP_n) or 32.5 per cent (w/w) (lower DP_n). Thus, the width of the existence region of the LC phase becomes smaller for smaller DP_n . The formation of a solid phase at higher concentration of the solution is indicated by UV/VIS spectra D and E in figure 2: A new peak appears at much higher wavelength.

3.2. Texture

Figure 3 displays a typical example of a schlieren texture, well-known from studies of low molecular weight nematic systems. It indicates clearly that, beyond a critical concentration, P-4-BCMU forms a polymer nematic phase in chloroform solution. Here we use the term 'polymer nematic' to replace nematic, as the molecular order in LMWLCs and stiff LCPs is not the same as will be demonstrated later. To bring out the liquid crystal texture in such a clear fashion, the P-4-BCMU film ($DP_n = 425$) was cast from chloroform solution to provide a thickness of about 10 μm and allowed to anneal under a controlled atmosphere of chloroform/air for more than 200 h at room temperature. Figures 3(a) and (b) correspond to two different orientations of the crossed polarizers. The dark brushes in figure 3 start from points which do not change their position when the polarizers are rotated. These points are the positions of disclinations or singularities [27–30]. Evidently there are different types of disclinations present. The strength of a disclination is

Phases observed in the two component system P-4-BCMU/chloroform at room temperature for two polymer samples differing in DP_n .

Sample A ($DP_n = 425$)		Sample B ($DP_n = 110$)	
Concentration/% w/w	State of system†	Concentration/% w/w	State of system†
5.0	L	15.0	L
7.5	L	17.5	L
10.0	L+LC	20.0	L
12.5	LC	22.5	L
15.0	LC	25.0	L+LC
17.5	LC	27.5	LC
20.0	LC	30.0	LC
22.5	LC+S	32.5	LC+S
25.0	LC+S	35.0	LC+S

† L = liquid; LC = liquid crystal; S = solid in gel form.

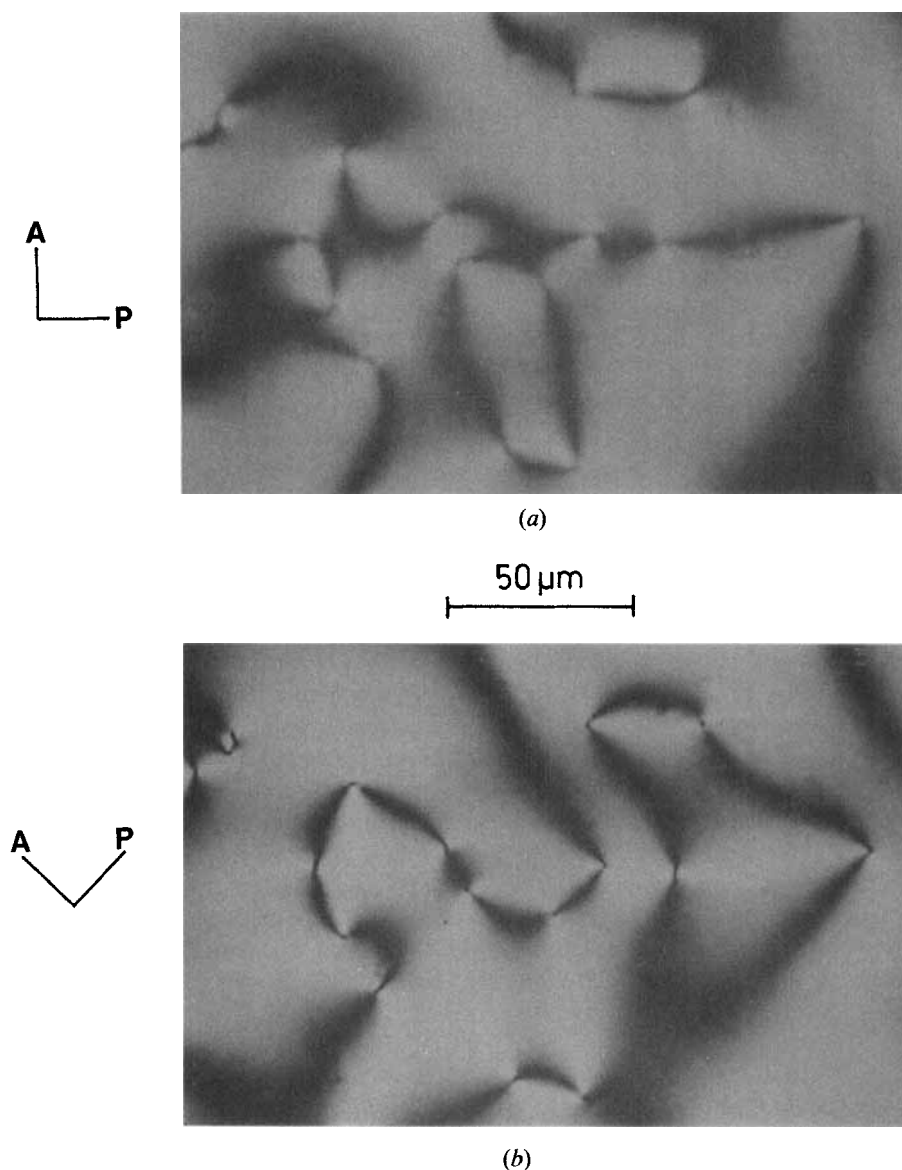


Figure 3. Optical micrographs of a *c.* $10\ \mu\text{m}$ thick film of the lyotropic phase annealed for 2 weeks at 25°C . The position of the analyser and polarizer is indicated. The same area is seen in the micrographs (a) and (b) with only the position of the polarizers rotated.

defined by a number of s , the modulus of which is equal to one-fourth of the number of dark brushes which start from the disclination. The sign is positive when the brushes turn in the same direction as the rotation of the polarizers, and negative when they turn in the opposite direction. Only disclinations with $s = +\frac{1}{2}$ and $-\frac{1}{2}$ can be seen. Occasionally we observed a few disclinations with $s = +1$. They are unstable and dissociate into $s = +\frac{1}{2}$ disclinations because their energy is proportional to $|s|^2$. Disclinations with $s = -1$ were observed only very rarely.

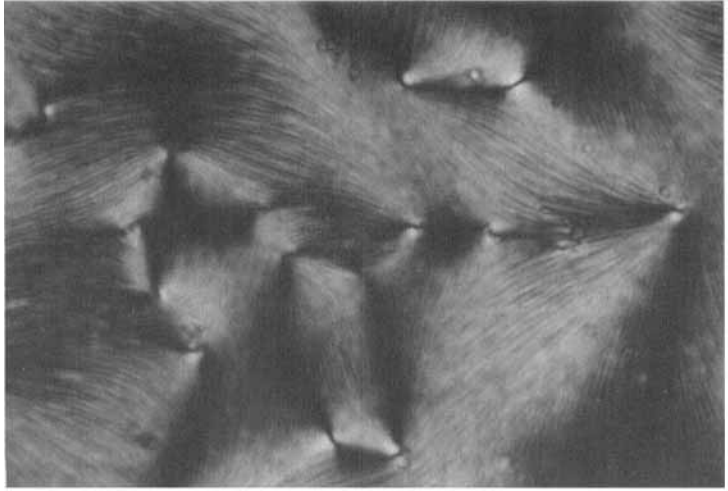
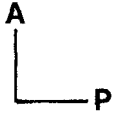
Figures 4(a) and (b) display a set of micrographs taken between crossed polarizers from the same film and same area as figure 3, but after complete evaporation of the chloroform. The film has undergone a transition from the liquid crystal to the solid state. Basic features, i.e. schlieren texture and red brushes, are just as in figures 3(a) and (b), indicating that the local orientation of the molecular axes does not change when the chloroform is evaporated. However, additional stripes have appeared. The colour variation seen in the micrographs originates from an interplay between birefringence and dichroic behaviour of the solid P-4-BCMU. A similar stripe texture was reported recently from a thermotropic main chain LCP [31]. The width of the stripes is a function of film thickness, domain size, evaporation rate of the chloroform and the molecular weight. Wider stripes are formed in thicker films, in films with larger domains, of higher molecular weights or in films prepared at faster evaporation rates. They may be considered as a kind of decoration effect. This can be seen from the dichroic contrast of figures 4(c) and (d). The transition moment for absorption of visible light is parallel to the chain direction in all polydiacetylenes. Thus, the chain direction in solid samples can be readily identified from the local dichroism. It can be identified within the stripes as being parallel to their longest axes, when images in linearly polarized light are obtained. It is of extreme importance for the later electron microscopic investigations to point out that the relative position of the disclinations and their strength do not change when the solvent is rapidly evaporated, once a particular texture has been formed by extended annealing in the lyotropic LC phase. This is clearly shown by comparing figures 3(a) and (b) with figures 4(a) and (b). The contrast from disclinations in unpolarized light is higher in the solid than in the liquid crystalline film. It is worth noting that not only can we detect directly the spatial position of the disclinations, but also we can identify their type from micrographs taken in unpolarized light (cf. figure 7.D(3)). The stripe pattern is an immediate image of the molecular director field and of the spatial distribution of positive and negative disclinations. Figure 4(e) shows the stripes and the location of disclinations with strengths $s = +\frac{1}{2}$ and $-\frac{1}{2}$ as a sketch taken from an image in unpolarized light corresponding to the same area as depicted in figures 4(a) and (c).

