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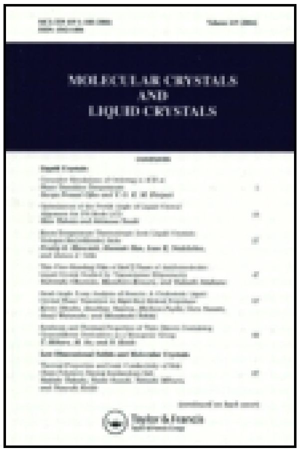

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Phase Transitions in Smectic Poly(Ester Imide)s Derived from 4-Aminocinnamic Acid Trimellitimide and Long Aliphatic Spacers

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Phase Transitions in Smectic Poly(Ester Imide)s Derived from 4-Aminocinnamic Acid Trimellitimide and Long Aliphatic Spacers

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The phases behavior of poly(ester imide)s (PEI) based on trimellitic anhydride, 4-aminocinnamic acid and α,ω-dihydroxydodecane ($n = 12$) or α,ω-dihydroxyhexadecane ($n = 16$), resp., have been investigated by X-ray measurements employing synchrotron radiation. Both PEIs form monotropic LC phases which can be quenched into the glassy state. Due to the regular sequence of rigid, polar mesogens and flexible, non-polar spacers smectic phases are formed in the melt and in the solid state, giving rise to sharp X-ray reflections. During transition from the smectic LC phase to the higher ordered smectic crystalline phase these layer reflections shift towards larger scattering angles indicating a narrowing of the layers due to tilting of the mesogens with respect to the layer plane. X-ray fiber pattern indicate that this tilting already occurs in the frozen LC phase (S_C). The chains are oriented preferably parallel to the fiber direction while the staggering of the mesogens orients the layers inclining an angle of about $\beta = 20°$. During crystallization the mesogens reptate longitudinally in order to fit the lateral lattice and the tilt angle increases up to 41° ($n = 12$) and 35° ($n = 16$) (S_H). Isothermal experiments reveal that PEI ($n = 12$) is capable of forming two different smectic-H phases depending on the thermal treatment. Above 130°C S_{H1} ($\beta = 32°$, $d = 27$ Å) is formed preferably whereas S_{H2} ($\beta = 41°$, $d = 24$ Å) dominates below 140°C.

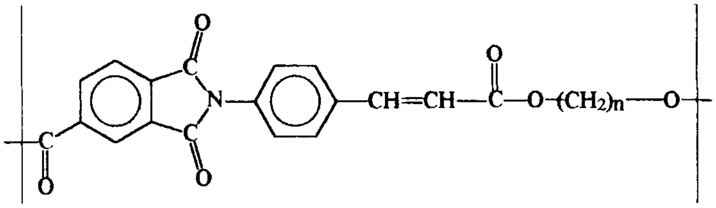
Keywords: LC-polymer; smectic; monotropic; X-ray scattering

INTRODUCTION

Several authors have demonstrated in previous studies [1–7] that poly(ester imide)s consisting of a regular sequence of polar, rigid imide mesogens and non-polar, flexible alkane spacers tend to form smectic layer structures giving rise to reflections in the middle angle X-ray scattering (MAXS,

$2\theta = 1-5°$). Various smectic phases can be formed in the molten and solid state depending on the chemical structure of the mesogen, the spacer length and the thermal treatment of the polymer.

A previous publication [8] reported on synthesis and properties of poly(ester imide)s (PEI)s derived from trimellitic anhydride, 4-aminocinnamic acid and α,ω-dihydroxyalkanes. Compared to the PEI based on aminobenzoic acid the incorporation of the double bond introduces photoreactivity and improves the mesogenic character. Whereas the PEIs containing odd-numbered spacers form an enantiotropic smectic LC-phase which is frozen in the solid state, the PEIs having even-numbered spacers form a monotropic LC phase. Further cooling yields a higher ordered, quasi-crystalline smectic phase which can be also called condis-crystalline [9, 10].



PEI n = 12, 16

The layer distances (*d*-spacings) of the smectic-crystalline phases was found to be much shorter compared to the smectic LC phases, suggesting a tilting of the mesogens with respect to the normal of the layer plane (S_H). On the other hand, X-ray fiber pattern of quenched PEI ($n = 12$) indicated that the LC phase is already tilted (S_C) in agreement with the polarizing microscopic texture. The present paper is aimed at investigations of the phase transitions of PEI with long spacers ($n = 12, 16$) in more detail by time-resolved X-ray diffraction of fibers and isothermal experiments.

