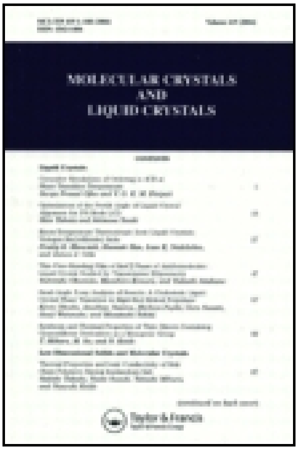

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Formation of Smectic Spherulites in Poly(ester imides)

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The formation of higher-ordered smectic-crystalline phases resulting directly from the isotropic melt is determined in different poly(ester imide)s (PEI). The microscopic extinction patterns and the results of H_v-light scattering and time-resolved X-ray diffraction during isothermal crystallization indicate that a spherulitic superstructure is formed if no intermediate LC-phase occurs. This phase behavior is found in PEIs based on aminobenzoic acid trimellitimide and long aliphatic diols and in PEI derived from pyromellitic acid anhydride, ω-aminoundecane acid and aromatic diols, resp., which form no LC-phase at all. Additionally, this smectic-spherulitic morphology is formed by PEIs based on aminocinnamic acid trimellitimide, which pass through a monotropic LC-phase upon cooling if the polymer is crystallized at temperatures above the LC-phase. The competition between LC phase formation and spherulitic crystallization is discussed on the basis of thermodynamical and kinetical influences. The spherulites formed have a lamellar structure of 100–400 Å giving rise to a SAXS reflection. Whereas the crystal lamellae contain an internal smectic layer structure of about 30 Å, the region between the lamellae is probably amorphous.

Keywords: PEI; SAXS reflection; liquid crystal; X-ray diffraction

INTRODUCTION

This paper is part of a broader study on polymers which form layer structures. Polymers with a regularly alternating sequence of rigid, polar mesogens and flexible, non-polar spacers in the main chain tend to form smectic layer structures. At this point, it should be emphasized that "smectic" is not synonymous with "liquid-crystalline". Besides the smectic,

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liquid-crystalline phases S_A and S_C, polymers can form so-called higher-ordered smectic phases in the solid state, which are denoted S_B, S_E, S_F, S_G, and S_H depending on the lateral order of the mesogens and their orientation with respect to the layer plane [1]. Up to now, several examples to these solid smectic phases exist which can be regarded as smectic-crystalline as well, due to their crystal-like packing of the mesogenic groups and the resulting wide angle X-ray reflections. Of course, the chains segments do not form a perfect, three-dimensional crystal, due to a remaining disorder in the spacer conformation [2]. These smectic-crystalline phases are often formed during the cooling of a smectic liquid-crystalline phase. But there are also examples for transitions between two different smectic-crystalline phases [3–5].

The phase behavior of main-chain LC-polymers strongly depends on the spacer length. Whereas polymers with shorter spacers form nematic phases, longer spacers favor the formation of smectic phases in a kind of nanophase separation of the polar mesogens and the non-polar spacers. Generally, one observes that the temperature gap of the LC phase, between the isotropic and the solid phase, becomes narrower with increasing spacer length. It has been suggested earlier [6] that the gap may vanish completely for very long spacers resulting only in one phase transition. In some cases, the existence of a very short-lived LC-phase has been suggested. In a previous paper [7], we have demonstrated that poly(ester imide)s based on aminobenzoic acid trimellitimide and long aliphatic diols do not form such a short-lived LC-phase. Instead, the solid smectic phase is formed directly from the isotropic melt with a spherulitic superstructure. This process needs several minutes up to hours and, therefore, excludes the formation of an intermediate LC-phase, which would produce a completely anisotropic texture (schlieren, fans, bâtonnets *etc.*) much faster. The formation of mesophase domains from the isotropic melt has been observed also by Gedde *et al.* [8] in polyethers. The pecularity of this spherulitic morphology is the fact that it contains an internal smectic structure. This observation proves that the formation of smectic layers is not necessarily a consequence of liquid-crystallinity. The nano-phase separation can also occur during a nucleation-induced spherulitic crystallization, provided that the difference in polarity (amphiphily) between the mesogen and the spacer is large enough.

This paper is aimed at demonstrating, that the observed formation of smectic spherulites is not an individual case of special polymers, but rather a consequence of a certain thermodynamical relationship. Furthermore, the internal structure of the smectic spherulites will be investigated in more detail. And finally, this paper will answer the question, whether the absence of a LC-phase prior to smectic-spherulitic crystallization means that only the polymers which form no LC phase under any condition are capable of forming smectic spherulites.

EXPERIMENTAL

Materials

All poly(ester imide)s were synthesized by H. R. Kricheldorf *et al.*, by polycondensation in solution. The detailed synthetic route and properties of the PEIs have been reported in previous publications [9–12].

Measurements

Microscopic extinction patterns were obtained between crossed polars with an Olympus BH-2 optical microscope on Agfa Pan 400 film. The polymers were fused between glass plates on a Linkham hot-stage (THM 600/s), cooled rapidly to the crystallization temperature and kept there isothermally.

Time resolved X-ray scattering was performed employing synchrotron radiation at HASYLAB/DESY at a wave length of $\lambda = 1.54$ Å and two, one-dimensional, position-sensitive detectors with 30 s acquisition time registering simultaneously either small and wide angle scattering (SAXS/WAXS) or middle and wide angle scattering (MAXS/WAXS). The scattering patterns were normalized with respect to primary beam intensity.

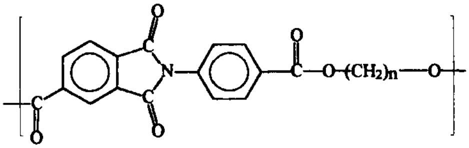
H_v-light scattering patterns were acquired using a Melles-Griot He/Ne laser (λ = 632.8 nm, 2 mW) and a CCD-camera. The polymers were fused between glass plates, mounted on the Linkham hot-stage, heated up to the isotropic melt, cooled rapidly to the crystallization temperature and kept there isothermally. The vertical polarized laser beam passes through the sample and the horizontal analyzer. The H_v-light scattering pattern is acquired by the CCD-camera all 30 s. Due to the limited number of scattering entities and the coherent radiation, the interference results in a speckled scattering pattern. In order to equalize the speckles, the patterns are averaged over the four quadrants and smoothed by a low-pass filter.

Differential scanning calorimetry (DSC) traces were recorded with a Perkin-Elmer DSC-4 in aluminium pans under nitrogen at heating and cooling rates of 10°C/min.

RESULTS AND DISCUSSION

Evidence of Smectic Spherulites

The poly(ester imide)s (PEIs) of the chemical structure 1 form particularly stable smectic layer structures in the liquid-crystalline phase as well as in the solid state due to the large polarity of the imide group [13]. With increasing spacer length the temperature gap of the LC-phase becomes narrower and finally vanishes completely. Whereas the PEI 1 ($n = 12$) passes through a monotropic meso-phase upon cooling, the analogous PEI with spacer lengths of $n = 22$ and $n = 16$ form a higher-ordered solid smectic phase (S_E) with a spherulitic superstructure resulting directly from the isotropic melt. The incorporation of longer spacers by copolymerization has the same effect as demonstrated previously [7] for the random co-PEI 1 ($n = 12/22$).



PEI 1 (n=12,16,22)

In addition to the microscopic texture, the light scattering measurements and the time-resolved X-ray scattering using synchrotron radiation during isothermal crystallization indicate the formation of smectic spherulites. The

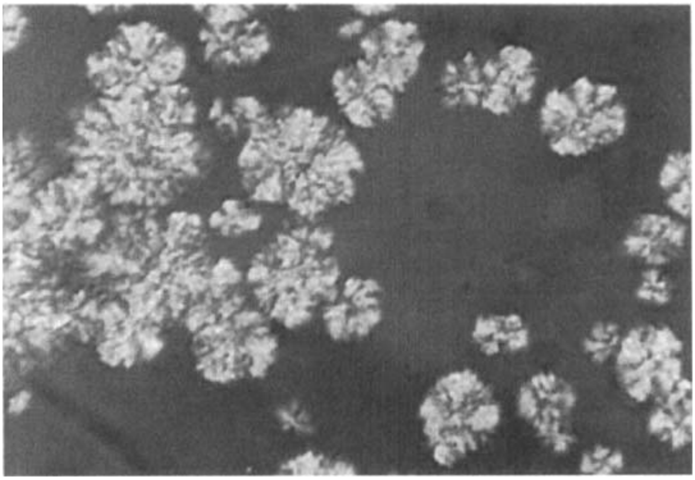


FIGURE 1 Polarizing optical micrographs of PEI 1 ($n = 22$) after 70 minutes at 149°C.

microscopic extinction pattern between crossed polarizers of PEI 1 ($n = 22$) after annealing at 149°C for 70 mm (Fig. 1) depicts spherulites of about 50 μm in diameter within an isotropic matrix. Inspite of the irregular internal structure, the typical cloverleaf-shaped pattern [14] is detected in the H_V-light scattering in Figure 2 for PEI 1 ($n = 22$) crystallized at 135°C for 30 s (a), 45 s (b), 60 s (c), and 75 s (d). Caused by the growth of the spherulites the overall scattering intensity increases with time while the maximum shifts slightly towards smaller scattering angles. The scattering maximum occurs under an azimuthal angle 45° with respect to the direction of polarization, which indicates that the optical axis of the spherulite is tangentially oriented.