The stripe texture causes a surface topology which occurs when the solvent is completely evaporated. This can be seen in the micrograph of figure 5 which was taken in reflected light. In this optical micrograph, we can directly and easily determine the positions, strengths and signs of the disclinations.

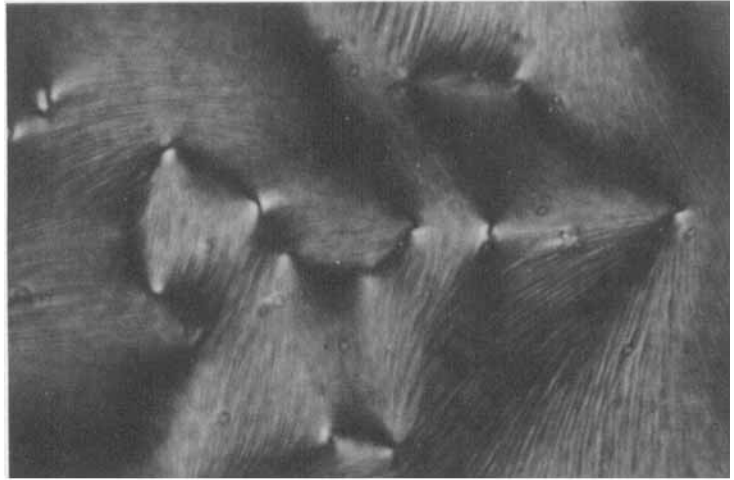
A droplet texture could also be formed under special circumstances; this corresponds to similar textures conventionally seen in LMWLCs. When a droplet of a dilute solution of P-4-BCMU in chloroform was put on a glass surface and the chloroform allowed to evaporate, an extinction cross was seen between crossed polarizers. Even more interesting, was the observation of a texture, that we call the 'anti-droplet' texture. The anti-droplet texture was formed when a droplet of chloroform was put onto the surface of a solid film of P-4-BCMU and allowed to evaporate slowly. The texture formed is seen in figure 6. In the droplet or anti-droplet textures, a disclination with $s = +1$ is formed.

3.3. Disclination density

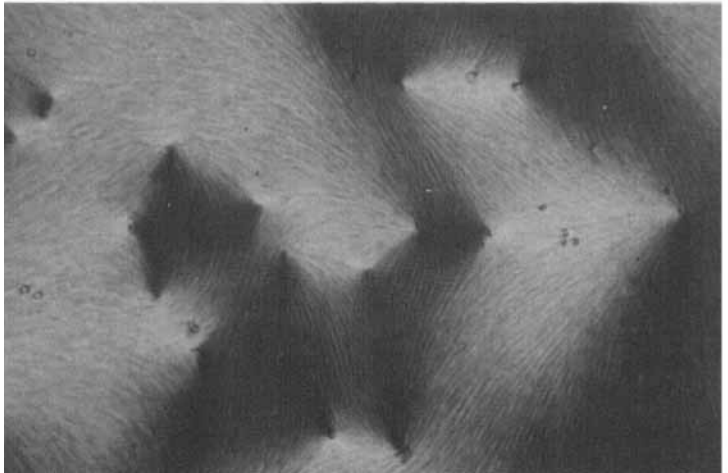
The development of the polymer nematic texture at 25°C was investigated as a function of time. The films to be studied were prepared by concentrating a dilute solution of P-4-BCMU in chloroform. The film preparation method influences



(a)



(b)



(c)

50 μ m

A scale bar consisting of a horizontal line with vertical end caps, indicating a length of 50 micrometers.

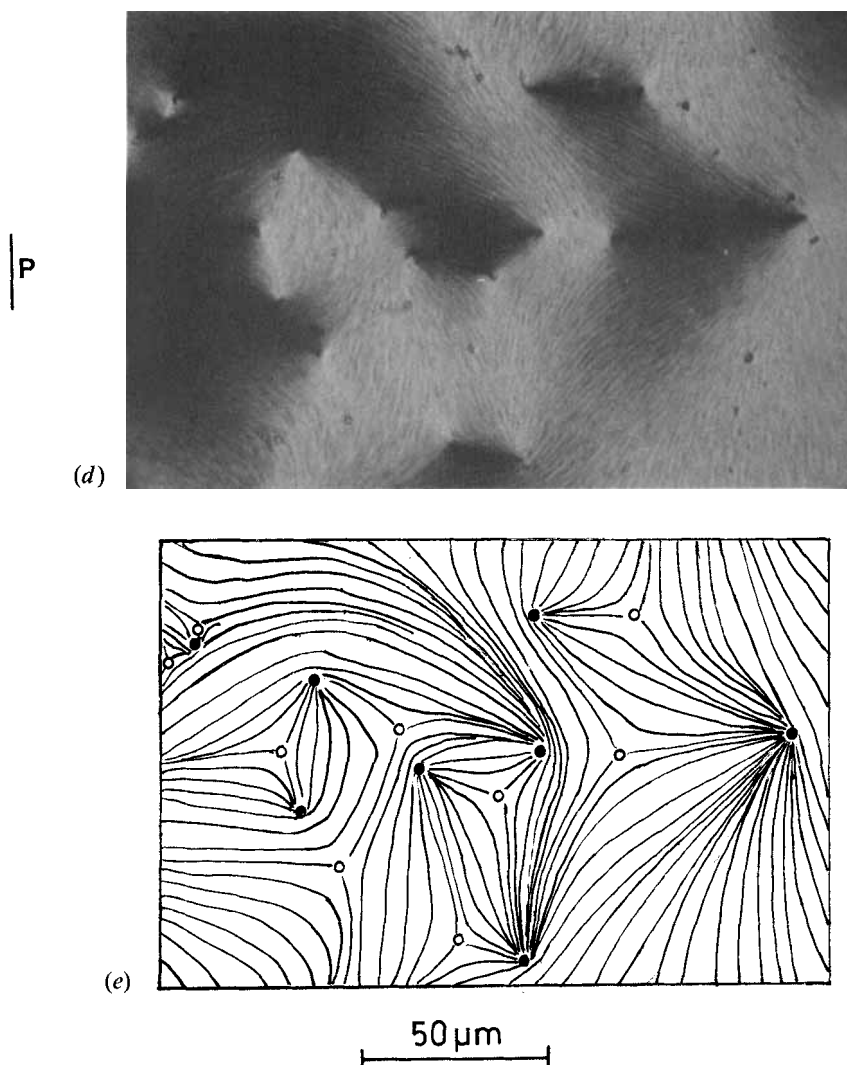


Figure 4. (a) and (b) Optical micrographs (crossed polarizers and relative position indicated) of the same field of view as in figures 3(a) and (b) after complete evaporation of the solvent. (c) and (d) Dichroism of the texture; the same field of view as in figures 4(a) and (b) is depicted. (e) Schematic drawing showing the positions of disclinations of (\circ , $s = -\frac{1}{2}$; \bullet , $s = +\frac{1}{2}$) and the director field labelled by stripes. Taken from (a) to (d).