EXPERIMENTAL

Materials

Both poly(ester imide)s were synthesized by Probst and Kricheldorf as described previously [8].

Measurements

Time resolved X-ray scattering was performed at HASYLAB/DESY employing synchrotron radiation at $\lambda = 1.5$ Å. Middle angle X-ray scattering (MAXS

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$2\theta = 1°-10°$) and wide angle X-ray scattering (WAXS, $2\theta = 10°-35°$) were detected simultaneously by two one-dimensional position sensitive wire-counters (Gabriel-detectors) at an acquisition time of 30 s.

RESULTS AND DISCUSSION

Both PEIs ($n = 12$ and 16) form monotropic smectic-LC phases as revealed by DSC measurements [8]. The middle angle X-ray scattering (MAXS) illustrated in Figure 1 exhibits the change of MAXS during heating and cooling PEI ($n = 12$) at a heating rate of 10°C/min. Upon heating the broad MAXS reflection at $2\theta = 3.6°$ corresponding to the solid smectic layer structure disappears at 165°C in good agreement with the DSC melting point [8]. The development of the sharp MAXS reflection at $2\theta = 2.9°$ upon cooling below 145°C can be attributed to the formation of the smectic LC phase. At 100°C this MAXS reflection vanishes while another reflection at $2\theta = 3.7°$ develops indicating that the phase transition into the solid smectic phase involves a reorientation of development of weak reflections in the wide angle X-ray scattering (WAXS) which was detected simultaneously (see Fig. 2).

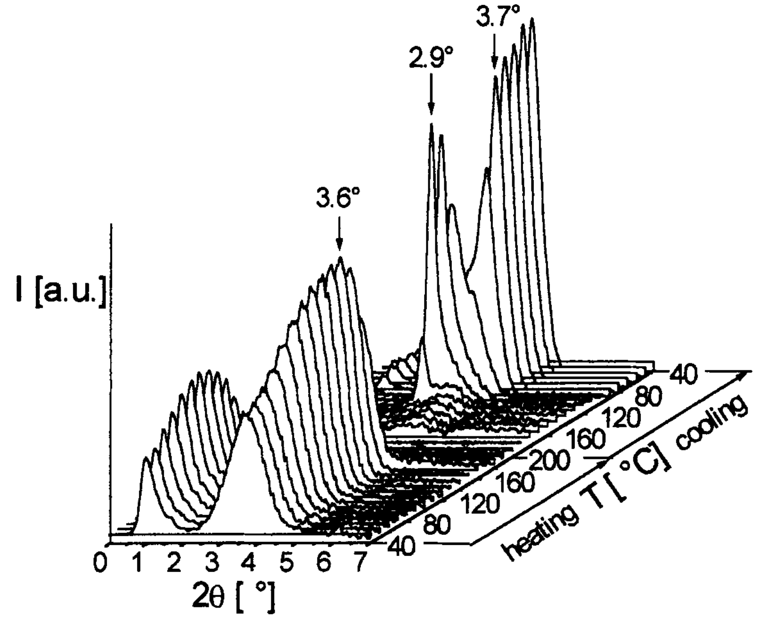

FIGURE 1 MAXS of PEI ($n = 12$) during heating and cooling with 10°C/min.

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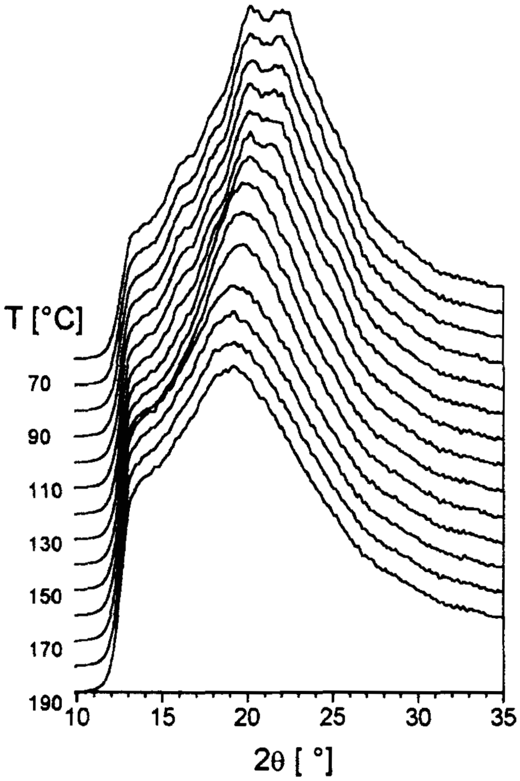

FIGURE 2 WAXS of PEI ($n = 12$) during cooling with 10°C/min.