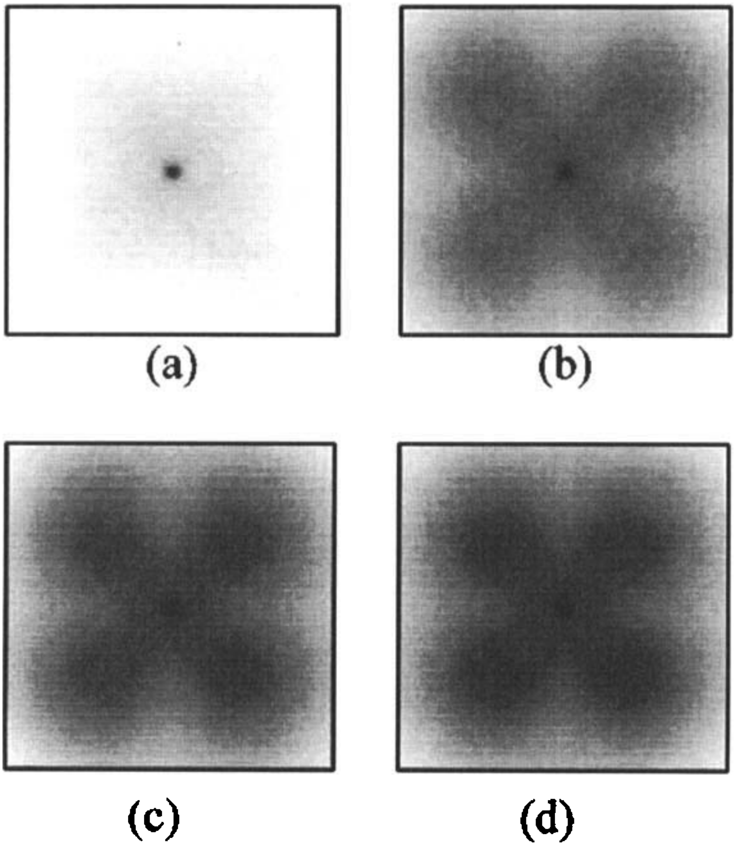
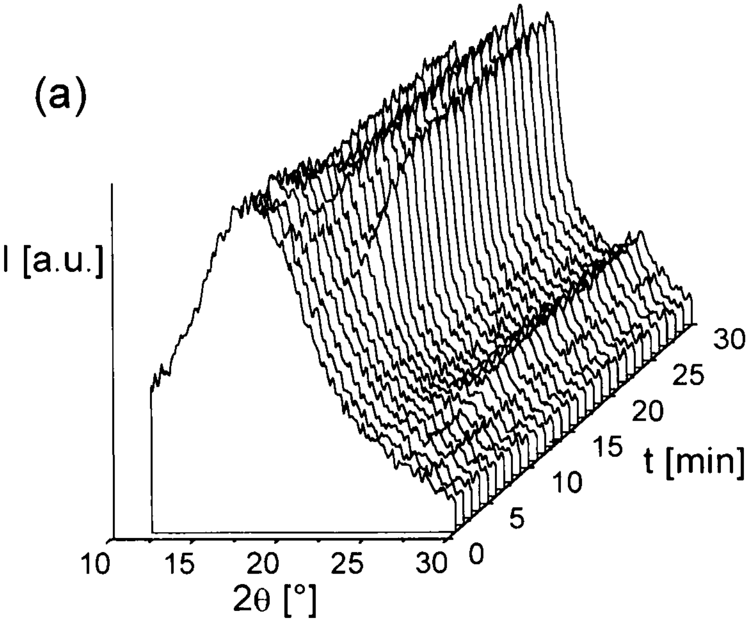
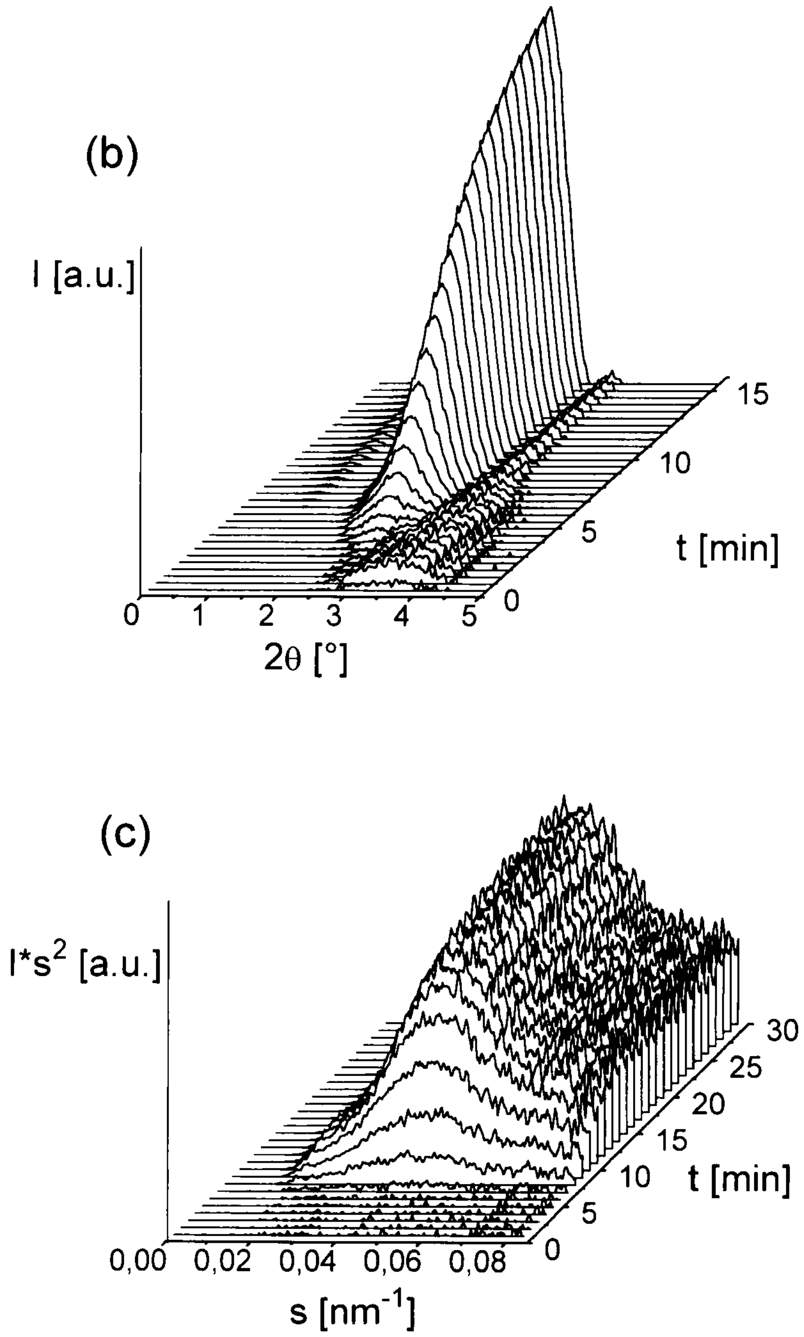


FIGURE 2 H_V-light scattering patterns of PEI 1 ($n = 22$) at 140°C after 5 min. (a), 7 min. (b), and 9 min. (c).