strongly the formation and density of disclinations in the liquid crystalline state. The key factor in establishing an initial and reproducible density of disclinations is the rate of evaporation of the solvent during the formation of the liquid crystal phase on going from the thin layer of isotropic solution to the liquid crystal film. In our experiments, it took typically 5 h at 25°C to go from the thin liquid film, at an initial concentration of 5 g l⁻¹ of the polymer to the liquid phase characterized by the micrograph shown in figure 7A(1). Undiscernible patterns were obtained when the liquid crystal phase was formed over shorter times. The density of disclinations and

their annihilation by isothermic annealing could be determined from micrographs taken after various times from the same area of the liquid crystal film. As pointed out above, the disclinations and their sign can be better analysed when the films are rapidly dried after a desired density of disclinations has been reached. A set of micrographs illustrating the decrease in disclination density with annealing time is reproduced in figure 7. A, C and D refer to the respective points in figure 8 in which the time dependence of the disclination density is reported for the sample of $DP_n = 145$. In the case of the sample with $DP_n = 425$, the annihilation kinetics were so slow that a similar curve could not be obtained. The curve in figure 8 allows us to classify three regimes, assigned to the initial slow annihilation (A-B) the subsequent fast annihilation (B-D) and the final slow annihilation (D-E) regime.

3.4. Characterization by electron microscopy

In the following, we want to correlate observations by optical microscopy with molecular features obtained by electron microscopy. We have already shown that it is possible to identify lamellae in a thin film of P-4-BCMU by means of transmission electron microscopy [23–25]. The lamellar thickness is closely correlated with the lengths of the macromolecules. The chain direction was found perpendicular to the lamellar surface and parallel to the substrate on to which the film was cast. Within the lamellae, the side chains are mainly directed towards the substrate. Contrast between lamellae and interlamellar regions, in particular in samples which were solidified after short dwell times in the anisotropic solution state, is enhanced by selective beam damage in the disordered interlamellar regions, where chain ends, ciliae, and probably very short chains are accumulated. For these samples we can see, at very low beam intensity, that the contrast between lamellar cores and boundary regions is initially not sufficient to obtain clear images. Thus we should address beam damage as a means of contrast formation, but this effect should be

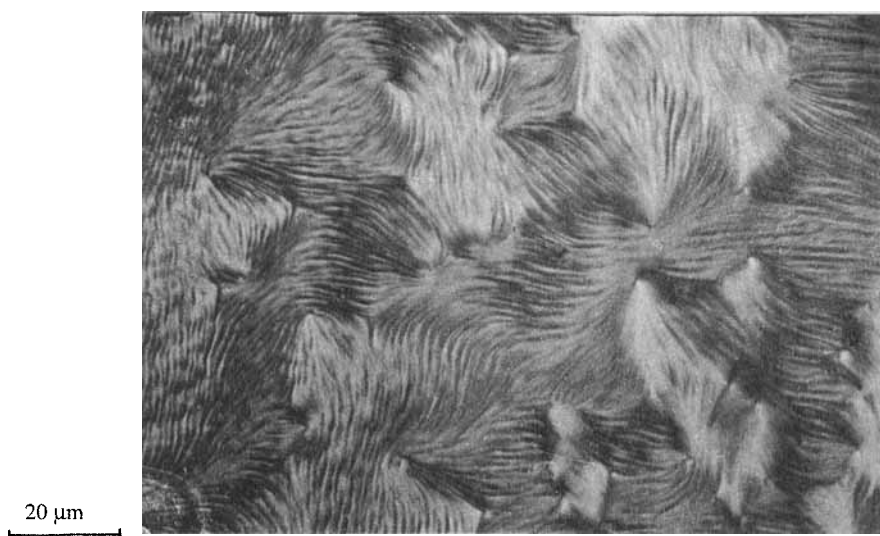


Figure 5. Optical micrograph in reflected light of the solid film obtained when all solvent was evaporated from the annealed lyotropic phase.

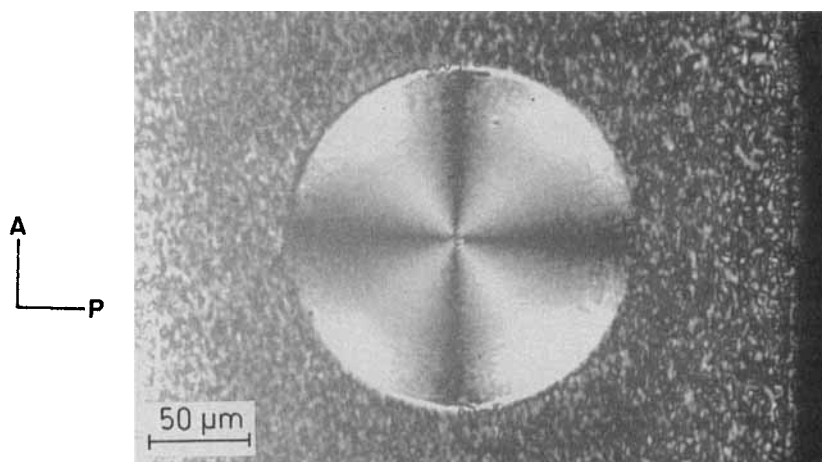
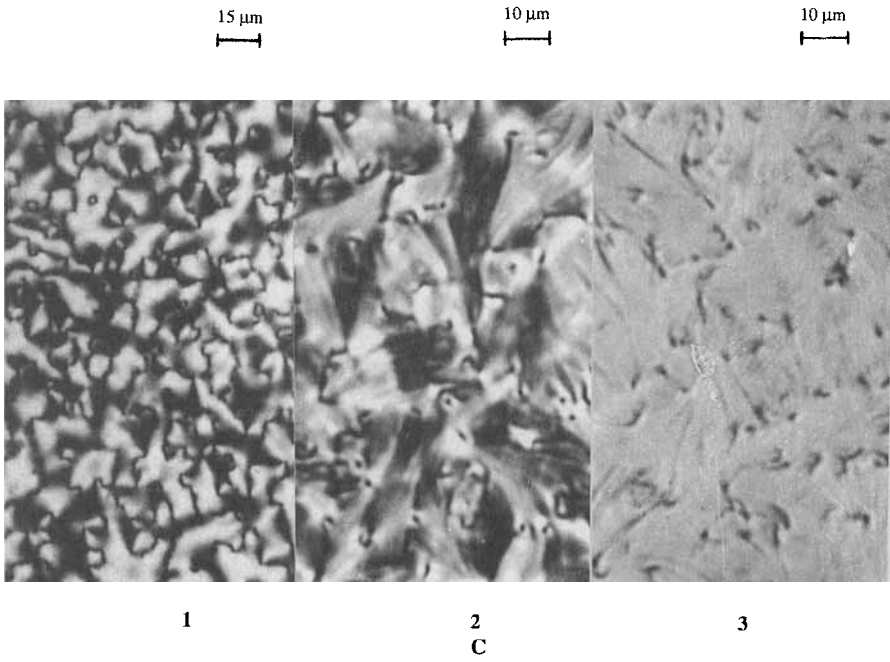
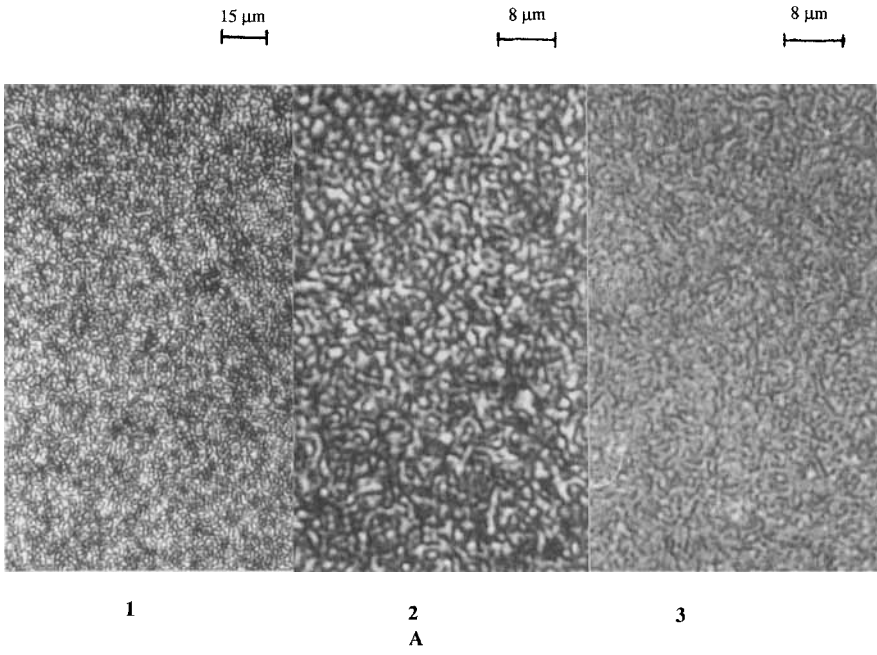