Calculating the thickness of the smectic layers (d-spacing) from the position of the MAXS reflections via the Bragg equation results in a decrease of the d-spacing from 30 Å to 24 Å during this phase transition. This narrowing of the smectic layers can be explained by a stronger tilting of the mesogens with respect to the normal of the layer plane during the proposed phase transition from smectic-C to smectic-H.

Since the tilt angle between mesogens and smectic layers can be visualizes by X-ray fiber pattern Lit), the rearrangement of the molecular chains during the phase transition can by studied more precisely by on-line X-ray diffraction of the fiber in the middle angle region. Investigations of the oriented LC phase would involve on-line experiments during fiber spinning, which need unproportional expenses and large amounts of polymer. However, it can be assumed that the polymer undergoes the same phase transition with the same structural changes when the LC phase is frozen into a

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smectic glass by quenching and subsequently annealed above glass transition temperature T_g. Previous investigations [8] revealed that it is possible to quench the PEIs $n \leqslant 12$ avoiding crystallization. Figure 3 depicts the change of MAXS during heating of the quenched PEI ($n = 12$). The frozen smectic LC phase gives rise to a layer reflection at $2\theta = 2.9°$ which is identical to the MAXS of the LC phase obtained upon cooling in Figure 1. Often, for the LC phase a non-symmetrical shape of the MAXS reflection is found which must be caused by a non-symmetrical distribution of d-spacings. In the LC phase the variation of local mesogen orientation with respect to the director allows a narrowing of the layers which is reflected by the slope of the peak towards larger angles, while the sharp limit at lower angles correspond to the maximum d-spacing of extended repeat units. This accounts for S_A phases as well as for S_C phases in which the variation of orientation about the director is large compared to the tilt angle of the director relative to the normal of the layer plane. However, upon heating above T_g the MAXS reflection of the frozen LC phase vanishes above 70°C and the layer reflection of the quasi-crystalline smectic-H phase develops at

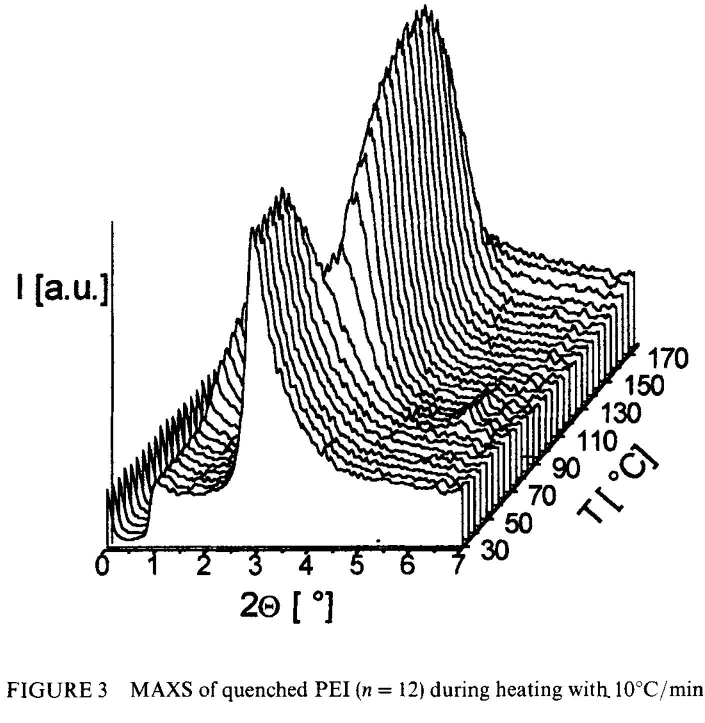

FIGURE 3 MAXS of quenched PEI ($n = 12$) during heating with 10°C/min.

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$2\theta = 3.7°$. At 165°C the MAXS reflection disappears again due to transition into the isotropic phase.