Further evidence of the direct crystallization from the isotropic melt and of the internal structure is the simultaneous development of the smectic layer reflection and the crystal reflections in the time-resolved X-ray scattering. Whereas a short-lived LC-phase may not be detected in a DSC or X-ray scattering experiment during cooling with 10°C/min, the slow simultaneous development of the layer reflection and the crystal reflections during isothermal treatment excludes an intermediate formation of a smectic LC-phase. Figure 3 exhibits the change of the X-ray pattern in the wide angle (WAXS) (a), middle angles (MAXS) (b), and small angle (SAXS) (c) range as a function of time during isothermal crystallization of PEI 1 ($n = 22$) at 144°C. In Figure 3a one can clearly see that the crystal reflections grow slowly with a half time of about 10 minutes at the expense of the amorphous halo. Simultaneously, the smectic layer reflection develops in Figure 3b in the middle angle region at $2\theta = 2.6°$ corresponding to a spacing of 34 Å. Additionally, a long period reflection occurs in the SAXS (Fig. 3c), which indicates that the spherulites consist of lamellar two-phase system with a spacing of about 250 Å.



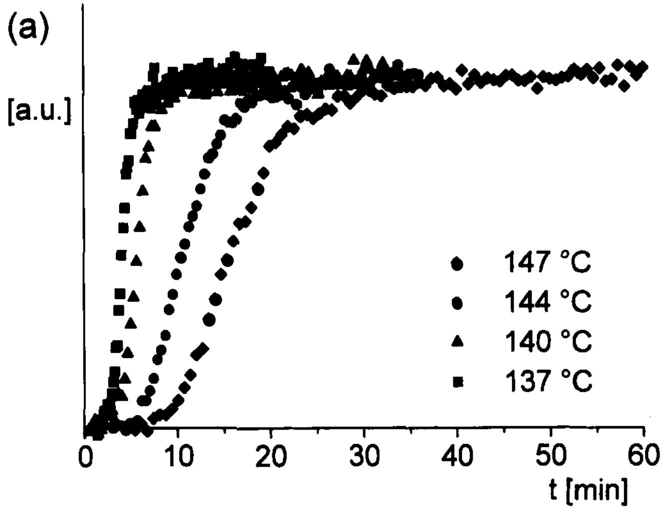
FIUGRE 3 Change of WAXS (a), MAXS (b), and SAXS (c) of PEI 1 ($n = 22$) during isothermal crystallization at 144°C.



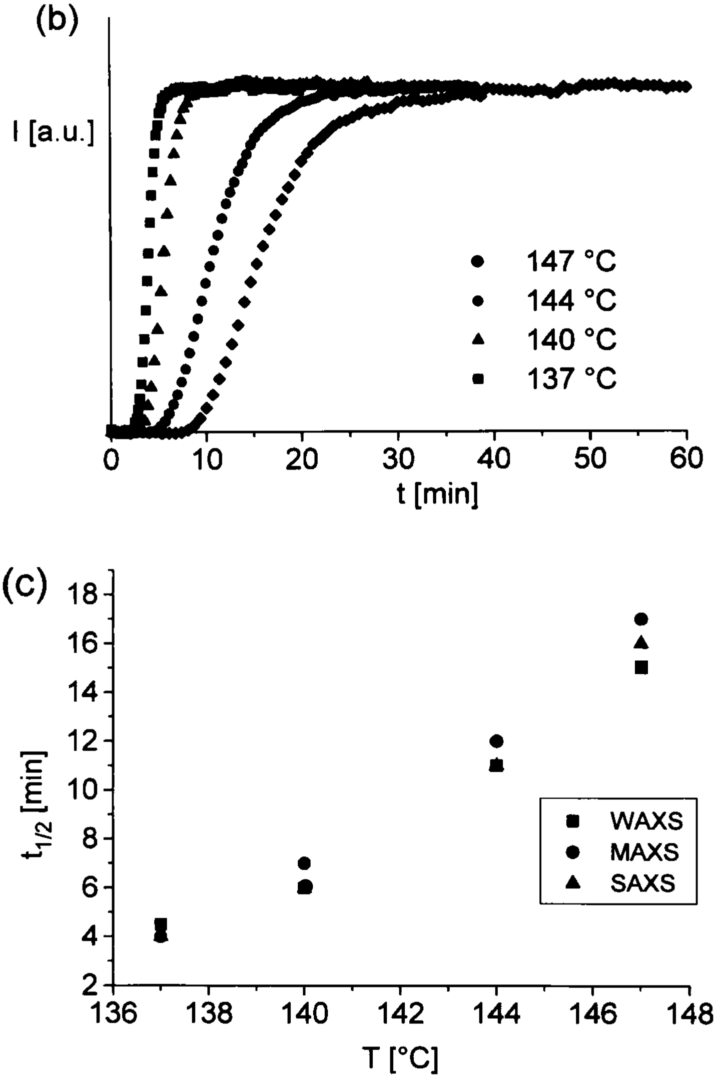
FIUGRE 3 (Continued).

It has to be concluded that the spherulites are formed by crystal lamellae, which in their part consist of smectic layers of approximately 30 Å, as it has been previously [7] represented in the model. The fact that the integral intensities of the reflections in all three angular regions increase simultaneously and an evaluation according to Avrami-equation always results in exponents of n close to 3, indicates that the formation of the crystals, as well as development of the smectic layers and the lamellar structure is a consequence of the growth of the spherulitic superstructure. In other words, the spherulites grow within the isotropic phase starting from nuclei and during the growth their internal structure does not change significantly. Figure 4 represents the integral intensities of the WAXS reflections (a), and SAXS reflection (b) as a function of time, and the half times of crystallization (c) of PEI 1 ($n = 22$) at different temperatures. The slow rate of crystal growth and the low temperature dependence are indicative for the formation of a solid phase from the isotropic melt, because such a process is induced by nucleation and has consequently a relatively high activation energy.

At this point, the question arises what the structure between the lamellae is like. The small angle X-ray scattering is a result of periodic fluctuations in the electron density of a lamellar two-phase system with a spacing of a few hundred Å. If the crystalline phase, which gives rise to the WAXS



FIUGRE 4 Integral intensity of WAXS (a) and SAXS (b) reflections as a function of time and half times of crystallization (c) at different temperatures.



FIUGRE 4 (Continued).

reflections, has the higher electron density, what is then the nature of the less dense phase?

One the one hand, this class of polymers do not tend to form amorphous phases, as it would be equivalent to a molecular mixture of the polar mesogens and the non-polar spacer which is thermodynamically unfavorable. Rapid quenching of the isotropic melt results in a frozen smectic LC-phase for shorter spacers ($n = 6-12$). For longer spacer ($n = 16{,}22$) crystallization cannot be suppressed at all. Consequently, it can be suggested that this second phase may also contain a smectic layer ordering but without lateral crystal-like packing of the mesogens. The formed structure would be a frozen smectic LC-phase below T_g. In this case, however, the difference between the electron densities of the LC-phase and the crystal phase would be rather low and the resulting X-ray scattering extremely weak.

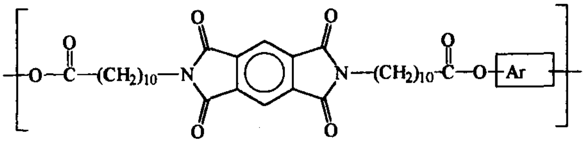
On the other hand, the formation of an amorphous phase cannot definitly be excluded, because the entanglements of the molecules, which limit the crystallization in the case of conventional semi-crystalline polymers, can occur in this case as well since the crystals grow from the isotropic melt. During the formation of a LC-phase, major parts of the molecules are oriented within the domains and entanglements can be solved due to the high molecular mobility. Therefore, thermotropic LC-phase are homogeneous as a rule. In contrast, for the lamellar crystallization the lateral interaction of the mesogenic groups is the only driving force. Therefore, the entanglements cannot be solved subsequently to lateral packing and, thus, limit the extend of the crystallization.

In any case, the formation of crystal lamellae partly involves chain folding and the third explanation for the SAXS is based on the assumption that the low density phase does not contain mesogens at all, but is mainly formed by spacers loops. This model has been applied also to explain the SAXS reflection caused by a higher-ordered smectic phase with LC-texture [15]. Actually, this fold phase would be very thin and the long period calculated from the position of the SAXS reflection would be equivalent to the thickness of the crystal lamellae. This latter model is supported by the observation that the SAXS reflections of all samples does not exhibit the regular gaussian shape but a long tail towards larger scattering vectors. This asymmetrical shape indicates that one of the phases is extremely thin.