Figure 6. Optical micrograph of an anti-droplet texture of P-4-BCMU.

distinctly differentiated from the process of formation of the lamellae. The fact, already amply discussed in the previous section, that the texture of the lyotropic liquid crystal phase is conserved on rapid evaporation of the solvent allows a detailed study of the types and interactions of the disclinations by electron microscopy. Thus, thin films of P-4-BCMU solution were prepared and the desired liquid crystalline phase was obtained by slow solvent evaporation in order to adjust the disclination density as described by figure 8. The solvent was then rapidly evaporated to quench the texture which was subsequently investigated by electron microscopy.

The first discernible texture could be obtained when the samples had been annealed to match approximately the conditions of A in figure 8. Micrographs obtained from such samples show numerous black stripes the length of which corresponds approximately to the molecular length as demonstrated by figure 9(a). The onset of parallelization of the macromolecules is seen, but the overall degree of parallelization and aggregation is still rather small. However, first signs of formation of lamellae are already seen. In the optical microscope, only granularity was seen, indicating the presence of a very large number of small domains. When a liquid crystalline film was allowed to anneal for such a time that its disclination density corresponded to the region between A and B in figure 8, a network of lamellae was seen by TEM. This is shown in figure 9(b). The contrast is still weak and striations of 20–40 nm in width are superimposed. The lamellar thickness corresponds to the chain length. Disclinations can hardly be detected, because directors of neighbouring lamellae point, even within small areas, in different directions.

Lamellae became more clearly visible when the liquid crystalline film was allowed to anneal for a length of time exceeding B in figure 8. This is displayed in figure 9(c). Striations are now finer (~ 10 nm in width) and the directors change orientation slowly. From this stage on, disclinations are identified clearly. Their positions are indicated in figure 9(c) by white arrows for strength $s = +\frac{1}{2}$ and by black arrows for $s = -\frac{1}{2}$. It is worth noting that the thickness of individual lamellae is not uniform. At some sites (for example, A in figure 9(c)), a thick lamella is split into two thinner



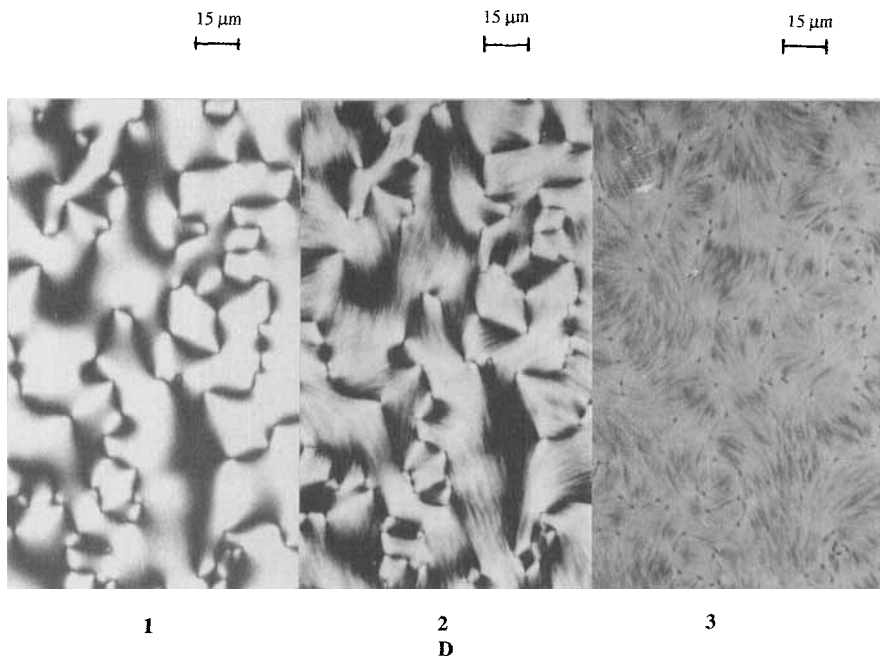


Figure 7. A set of micrographs demonstrating the decrease in disclination density, and changes in texture and growth of domains as a function of the time of annealing of the lyotropic phase; all micrographs marked 1 are taken in the lyotropic state and the micrographs marked 2 and 3 are taken after the solvent has been evaporated; 2 under crossed polarizers, 3, taken in unpolarized light. Capitals A, C and D correspond to figure 8.

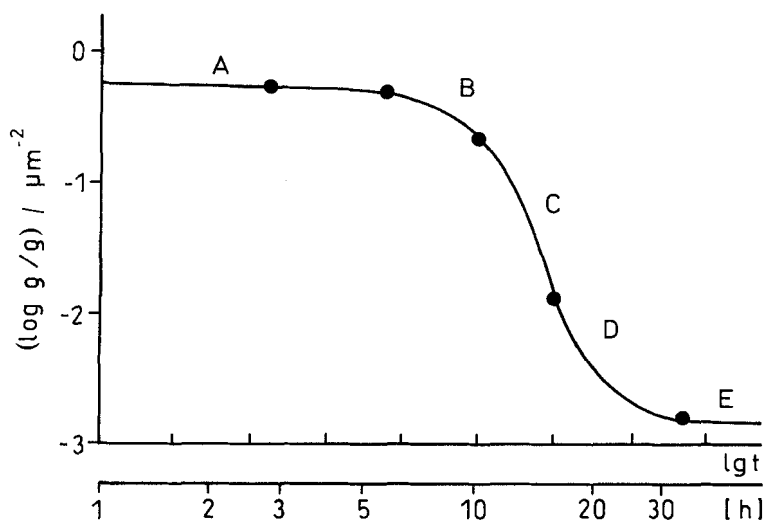
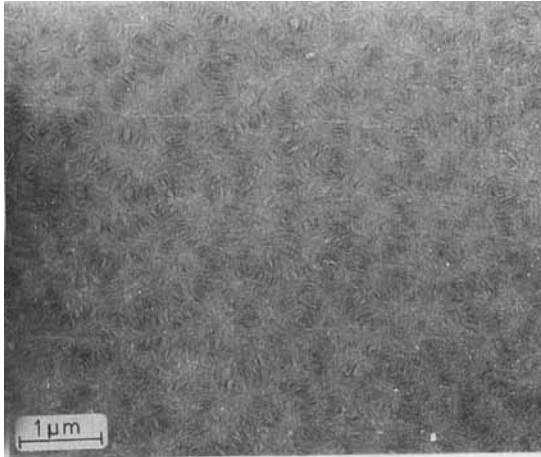
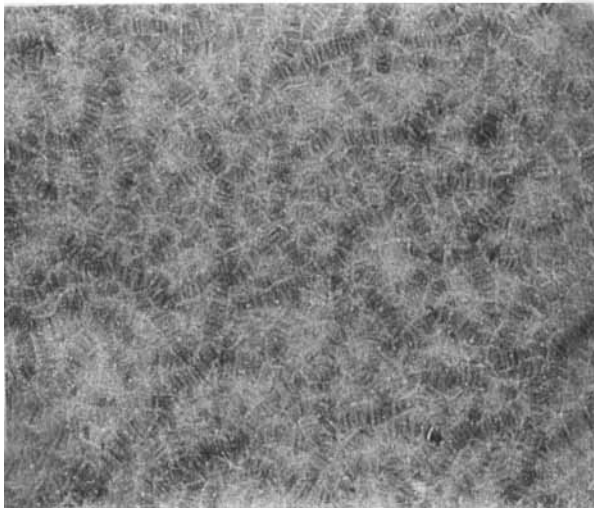


Figure 8. Disclination density determined from the optical micrographs (cf. figure 7) as function of the annealing time. The polymer used has $DP_n = 145$; for an explanation of regimes A-E see the text.