The same thermal treatment was applied to PEI fibers which had been drawn from the LC phase. In fact, there is no difference to fibers drawn from the isotropic melt, because it is not possible to freeze in the isotropic phase. Figure 4 represents the X-ray diffraction pattern in the middle angle region of the PEI ($n = 12$) fiber during heating at different temperatures (vertical fiber direction). Between ambient temperature and 65°C there are no changes in the MAXS observable, the pattern exhibits a four point diagram. The azimuthal splitting of the reflections prove the existence of a tilted frozen smectic-C phase in agreement with previous microscopic results [8]. Assuming that the molecular chains are oriented preferably parallel to the fiber direction a smectic phase with upright mesogens (S_A, S_B, S_E) gives rise to MAXS reflections on the meridian of the pattern. On the other hand, a tilt of the mesogens with respect to the normal of the layer plane (S_C, S_F, S_H) forces the smectic layers to take orientations inclining a certain angle with the fiber direction, which is detectable by the azimuthal splitting angle of the MAXS reflections β. The fiber pattern at 65°C exhibits a

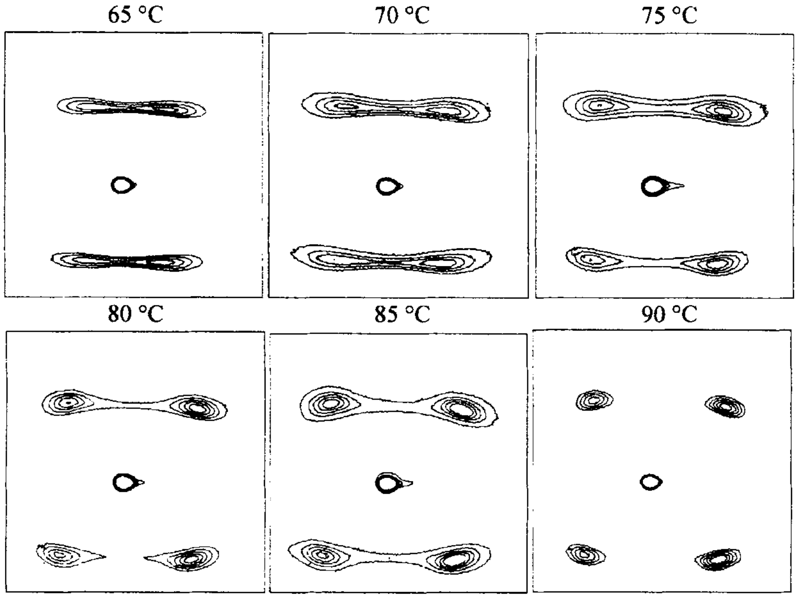

FIGURE 4 X-ray diffraction pattern of PEI ($n = 12$) fiber during heating at different temperatures.

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splitting of $\beta = 23°$, upon further heating the splitting of the MAXS reflections increases up to an angle of $\beta = 41°$. During this process of reorientation the reflections do not move azimuthally on a concentric circle but remain on the same layer line, so that their radial scattering angle 2θ changes as observed previously in the powder pattern (Fig. 3) corresponding to a decrease of layer spacing in direction normal to the layer plane. Figure 5 exhibits the tilt angle and the normal *d*-spacing of the quenched PEI ($n = 12$) fiber during annealing. During the crystallization above T_g between 65°C and 75°C the tilt angle increases from 23° to 41° while the layer thickness decreases from 30 Å to 24 Å.

The invariance of the meridional scattering angle in the fiber patterns (Fig. 4), on the other hand, indicates that the *d*-spacing in fiber direction remains constant at a value of 32 Å which is in good agreement with the monomer length of 18 Å for the mesogen calculated by force field program [8] and $12 \times 1.2 = 14.4$ Å for the spacer [11]. Hence, this phase transition does not involve rotational reorientation of the mesogens (or spacers) but longitudinal reptations of neighboring chains, resulting in a stronger tilting of the smectic layer planes with respect to the fiber direction (represented schematically in Fig. 6). The driving force of this process is the gain in