In the case of PEI $\underline{1}$ ($n = 22$) crystallized at 144°C, a long period of 270 Å and a smectic layer distance of 34 Å results in an average backfolding rate of about 8. For PEI $\underline{1}$ ($n = 16$) crystallized at 145°C, the long period amounts to 240 Å and the smectic d-spacing to 30 Å. From these values a lamellar thickness of 8 mesogens can be calculated once again. Similar values have been found in other samples. However, the long period depends strongly on the temperature while the layer spacing remains constant.

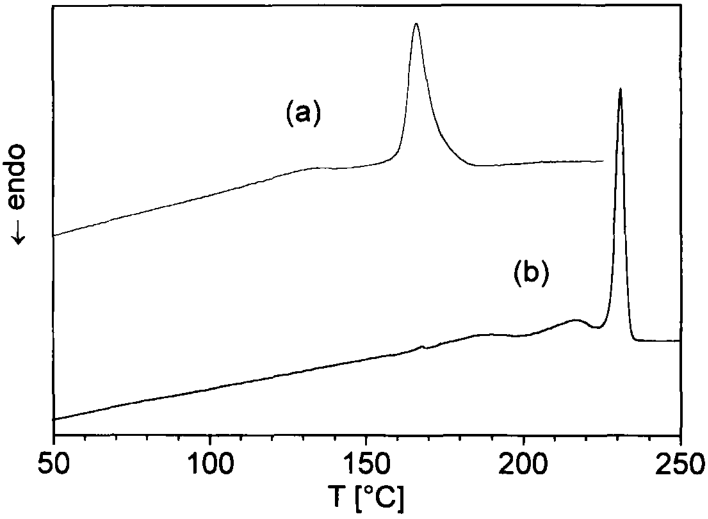
Particular important is the question whether the smectic-spherulitic crystallization of PEI $\underline{1}$ represents an individual case or a consequence of a distinct thermodynamical relationship. The above observations indicate that at least all polymers are suitable for the formation of this morphology which form smectic phases due to a regular sequence of very polar mesogens and flexible spacers, but do not pass through a LC-phase.

Another class of particularly polar mesogens are pyromellitimides. In a series of experiments pyromellitic anhydrid has been reacted with different ω-amino-carbon acids. The resulting dicarbonacids have been polycondensed with different aromatic diols yielding poly(ester imide)s of the structure PEI 2 [11].

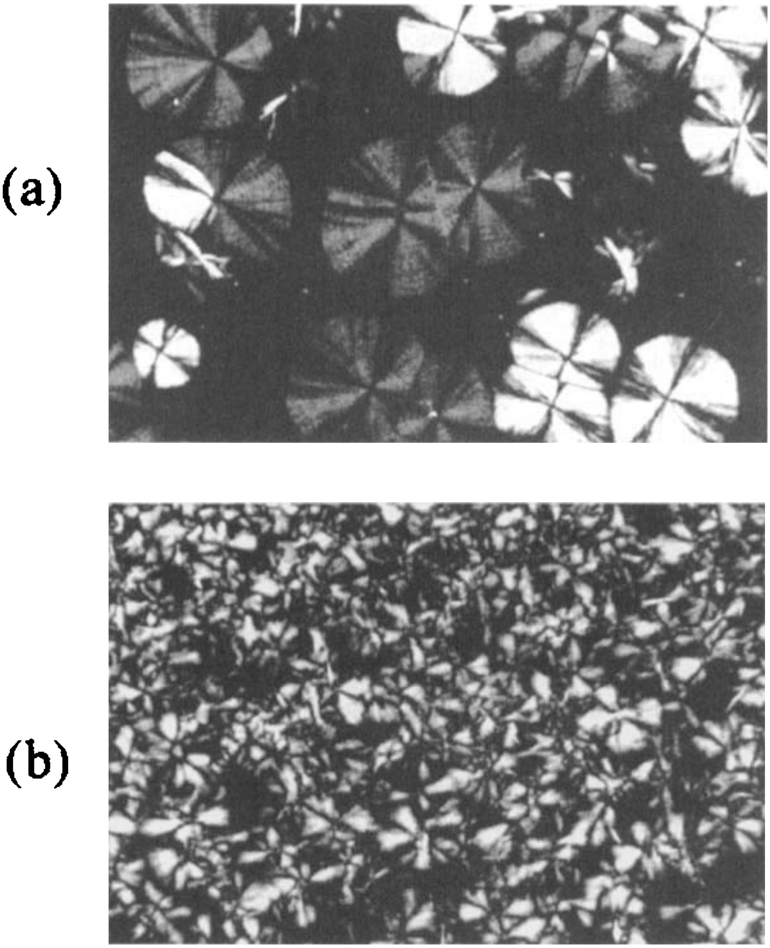


PEI 2a: Ar = naphthyl-
PEI 2b: Ar = biphenyl-

For this investigation, the polymers based on ω-aminoundecanoic acid (PEI 2a and 2b) are of interest. Both exhibit only one exothermal peak in the DSC upon cooling, PEI 2a at 165°C and PEI 2b at 230°C (Fig. 5). In fact, both polymers form spherulites upon cooling the isotropic melt without passing through a LC-phase. Figure 6 displays the polarizing microscopic patterns of 2a at 200°C for 30 minutes (a) and 2b after 12 minutes at 250°C (b). The spherulites of 2a measure about 100 μm in diameter and exhibit a distinct maltese cross which is characteristic for a regular internal structure.



FIUGRE 5 DSC cooling traces of PEI 2a (a) and 2b (b) at 10°C/min.



FIUGRE 6 Polarizing optical micrographs of PEI 2a after 30 minutes at 200°C (a) and PEI 2b after 12 minutes 15 250°C (b).

Obviously, two different classes of spherulites are formed, one highly birefringent having a radial fibrillar texture, and the other low birefringent with a banded texture and a zig-zag-shaped maltese cross. However, these differences should not be discussed at this point. In the microscopic texture of PEI 2b the spherulites are less clearly recognizable, because they are sometimes fan-shaped resembling axialites and they impinge on each other. Nevertheless, a spherical shape is confirmed by the cloverleaf-shaped H_v-

light scattering patterns at 232°C depicted in Figure 7. From the radial scattering angle at the maximum intensity, an average spherulitic radius R of 34 μm can be calculated by Eq. (1) [14] in which λ is the wave length of the used laser and θ_{max} is the radial scattering at the maximum intensity.

$$R = \frac{4.1 \cdot \lambda}{4\pi \cdot \sin(\theta_{max}/2)} \tag{1}$$

Once more, the simultaneous formation of the internal semi-crystalline and smectic structures can be detected only by the time-resolved X-ray diffraction. Figure 8 reveals that the reflections of the crystals in the WAXS (a), the smectic layers in the MAXS (b), and the lamellae in the SAXS (c) develop simultaneously during isothermal crystallization of PEI 2a at 200°C. The single crystal reflection at $2\theta = 20.2°$ indicates the formation of higher-ordered smectic-crystalline phase with a hexagonal lateral (S_B). The position of the MAXS reflection at $2\theta = 5.2°$ corresponds to a layer spacing

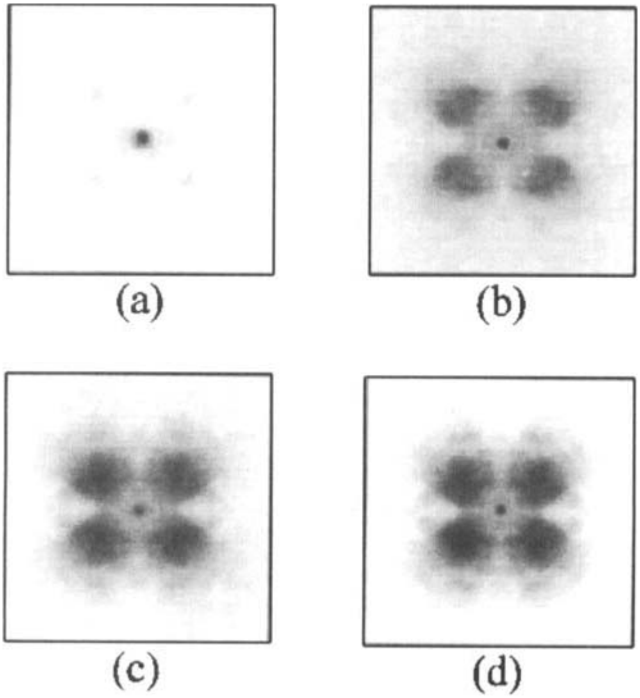


FIGURE 7 H_v-light scattering patterns of PEI 2b at 232°C after 1 min. (a), 2 min. (b), 3 min. (c), and 5 min. (d).