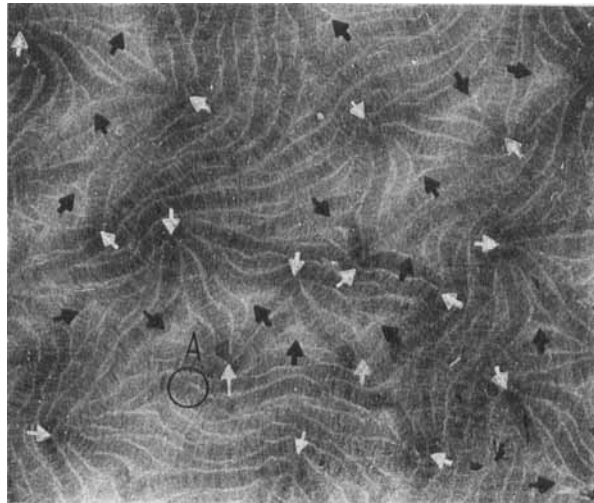
(a)



(b)



(c)



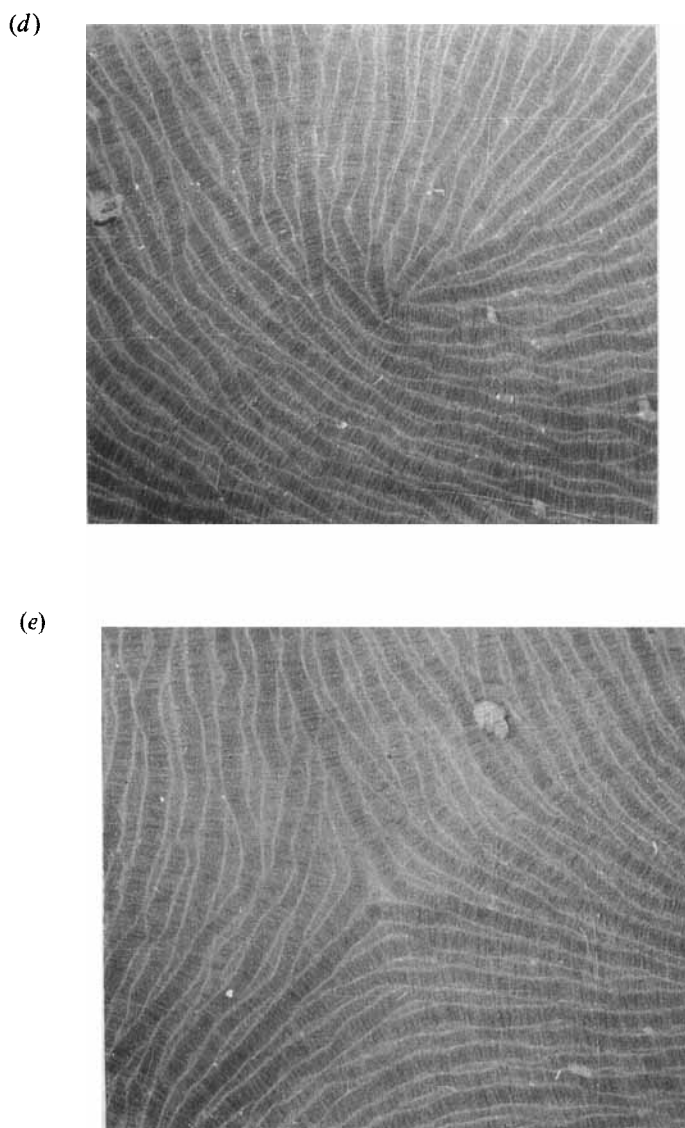
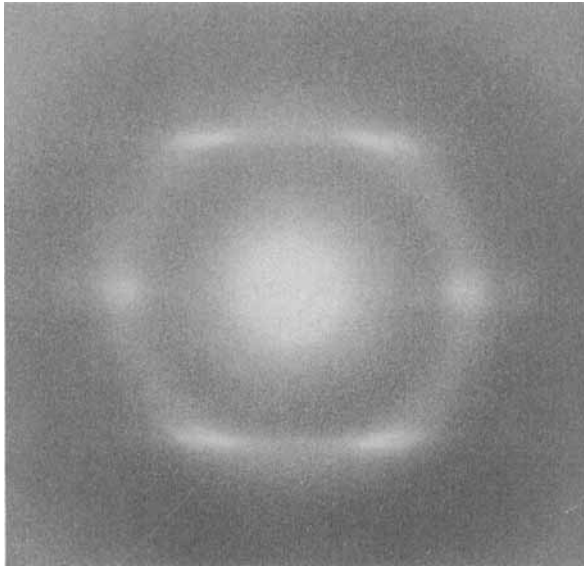


Figure 9. A set of TEM micrographs of thin polymer films demonstrating the change of supramolecular structure with annealing time. (a) Film as cast and briefly annealed in the lyotropic phase; (b) after annealing to the regime B (cf. figure 8); (c) after annealing to the regime between B and C, the arrows indicating disclinations; (d) and (e): two disclinations of $s + \frac{1}{2}$ and $-\frac{1}{2}$, respectively, and formation of extended lamellae in the regimes D and E of annealing time.

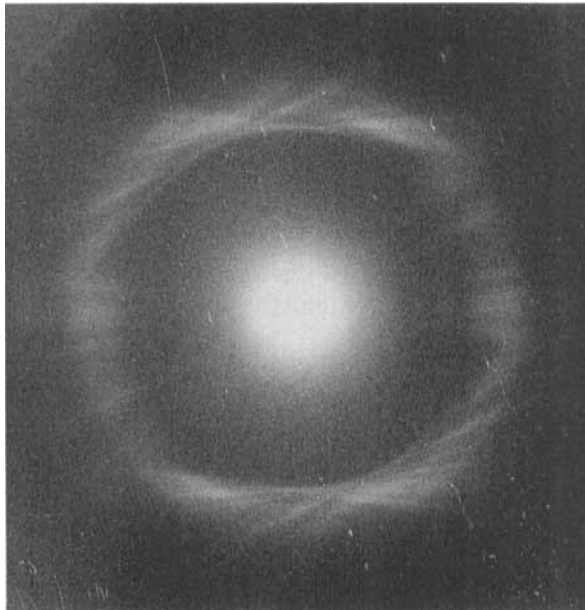
ones. Frequently the thickness of individual lamellae decreases towards their ends. With further increasing annealing time, more and more disclinations become annihilated and it becomes very rare that two disclinations are only such a distance apart that they can both be imagined in a single frame at 10 000 fold magnification. Figure 9(d) and (e) shows disclinations with $s = +\frac{1}{2}$ and $s = -\frac{1}{2}$, respectively, in samples obtained near E in figure 8. The variations in the thickness of individual lamellae is assumed to reflect the molecular weight distribution of the sample. In other words segregation according to chain length is considered to be the origin of thickness fluctuations. Most of the lamellae are pointed, i.e. they end in tips, because short chains tend to migrate towards the outer part of the lamellae. The particular shape of their surface facilitates the formation of curvature in the vicinity of the disclination cores. At the $s = -\frac{1}{2}$ disclination, the core itself seems to consist of short chains (see figure 9(e)). Another conspicuous feature towards chain segregation is an alternating sequence of thick and thin lamellae, seen in figures 9(d) and (e). These figures display a further interesting phenomenon. The morphological features seen around the disclination core can be grouped into two systems which are reciprocal to each other. There are curved lamellae and dark striations perpendicular to them. The latter can be used to characterize the bent director field round the core of the disclination. Nevertheless, the molecules inside the lamellae are straight as shown by electron diffraction, a topic which will be discussed later. Because extended molecules in two subsequent lamellae are inclined with respect to each other, in order to follow the director field, their ends contribute to the disorder in the interlamellar regions. It is reasonable to assume that most of the elastic energy caused by the bend in the director field is concentrated in these regions and may contribute to the enhancement of irradiation induced degradation of chain segments in these areas.