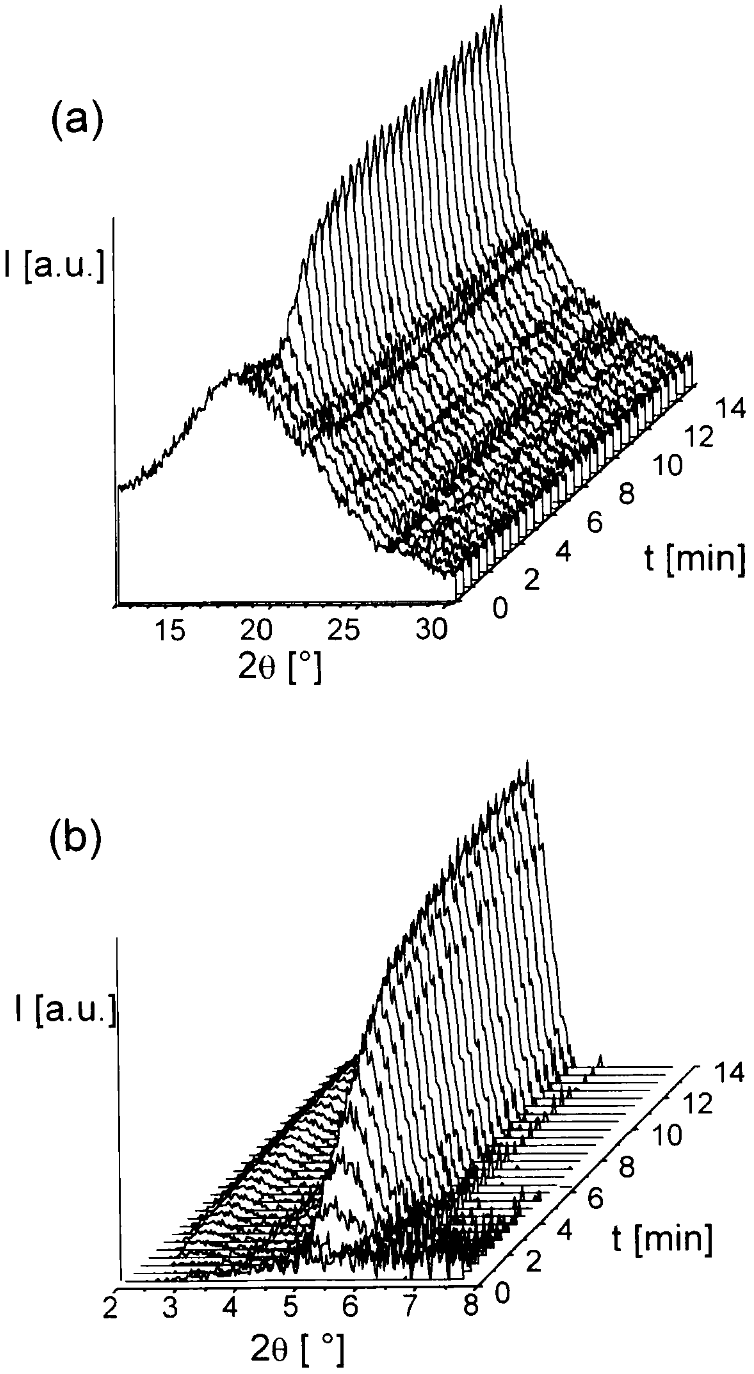


FIGURE 8 Change of WAXS (a), MAXS (b), and SAXS (c) of PEI 2a during isothermal crystallization of at 202°C.

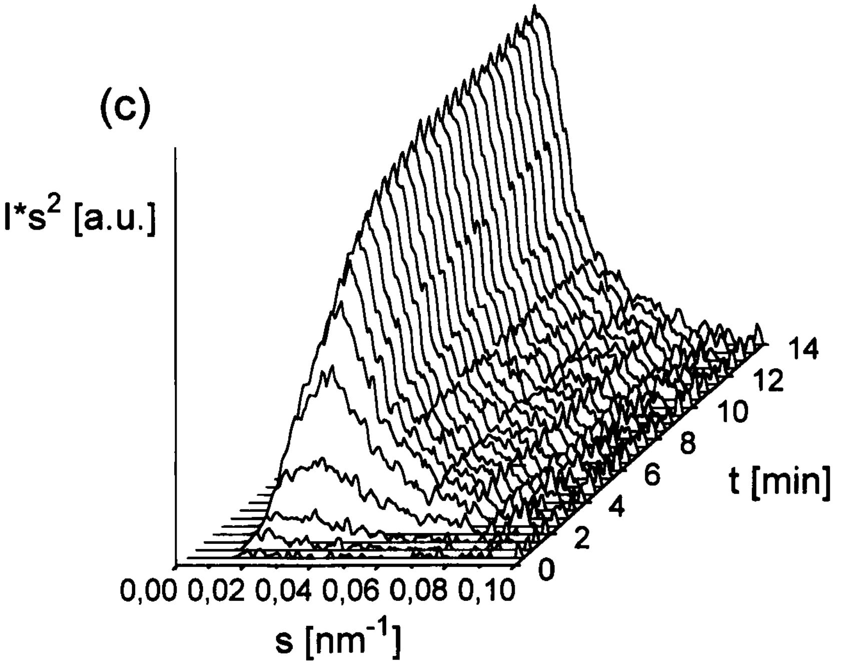


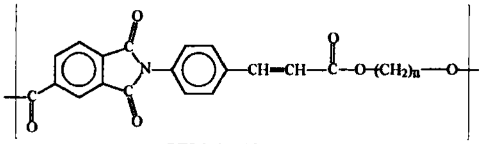
FIGURE 8 (Continued).

of 17 Å, which cannot be attributed clearly to the repeat units. From the position of the SAXS reflection a long period of 275 Å is calculated.

The time-resolved MAXS of 2b during isothermal crystallization at 240°C exhibits a slow development with a half time of 5 minutes of the layer reflection at $2\theta = 5.1°$ corresponding to a d-spacing of 17 Å, which confirms the smectic layer structure of PEI 2b.

Competition Between Smectic-spherulitic Crystallization and Formation of Monotropic LC-phase

In this section, the question will be clarified as to whether the occurrence of smectic spherulites implies that the respective polymer do not form a LC-phase under any circumstances. For this purpose another class of smectogenic poly(ester imide)s of the structure PEI 3 has been investigated.



PEI 3 (n=12,16,22)

Compared to PEI 1, they are based on aminocinnamic acid instead of aminobenzoic acid. The double bond improves the mesogenic character and allows a fixing of the smectic structure by subsequent cross-linking *via* exposure to UV-radiation.

It has been demonstrated previously that PEI 3 $n = 12$ and $n = 16$ form monotropic smectic LC-phases upon cooling of the isotropic melt [12]. Upon further cooling, they undergo a transition into higher-ordered smectic solid phases, at which the tilt angle between the mesogen axis and the smectic layer plane changes. Therefore, this phase transition is clearly detectable in the X-ray scattering by the change in the position of the layer reflection. For PEI 3 ($n = 22$) only one phase transition is detected in the DSC upon cooling with a rate of 10°C/min at 132°C.

Nevertheless, the polarizing microscopic pattern after 50 minutes at 180°C (see Ref. [7], Fig. 7c) exhibits a coexistence of small spherulites (2 μm) and larger LC-droplets. Obviously, the difference in free energy between the LC-phase and the smectic-crystalline phase is extremely low in this case. LC-droplets are formed by separation of shorter polymer chains which rather tend to form liquid-crystals than the long chains. Even more remarkable is the fact that the spherulites do not grow upon the droplet surface, although it could be assumed that the ordered LC-phase is suitable to induce crystallization. At higher temperatures, the spherulites are much larger (100 μm) and exhibit an irregular shape similar to dendrites. The coexistence of the LC-phase and the spherulites is also observable in the light scattering and X-ray diffraction. In the H_V-light scattering, the disclinations in the LC-phase very often result in a maximum scattering intensity under azimuthal angles of $\mu = 0°$ and 90°, which is both parallel and perpendicular to the direction of polarization [16]. In contrast, spherulites generally give rise to intensity maxima at $\mu = 45°$. Both patterns coexist in the H_V-light scattering patterns of PEI 3 ($n = 22$) at 142°C (Fig. 9). The spherulites grow slowly while the droplets remain constant in size. The rapid formation of the LC-droplets and the slow development of the smectic-crystalline phase is also clearly detectable in the time-resolved X-ray scattering. Figure 10 represents the change in WAXS (a), MAXS (b), and SAXS (c) of PEI 3 ($n = 22$) at 142°C. The two phases can be easily distinguished due to the different positions of their layer reflections in the MAXS (b) (analogous to PEI 3 $n = 12$, 16). The difference in the layer spacings of the LC-phase and the smectic-crystal phase can be attributed once more to a different tilt angle of the mesogens with respect to the layer plane [17]. Unfortunately, no oriented sample of PEI 3 ($n = 22$) could be obtained in order to confirm this tilt by X-ray fiber patterns, either due to a lower molecular weight or a fast relaxation

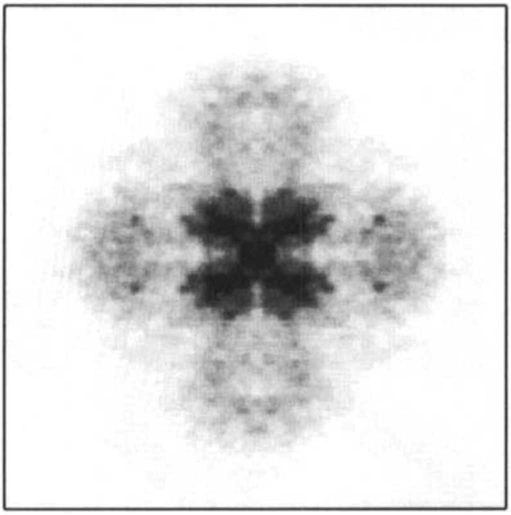


FIGURE 9 H_v-light scattering pattern of PEI 3 (n = 22) after 12 min at 142°C.

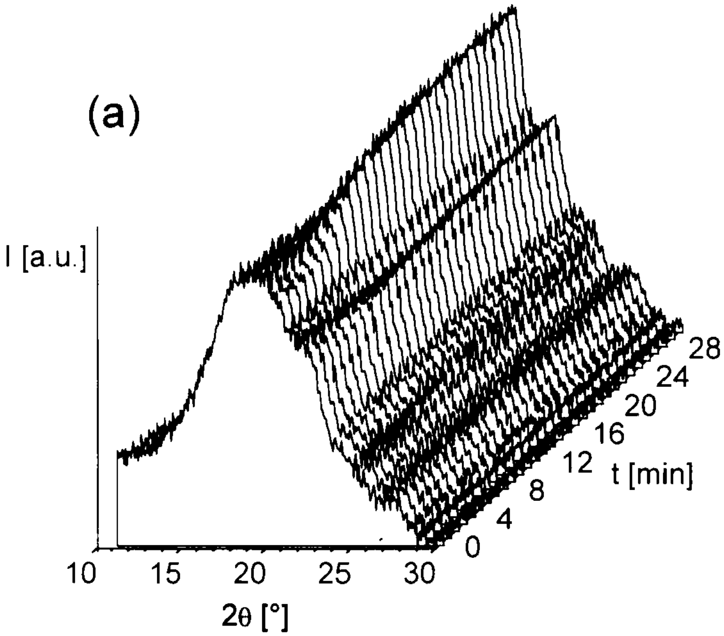


FIGURE 10 Change of WAXS (a), MAXS (b), and SAXS (c) of PEI 3 (n = 22) during isothermal crystallization at 142°C.

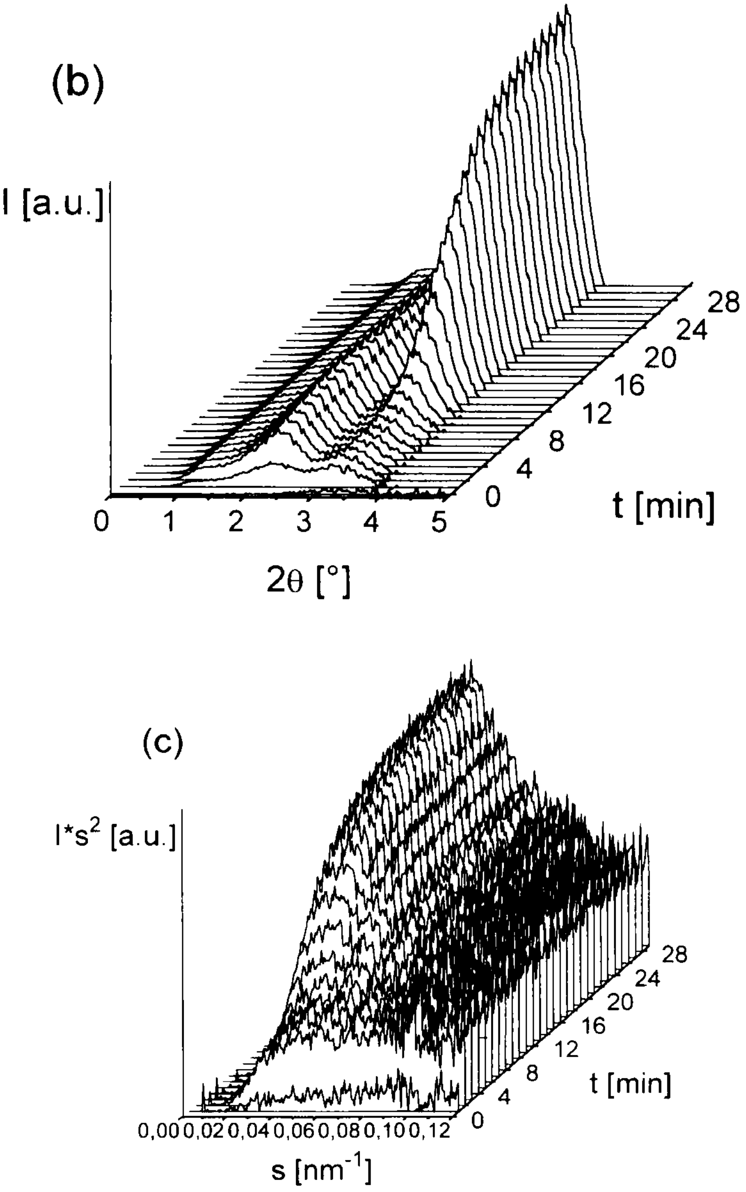


FIGURE 10 (Continued).

of the molecules. One can clearly see in Figure 10b that the layer reflection of the LC-phase at $2\theta = 2.2°$ (40 Å) occurs within the first minute, while the reflection of the smectic-crystalline phase develops at $2\theta = 3.2°$ (28 Å) with a half time of about 10 minutes simultaneously with the crystal reflections in the WAXS (Fig. 10a). The change in the SAXS is also remarkable. One can see that along with the first MAXS-reflection, a very broad SAXS peak occurs (Fig. 10c) after one minute which corresponds to a long period of about 150 Å. This observation indicates that a periodical chain-folding also exists in the LC-phase. However, this aspect will be discussed in more detail in a future publication. While the crystalline structure forms, an additional SAXS intensity appears at a lower angle from which a long period of about 250 Å can be calculated. With a smectic d-spacing of 28 Å the lamellar thickness once again amounts to 8 monomer units, in contrast to the backfolding rate of 4 in the LC-phase.

The different kinetics for the formation of the LC-phase and the smectic spherulites is demonstrated very clearly in Figure 11 representing the integral SAXS intensity of PEI 3 (*n* = 22) as a function of time at different temperatures. The abrupt increase of the SAXS within the first minute which is more or less irrespective of the temperature results from the formation of the LC-droplets. The subsequent slow increase corresponds to the spherulitic crystallization. Furthermore, it becomes obvious that the spherulites indeed grow slower at higher temperatures, even though the ratio of the LC-phase and smectic crystalline phase remains more or less constant.

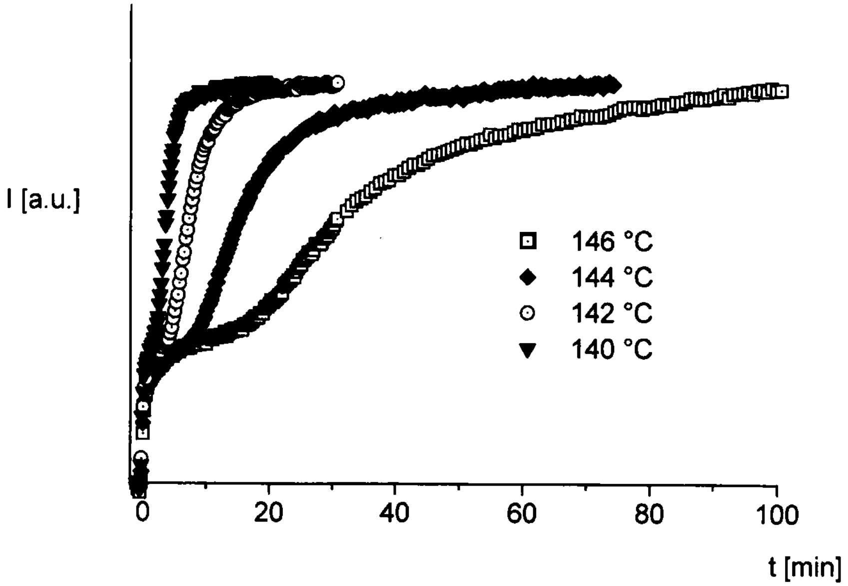


FIGURE 11 Integral SAXS intensity of PEI 3 (*n* = 22) as a function of time at different temperatures.