Figure 10(a) displays an electron diffraction pattern from an area the diameter of which was a bit larger than the width of a thick lamella. It was recorded in the nano-probe mode, i.e. the area was selected by a convergent beam limited by the condenser aperture, and not by an aperture in the imaging plane of the objective (conventional selected area diffraction). Diffraction patterns had to be taken at low beam intensities and exposure times insufficiently long to cause damage which would make the lamellae visible. It is therefore not possible to select an area deliberately at a desired place, for example in only one unique lamella or in the immediate vicinity of a disclination. Therefore, the diffraction patterns were taken 'blindly', i.e. without reference to particular morphological features. Continuous intensity along layer lines in figure 10(a) points to longitudinal shift disorder of adjacent chains packed together in bundles. The meridional distance of the layer lines corresponds to the chain repeat. The continuous intensity is superposed by sampling of intensity at the points of 001 reflections of staggered chains in register. The intense equatorial reflections relate to the side chain packing. Side chains point mainly towards the substrate, forming a layered structure parallel to the substrate. The periodicity of these layers is determined by the length and conformation of the side chains. At some places, lamellae are seen edge on and give rise to weak reflections on the innermost part of the equator.

Figure 10(b) is a diffraction pattern of an ensemble of strongly curved lamellae near the core of a disclination. It shows a distinct number of streaks rotated with respect to each other, instead of a continuous broad arc, giving evidence that the



(a)



(b)

Figure 10. Electron diffraction patterns obtained from thin films after annealing in the lyotropic phase. (a) Pattern obtained from an individual 'thick' lamellum (cf. figures 9 (d) and (e)). (b) Pattern from an ensemble of strongly curved lamellae near the centre of a disclination.

lamellae are not continuously bent. The underlying diffuse scatter is probably due to the chain ends in the disordered interlamellar region.

4. Discussion

4.1. Formation of lyotropic liquid crystals

Theories on the formation of lyotropic liquid crystals of rod-like macromolecules in solution have been developed by Onsager [32], Flory [22] and Di Marzio [33]. The following general requirements can be derived for the formation of anisotropic liquid crystalline solutions of polymers:

- (i) a rod-like conformation of the main chain;
- (ii) a minimum molecular length which may be expressed in terms of the axial ratio;
- (iii) a solvent that is capable of dissolving the polymer beyond a critical concentration at which the lyotropic phase will appear.

Point (i) is probably the requirement which needs detailed comment. The structure of P-4-BCMU is sketched in figure 1, and due to its main chain consisting of alternating multiple and single carbon bonds, the backbone is linear and rigid in the solid crystalline state. The long side chains make the PDA soluble in common organic solvents and do not affect the rigidity significantly. However, in dilute solution in chloroform, P-4-BCMU was shown to adopt the conformation of a worm-like chain [14]. The persistence length of P-4-BCMU in chloroform is close to 16 nm; the same value was measured in toluene at a higher temperature (about 80°C) [9]. It is common use to apply the term 'rod-like' to stiff macromolecules, the length of which does not exceed the persistence length. The form anisotropy of macromolecules of larger length is based on the persistence length as the critical parameter. The mean square radius of gyration of the chain cross-section which includes the space required by side chains is of the order of 0.6 nm² [9], i.e. the diameter is about 0.9 nm on average. Therefore, the axial ratio, x , of P-4-BCMU in chloroform is about 18, indicating the high anisotropy of the macromolecule. Flory *et al.* [34] calculated a value of 6.42 as the minimal axial ratio at which a nematic phase would be stable in a neat liquid consisting of hard rods. Although the samples investigated consisted of chains which were longer on average than the persistence length, we observe that the critical concentration is influenced by the average chain length. Therefore, the persistence length is obviously not the only parameter determining the value of the critical concentration c^* (see the table). In any case, regardless of whether the axial ratio is calculated from the full length of the chain or only from the persistence length, conditions (ii) and (iii) are fulfilled by the P-4-BCMU solutions in chloroform. This is not the case when tetrahydrofuran (THF) and dimethylformamide (DMF) are used as solvents for P-4-BCMU, instead of chloroform. Concentrated solutions of the polymer in THF or DMF were very viscous and gave isotropic gels. The high viscosity seems to prevent the molecular alignment necessary to form an ordered liquid crystalline solution. In addition, toluene is a solvent for P-4-BCMU at higher temperature (about 80°C). The solution cooled from 80°C is a red gel at room temperature. In the literature [10, 11], it has been reported that anisotropic particles were formed after ageing the red gel for some time. But in the red gel of P-4-BCMU in toluene, the rigid molecules are not mobile enough to form a real anisotropic liquid crystalline solution. Therefore, among the common solvents, only chloroform fulfils all the conditions, under which theory predicts the

formation of lyotropic liquid crystals, as a solvent for P-4-BCMU at room temperature. This system is a good example that textures well-known from nematic LMWLCs can also be observed in stiff main chain LCPs. In addition to optical microscopy, the phenomena can be studied at higher resolution by electron microscopy because of several favourable circumstances.

4.2. Structure, texture and disclinations

Several essential features concerning the state of order of P-4-BCMU can be extracted from the experimental data: optical microscopy shows that the liquid crystals are nematic. The curvature of the lamellae becomes less pronounced as the system approaches equilibrium. In addition, the thickness of individual lamellae shows variations. Dark field images over large areas in the light of one of the intensity maxima on the layer line have low contrast and never exhibit lamellar structures. This is an additional indication that the intensity sampling is not due to real crystallites, although some chains are in register. Therefore crystallization is not the essential feature and cannot be the reason for the morphology seen in bright field images. It is necessary to emphasize this point to avoid misinterpretation of the origin of the lamellar texture. In the particular case of P-4-BCMU, it was possible to freeze-in the basic feature of the LC morphology. It should be mentioned that crystallization occurs to a much higher degree when P-4-BCMU is recrystallized from the thermotropic state [35].

The case of a polymer nematic forming lamellae was treated for polymer chains of uniform length from a theoretical point of view by de Gennes [36]. Computer simulations exhibit lamellae as well as when the polymer exceeds a critical concentration [37]. Meyer introduced the expression 'supersmectic' for such systems, emphasizing the difference from low molecular weight smectics [38].

An important feature of a polymer is its molecular mass distribution, i.e. the distribution of chain lengths. This property is well-known, but its effect on ordering phenomena in LCPs is in the very early stages of theoretical treatment [39]. The TEM micrographs demonstrate convincingly that the molecules segregate in the lyotropic state with respect to their length when the system is allowed to relax. This process results in both the alternating sequence of thick and thin lamellae and the formation of pointed lamellae (for example in Figures 9(d) and (e)). In both cases, short chains are expelled from the interior of an aggregation of long chains. It seems that in the first case, the transport process is dominated by longitudinal motion of short chains. They accumulate in the interlamellar region between the lamellae of longer chains, forming there a thin lamella corresponding to the average length of the excluded molecules. In contrast to the longitudinal motion, the transport process leading to the pointed lamellae seems to work by a transversal migration of short chains. This type of motion seems only to be possible in a three-dimensional system and is not expected to take place in monolayers of rigid macromolecules.

In spite of the segregation according to chain length, the lamellar surfaces are not smooth. The less ordered interlamellar regions are characterized by a density deficiency. This detail is not always realistically reproduced in electron micrographs, because the lack of order makes the interlamellar regions less resistant to the impact of the electron beam. On the other hand, it is just the irradiation damage which gives the high contrast in the micrographs and makes the lamellar cores visible. (At low temperatures, irradiation damage proceeds much more slowly and the lamellar morphology is not seen at ordinary exposures. The films look homogeneous.

Contrast is present only for samples in the tail of the curve in figure 8, even without irradiation damage in the interlamellar regions.)