Perhaps the PEI 3 ($n = 22$) represents an individual case in which the distribution of chain length may be sufficiently broad so that this biphasic region occurs. But the question remains whether the analogous PEI 3 ($n = 12$ and 16) and the PEI 1 ($n = 12$), which display all homogeneous, but monotropic, LC-phases upon cooling with 10°C/min, can also form smectic spherulites under different circumstances. The following experiments prove that this is in fact the case. The necessary experimental condition is an annealing close below the melting temperature for several hours. Figure 12a

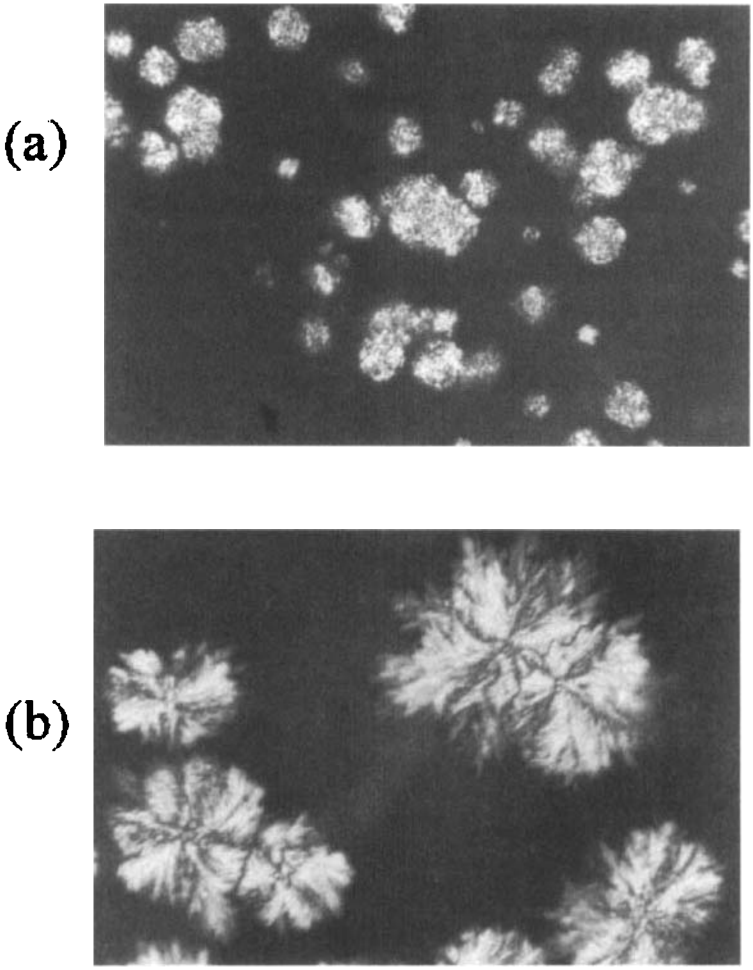


FIGURE 12 Polarizing optical micrographs of PEI 3 ($n = 16$) after 6 h at 156°C (a) and PEI 1 ($n = 12$) after 94 h at 160°.

displays the microscopic extinction pattern between crossed polars of PEI 3 (n = 16) after annealing at 156°C for 6 h. One can clearly see spherulites with a size of about 30 µm with a grainy internal texture. These spherulites develop within the temperature range of 142°C – 156°C, whereas the LC-phase is formed only below 142°C. Notwithstanding the grainy texture, the spherulites give rise to a cloverleaf H_v-light scattering pattern (Fig. 13) indicating that the main optical axis inside the spherulite is tangentially oriented.

A similar phase behavior has been observed for PEI 1 (n = 12) and PEI 3 (n = 12), which both form monotropic meso-phases as well. However, the temperature gap in which smectic spherulites are formed is very narrow and occurs above the melting point of the crystals grown from the LC-phase upon cooling. Therefore, the crystallization takes an extremely long time. Figure 12b shows the microscopic pattern of PEI 1 (n = 12) after isothermal crystallization at 160°C for 94 h. At this temperature, the spherulite growth

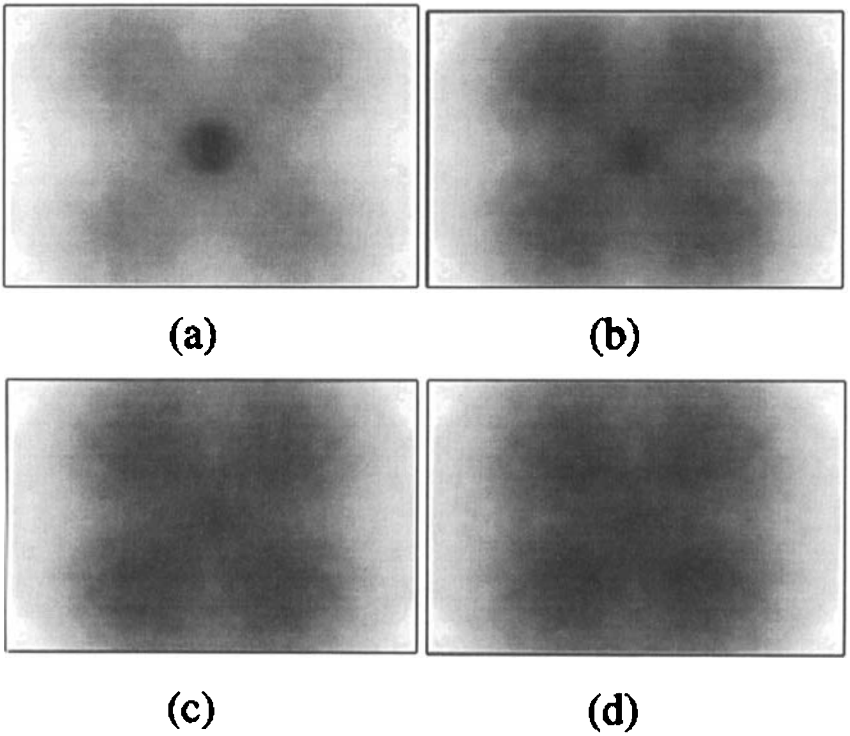


FIGURE 13 H_v-light scattering patterns of PEI 3 (n = 16) at 148°C after 9 min. (a), 12 min. (b), and 18 min. (c).

rate is 7 nm/mm. One can see large spherulites with a fringed shape. The maltese cross is sometimes oriented parallel to the direction of polarization, or sometimes is tilted.

A formation of spherulites and axialites during crystallization above the LC-phase has also been described but not depicted by Pardy *et al.* [18] for the smectic PEI 1 (n = 9) and by Heberer *et al.* [19] for nematic polyethers.

The competition between formation of a LC-phase and smectic solid phase becomes obvious in the following X-ray experiment. PEI 3 (n = 16) is cooled rapidly from the isotropic to 143°C and kept there isothermally. Figure 14 exhibits the change of the MAXS as a function of time for two experiments (a, b), which are carried out more or less the same way. In experiment (a), a layer reflections occurs after a short period of time at $2\theta = 3.0°$ which indicates the LC-phase. Yet, it disappears again after several minutes and another reflection develops at $2\theta = 3.2°$ indicating the formation of the solid smectic phase. However, in experiment (b) only this latter reflection at $2\theta = 3.2°$ develops after 10 minutes. Obviously, during

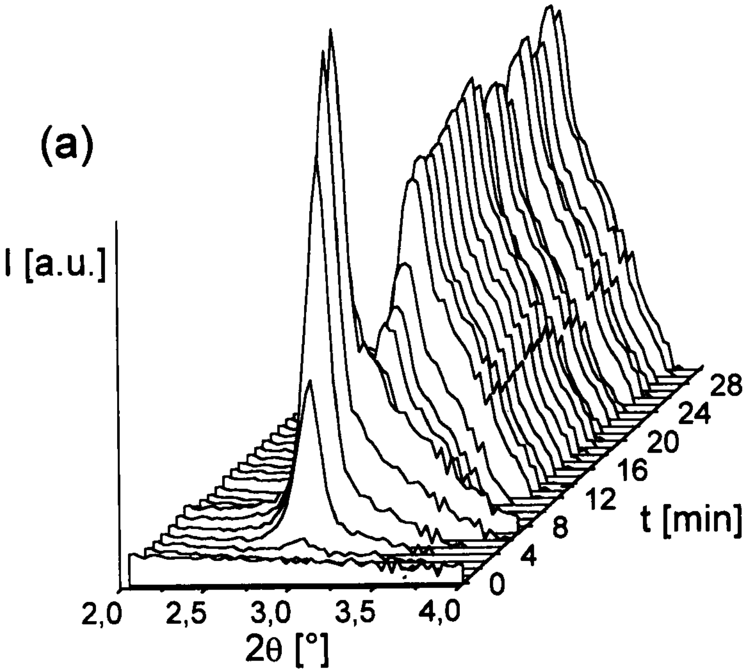


FIGURE 14 Change of MAXS of PEI 3 (n = 16) during two experiments (a) and (b) of isothermal crystallization at 143°C.

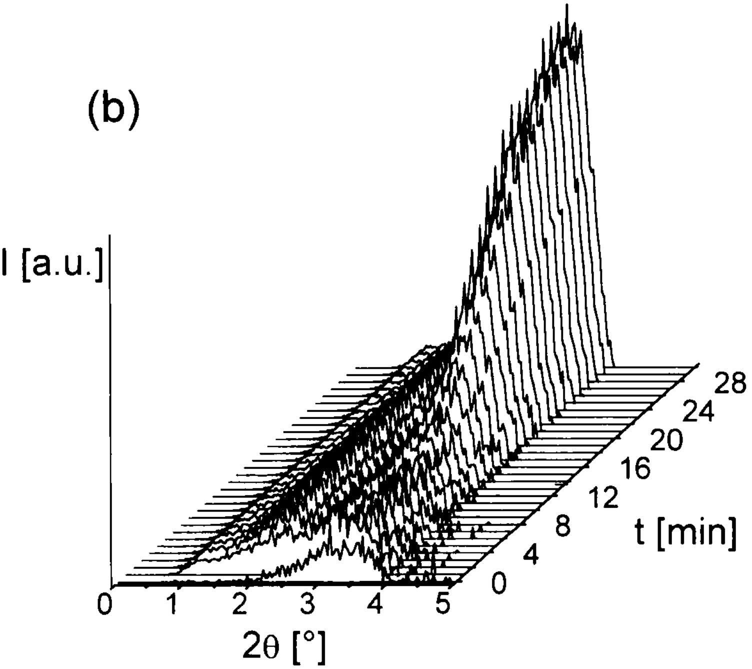


FIGURE 14 (Continued).

experiment (a) a slight supercooling has occurred resulting in a formation of the LC-phase which subsequently crystallizes. In contrast, the formation temperature of the LC-phase has never been reached in experiment (b) and, therefore, the smectic solid phase is formed directly from the isotropic melt with a spherulitic superstructure. By the comparison of these two experiments, one can see that the intermediate formation of the LC-phase in fact accelerates the crystallization process which is terminated after 12 minutes in experiment (a) but needs almost 30 minutes in experiment (b).

The above observations represent an interesting individual case of phase behavior, because, on first glance, the higher-ordered phase (smectic-crystalline) is formed at higher temperatures than the LC-phase with a lower structural order. In fact, this behavior wonderfully demonstrates the competition of thermodynamic and kinetic influences which is typical for phase transitions in polymers. The scheme displayed in Figure 15 demonstrates the conditions under which the formation of smectic-crystalline spherulites is possible. Of course, the regular sequence of polar mesogens and non-polar spacers is a basic requirement. Figure 15(a) represents the case in which the polymer does not form any LC-phase at all,

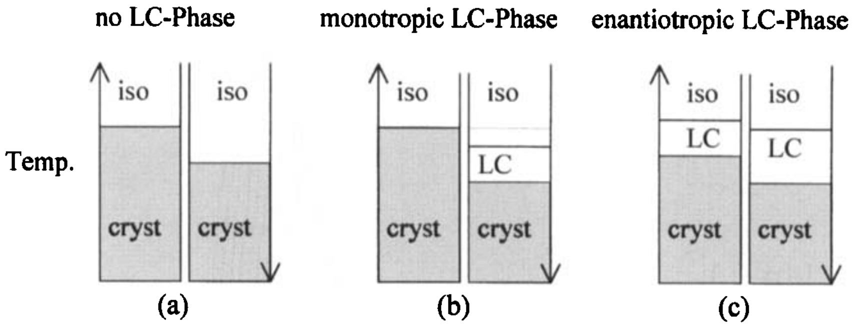


FIGURE 15 Schematic representation of the phase behaviour of polymers without LC-phase (a), forming a monotropic LC-phase (b) and passing through an enantiotropic LC-phase (c).

as observed in PEI 1 (n = 16, 22). The smectic-crystalline phase is the only stable phase besides the isotropic melt. Upon moderate cooling the crystalline phase is formed at a temperature below the melting point due to kinetic hindrance. In case (c), the enantiotropic LC-phase is thermodynamically stable and therefore, is formed upon heating and cooling. Upon cooling, the LC-phase is formed close below the clearing point, as the activation energy is very low. However, the subsequent crystallization exhibits once again a significant supercooling with respect to the melting temperature. As soon as the formation temperature of the LC-phase is reached, even under rapid cooling conditions, the LC-phase is formed much faster than the smectic-crystalline phase (higher activation energy) and consequently crystallization occurs exclusively from the LC-phase with a corresponding microscopic texture. In other words, a stable, enantiotropic LC-phase always prevents the formation of smectic spherulites. This is different in the case of a monotropic LC-phase (b), which is meta-stable and develops upon cooling only because the crystallization is kinetically hindered. Upon cooling at a rate of *i.e.*, 10°C/min, it is formed much faster than the crystals and determines the microscopic texture. But with time, the transition into the thermodynamically-stable crystalline phase occurs without significant changes in the texture. Only in some exceptional cases, the formation of spherulites has been observed to develop the schlieren-, batonnet- or grain-texture in the LC-phase during crystallization [19, 20].

However, when the anisotropization temperature of the monotropic LC-phase is lower than the melting point of the crystals, a temperature gap exists in which the crystals are stable but not the LC-phase. If such a polymer (*e.g.*, PEI 3 (n = 16)) is cooled from the isotropic melt and kept isothermally within this gap, the crystals develop directly out of the isotropic melt and that with a spherulitic morphology.

The above investigations of PEI 3 (n = 12, 16) give a hint concerning the molecular structure between the crystal lamellae within the spherulites. As mentioned above, the tilt angles of the smectic LC-phase and the smecticcrystalline phase are different in both polymers, as indicated in Figure 17a for (n = 16) by the positions of the MAXS reflections. Since the reflection of the smectic-crystalline phase at $2\theta = 3.2°$ develops exclusively during the crystallization with a spherulitic superstructure, one has to assume, that the regions between the lamellae are rather not smectic liquid-crystalline but amorphous. One has to assume that the repation of the molecular chains which is required for the growth of the lamellae exert constrains upon the coiled and entangled chain segments which prevent not only further crystallization but also a nano-phase separation of the mesogens and the spacers.

CONCLUSION

The development of the smectic-crystalline phase (S_E, S_H) directly out of the isotropic melt indicates that liquid-crystallinity is not a basic requirement for the formation of smectic layers. Moreover, the formation of a smectic-crystalline phase with a spherulitic superstructure is a consequence of two facts. On one hand, the difference in the polarity between the mesogens and spacers has to be large enough so that a high tendency exists to form smectic layers due to nano-phase separation. On the other hand, no LC-phase must be formed prior to crystallization. This is the case, if either no LC-phase is formed at all, or if the LC-phase is only monotropic respectively meta-stable and its formation temperature upon cooling is lower than the melting point of the smectic crystals during heating. Then, smectic spherulites are formed during isothermal crystallization within this temperature gap.

The spherulites exhibit a lamellar structure of the order of a few hundred Å giving rise to a SAXS reflection. Whereas the crystal lamellae comprise 4–8 higher-ordered smectic layers, the low-density phase between the lamellae is probably amorphous.

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