From the inspection of TEM micrographs alone, we would not hesitate to describe the morphology as a smectic structure, although the length scale is quite different from lamellar structures of LMWLCs. The thickness of P-4-BCMU lamellae exceeds 200 nm, for example, in figures 9(d) and (e). The question why a well-shaped lamellar system of stiff macromolecules has to be classified as nematic is answered by study of the disclinations.

A growing liquid crystal incorporates inevitably defects, the most prominent of them being disclinations. Their type, strength and distribution are the factors which determine the texture observed. Disclinations give rise to elastic deformations in their vicinity. The mechanisms discussed for these deformations in LMWLCs are: bend, splay and twist. For a thin LC film twist deformation does not occur.

The usual models of elastic deformations are problematic for LCPs when the assumption of constant density within the liquid crystal is made. But chain deformations are probably smaller than expected, because space filling can be realized by taking advantage of the curvature of the lamellar surfaces due to the length distribution of the polymer. At least in the frozen liquid crystalline state, electron diffraction patterns justify the treatment of rigid macromolecules as being rod-like. We infer from this observation that residual bend of molecules may be concentrated in the disordered interlamellar region, being an additional source of disorder. Nevertheless the director field is bent.

For smectic LMWLCs (typical molecular length 3 nm), only the disclinations exist and focal-conic domains are formed because splay is the only mode of deformation. For polymer lyotropic liquid crystals, like P-4-BCMU, however, mainly disclinations with strengths $s = +\frac{1}{2}$ and $s = -\frac{1}{2}$ are predicted by Kléman [40] because the anisotropy of the molecules is high and mainly bend deformation occurs. Disclinations with strength $s = +1$ are unstable because the deformation energy is proportional to s^2 . Therefore disclinations with $s = +1$ have a strong tendency to split into those with $s = +\frac{1}{2}$. Since the energy required to produce a splay deformation is obviously very high in liquid crystals of rod-like macromolecules, the strength of disclinations with $|s| \neq \frac{1}{2}$ may be even larger.

These predictions are realized in the case of P-4-BCMU. We observe mainly disclinations with $s = +\frac{1}{2}$ and $-\frac{1}{2}$ (see for example, the sketch in figure 4(e)) and some disclinations with $s = +1$. Disclinations with $s = -1$ are rarely detected. We suggest that in the core region of an integral disclination with negative sign the necessary curvature cannot be achieved by elastic deformation. In general we observed only two schlieren brushes.

It may be of interest to compare the results presented with those obtained for other polymer systems, with regard to a detailed description of the optically characterized disclinations. Only observations on liquid crystalline solutions of aromatic polyamides in concentrated sulphuric acid are reported in the literature [41, 42]. For the lyotropic nematic phase of the poly(*p*-phenylene terphthalamide)/sulphuric acid system, for example, defects are observed which display closed loops. For thermotropic main chain polymers with flexible spacers, disclinations with $s = +\frac{1}{2}$ and $-\frac{1}{2}$ predominate too [14, 18, 43–46]. But rigid macromolecules and those with flexible spacers might behave essentially differently and it is not sure whether they can be compared with each other.

4.3. Formation and annihilation of disclinations

The formation of the liquid crystal phase with its distinct pattern of disclinations is characterized—like all ordering phenomena—by time dependent effects influenced by a large variety of parameters. The first step is parallelization of the backbones during which the molecules arrange themselves with a large shift disorder. The quality ‘large’ is here to be understood on the scale of molecular length. Figure 9(a) shows a micrograph where this degree of molecular order dominates. Chain length distribution is, in this state, only of minor importance. It becomes important, however, in the next step when the system separates into cores of high order at the expense of regions where disorder is concentrated. During this interval of time, lamellae are formed. The first signs of this transition are already recognizable in figure 9(a). Lamellae, however, become a dominant feature of the morphology only at a time beyond A as demonstrated in figure 9(b). Formation of lamellae is about to be accomplished at point B and domains have formed. During this step, demixing of the chains with respect to their length already takes place. To improve order within the domain, disorder (on the length scale of domains) is concentrated in the environment of disclinations. Domain growth can best be observed by the decrease of disclination density in the regime B to D.

The process of annihilation of the disclinations is very complicated and not fully understood on the molecular level. We suggest that the annihilation process for a liquid crystalline solution of rod-like macromolecules does not involve complete disintegration of lamellae. Only a continuous sequence of shifts and slight rotations of single molecules or bundles of molecules within the lamellae between disclinations of opposite sign is necessary, joined to the decrease of distance between the disclinations until they annihilate. Due to the segregation of chains with various lengths, the molecules belong afterwards to new lamellae. First those disclinations of opposite sign annihilate; the distance for this is small, because the defect energy in their vicinity is highest. This leads to the high annihilation rate which is observed in the regime B to D of figure 8.

The electron micrographs of figures 9(d) and (e) display the situation in the vicinity of a pair of disclinations of strength $s = +\frac{1}{2}$ and $-\frac{1}{2}$ for a time when the disclination density approaches a small number. In addition to the lamellae of varying widths, we can observe the orientation of the directors recognizable by the fine black lines. The variation of their direction seems to be continuous. Closer inspection, however, exhibits that the arcs are segmented into straight parts. The electron diffraction pattern of figure 10 confirms these facts by the appearance of only a distinct number of streaks rotated with respect to each other, each set of streaks belonging to one lamella.

Disorder in a LC system of rigid macromolecules can in fact be observed on three different length scales: disorder at the boundaries of domains concentrated near disclinations is seen on the largest scale. The curvature of the lamellae is mainly curvature of lamellar surfaces and does not affect molecular conformation within the lamellar core. It involves simultaneously the disorder on the smallest scale, which is the scale of the chain repeat. This disorder expresses itself in the streaks of the diffraction patterns. Sometimes varying stagger of chains in register can be observed within a lamella. In such a case, the sampling of intensity seen on electron diffraction patterns is shifted asymmetrically along the layer lines. The disorder on the medium length scale, the scale of chain length, is important during formation of

the polymer nematic, but does not seem to play an essential role after lamellae have been formed and segregation of chains of various lengths has taken place.

The strength of interaction between two disclinations is inversely proportional to their distance. Accordingly, disclinations of opposite sign attract and those of equal sign repel each other. Therefore a disclination always selects the nearest opposite disclination to annihilate. The statistical units are larger after this step and so are the mutual distances between the disclinations. The annihilation rate slows down and approaches zero when the energy needed for reorganization of the lamellae is higher than that released by healing the defects. The texture will no longer change. In the light of this model, the shape of the curves in figure 8 can be qualitatively explained.

Investigations about the formation and annihilation of disclinations or the formation and growth of nematic domains in LCPs are reported in the literature by Hashimoto *et al.* [18] and Stein *et al.* [47]. They infer from their observations that the domain size follows a power law with time, the scaling exponents being 0.35 and 0.37 for a copolyester composed of *p*-hydroxybenzoic acid and ethylene terephthalate (X-7G) and for *p*-methyl substituted PSHQ, a thermotropic LCP, respectively. This relationship, however, does not seem to be universal law. Rojstaczer and Stein [20] found recently that the relation between domain size and annealing time in the unsubstituted PSHQ could not be described by a single scaling parameter. Also our experiments do not show a power law behaviour.

4.4. Stripe texture

Figures 4 and 5 showed that typical LC features are decorated by stripes when the solvent was evaporated from a lyotropic liquid crystal. The width of the stripes is a function of a large number of parameters, as described in the previous section. The stripes are always oriented parallel to the director field. This is best seen, in the particular case of P-4-BCMU, from the dichroism which has its maximum parallel to the main chains. Since film thickness, the distance between the disclinations and evaporation rate are essential parameters for stripe formation, we suggest that the occurrence of stripes is a consequence of the volume deficiency when the solvent evaporates. Adhesion to the substrate prevents uniform shrinkage in three dimensions. Therefore the volume deficiency is mainly compensated by film thinning and this process is not uniform throughout the whole lamella in particular when relaxation times are long as is the case for rigid macromolecules. This might be the reason why a stripe texture is never observed for LMWLCs, the relaxation times of small molecule systems being much shorter. Formation of stripes is also observed for thermotropic LCs where the volume deficiency is much smaller [31].

The stripes disappear when the film is brought back into a chloroform atmosphere in the closed glass container, because the stress due to volume shrinkage is released. Under crossed polarizers, the undecorated schlieren texture is seen again. This behaviour is reversible as long as the chloroform concentration does not reach saturation. This is an essential and important difference from the frequently observed 'banded' texture which appears in LCPs as a consequence of shear deformation in the LC phase. It is noteworthy that the banded texture can be seen in both the liquid crystal state and the solid state after shearing [48–53].

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References

- [1] WEGNER, G., 1980, *Faraday Discuss. chem. Soc.*, **68**, 494.
- [2] CHANCE, R. R., 1986, *Encyclopaedia of Polymer Science and Engineering*, Vol. 4, (Wiley, New York), p. 767.
- [3] BLOOR, D., and CHANCE, R. R. (editors), 1985, *Polydiacetylenes; NATO ASI Ser., Ser. E.*
- [4] RAO, D. N., CHOPRA, P., GHOSHAL, S. K., SWIARKIEWICZ, J., and PRASAD, P. N., 1986, *J. chem. Phys.*, **84**, 7049.
- [5] PATEL, G. N., CHANCE, R. R., and WITT, J. D., 1978, *J. Polym. Sci. Polym. Lett. Edn.*, **16**, 607.
- [6] PATEL, G. N., 1978, *Polym. Preprints Div. Polym. Chem., ACS*, **19**, 154.
- [7] PATEL, G. N., CHANCE, R. R., and WITT, J. D., 1978, *Polym. Preprints, Div. Polym. Chem., ACS*, **19**, 160.
- [8] WENZ, G., MÜLLER, M. A., SCHMIDT, M., and WEGNER, G., 1984, *Macromolecules*, **17**, 837.
- [9] RAWISO, M., AIME, J. P., FAVE, J. L., SCHOTT, M., MÜLLER, M. A., SCHMIDT, M., BAUMGARTL, H., and WEGNER, G., 1988, *J. Phys., France*, **49**, 861.
- [10] LIM, K. C., and HEEGER, A. J., 1985, *J. chem. Phys.*, **82**, 522.
- [11] LIM, K. C., KAPITULNIK, A., ZACHER, R., CASALNUOVO, S., WUDL, F., and HEEGER, A. J., 1985, *Polydiacetylenes, NATO, ASI Ser., Ser. E.*, edited by D. Bloor and R. R. Chance (Plenum), p. 257.
- [12] CHANCE, R. R., WASHBAUGH, M. W., and HUPE, D. J., 1985, *Polydiacetylenes, NATO, ASI Ser., Ser. E.*, edited by D. Bloor and R. R. Chance (Plenum), p. 239.
- [13] PEIFFER, D. G., CHUNG, T. C., SCHULZ, D. N., AGARWAL, P. K., GARNER, R. T., and KIM, M. W., 1986, *J. chem. Phys.*, **85**, 4712.
- [14] XU, R., and CHU, B., 1989, *Macromolecules*, **22**, 3153.
- [15] 1985, *Polymer Liquid Crystal Faraday Discuss. chem. Soc.*, **79**.
- [16] 1984, *Liquid Crystal Polymers I-III, Adv. Polym. Sci.*, **59** and **60**.
- [17] CIFERRI, A., KRIGBAUM, W. R., and MEYER, R. B. (editors) 1982, *Polymer Liquid Crystals* (Academic Press).
- [18] SHIWAKU, T., NAKAI, A., HASEGAW, H., and HASHIMOTO, T., 1990, *Macromolecules*, **23**, 1590.
- [19] KLÉMAN, M., 1989, *Liq. Crystals*, **5**, 399.
- [20] ROUSTACZER, S. R., and STEIN, R. S., 1990, *Macromolecules*, **23**, 4863.
- [21] VINEY, C., and WINDLE, A. H., 1982, *J. Mater. Sci.*, **17**, 2261.
- [22] FLORY, P. J., 1956., *Proc. R. Soc. A*, **234**, 73.
- [23] ALBRECHT, C., LIESER, G., and WEGNER, G., 1989, *Beitr. Elektronenmikroskop. Direktabb. Oberfl. (BEDO)*, **22**, 351.
- [24] ALBRECHT, C., LIESER, G., and WEGNER, G., *Prog. Colloid Polym. Sci.*, (in the press).
- [25] LIESER, G., WANG, W., ALBRECHT, C., SCHWIEGK, S., REHAHN, M., and WEGNER, G., 1992, *Polym. Prepr. (Am. chem. Soc., Div., Polym. Chem.)*, **33**, 294.
- [26] CHANCE, R. R., PATEL, G. N., and WITT, J. D., 1979, *J. chem. Phys.*, **71**, 206.
- [27] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Verlag Chemie)
- [28] DE GENNES, P. G., 1974, *The Physics of Liquid Crystals* (Clarendon Press).
- [29] NEHRING, J., and SAUPE, A., 1972, *J. chem. Soc. Faraday Trans. 2*, **68**, 1.
- [30] KLÉMAN, M., 1989, *Rep. Prog. Phys.*, **52**, 555.
- [31] CHEN, S., DU., C., JIN, Y., QIAN, R., and ZHOU, Q., 1990, *Molec. Crystals liq. Crystals*, **188**, 197.
- [32] ONSAGER, L., 1949, *Ann. N. Y. Acad. Sci.*, **51**, 627.
- [33] DI MARZIO, E. A., 1961, *J. chem. Phys.*, **35**, 658.
- [34] FLORY, P. J., and RONCA, G., 1979, *Molec Crystals liq. Crystals*, **54**, 289.
- [35] ALBRECHT, C., 1987, Diplomarbeit, Universität Mainz.
- [36] DE GENNES, P. G., 1977, *Molec Crystals liq. Crystals Lett.*, **54**, 289.
- [37] FRENKEL, D., 1988, *J. phys. Chem.*, **92**, 3280.
- [38] CIFERRI, A., KRIGNAUM, W. R., and MEYER, R. B. (editors), 1982, *Polymer Liquid Crystals* (Academic Press), Chap. 6.
- [39] ODIJK, T., 1986, *Macromolecules*, **19**, 2313.
- [40] KLÉMAN, M., 1990, *Fundamentals in Liquid Crystal Polymers*, edited by A. Ciferri (Academic Press), Chap. 5.

- [41] MILLAUD, B., THIERRY, A., and SKOULIOS, A., 1978, *J. Phys., France*, **39**, 1109.
- [42] WANG, W., HUND, M., WEGNER, G., and LIESER, G., 1993, *Polymer*, **34**.
- [43] KLÉMAN, M., LIEBERT, L., and STRZELECKI, L., 1983, *Polymer*, **24**, 295.
- [44] MAZELET, G., and KLÉMAN, M., 1986, *Polymer*, **27**, 74.
- [45] MACKLEY, M. R., PINAUD, F., and SIEKMAN, G., 1981, *Polymer*, **22**, 437.
- [46] NOEL, C., LAUPRETRE, F., FRIEDRICH, C., FAYOLLE, B., and BOSIO, L., 1984, *Polymer*, **25**, 808.
- [47] ROJSTACZER, S., HSIAO, B., and STEIN, R. S., 1988, *Poly. Prepr. (Am. chem. Soc., Div. Polym. Chem.)*, **29**, 486.
- [48] GRAZIANO, D. J., and MACKLEY, M. R., 1984, *Molec Crystals liq. Crystals*, **106**, 73.
- [49] DONALD, A. M., VINEY, C., and WINDLE, A. H., 1983, *Polymer*, **24**, 155.
- [50] VINEY, C., DONALD, A. M., and WINDLE, A. H., 1983, *J. Mater. Sci.*, **18**, 1136.
- [51] HUDSON, S. D., THOMAS, E. L., and LENZ, R. T., 1987, *Molec Crystals liq. Crystals*, **153**, 63.
- [52] VENEY, C., DONALD, A. M., and WINDLE, A. H., 1985, *Polymer*, **26**, 870.
- [53] ROCHE, E. J., ALLEN, S. R., GABARA, V., and COX, B., 1989, *Polymer*, **30**, 1776.