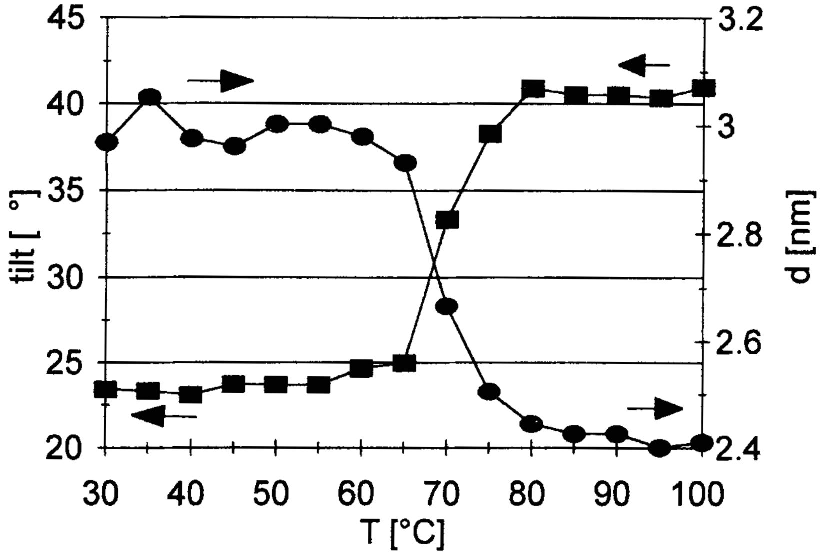

FIGURE 5 Tilt angle β and normal *d*-spacing of PEI ($n = 12$) fiber as function of temperature.

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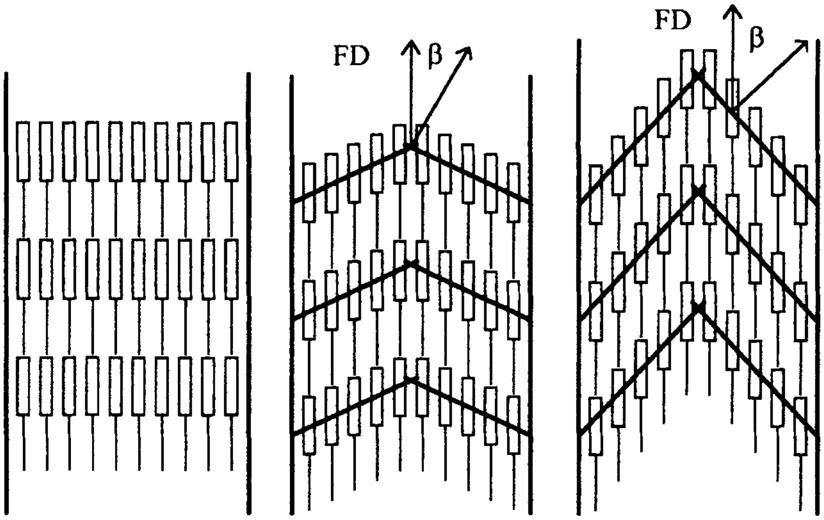

FIGURE 6 Schematic representation of layer orientation in tilted smectic fibers.

enthalpy by lateral interactions of the mesogens embedded into a quasicrystalline lattice. Obviously, the mesogens need a distinct staggering to minimizes their energy which depends on their molecular structure.

Additionally to the orientation of the smectic layers the X-ray fiber patterns of Figure 4 contains information about the morphology of the PEI fiber. In the pattern of the frozen LC phase at 65°C the envelope of the MAXS reflections has almost the shape of layer lines indicating a fibrous structure. Obviously, the smectic layers are well correlated in fiber direction but only little extended in lateral direction, resembling an oriented cybotactic nematic phase [12, 13]. Upon heating the envelope of the reflections changes gradually and simultaneously to the increase of the splitting. At 90°C the envelope of the four point diagram has the shape of an ellipsoid with the main axis on the equator indicating a cylindrical correlation of the smectic layers. Furthermore, the azimuthal the smectic layers has been improved during the phase transition. This finding can be explained by the above proposed mechanism of reorientation in which the mesogens, by longitudinal reptation and lateral interaction, can connect smectic layers that had been uncorrelated before.

The results up to now indicate that for PEI ($n = 12$) two descrete tilt angles between the mesogens and the normal of the smectic layer plane exist: $\beta = 23°$ for the LC phase (S_C) and $\beta = 41°$ for the higher ordered solid

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phase (S_H). Additional measurements with slower cooling rates and isothermal experiments, originally performed in order to study the kinetics of this phase transition, reveal that another descrete level of tilting can be captured. The change of MAXS during cooling of PEI ($n = 12$) with 5°C/min Fig. 7) reveals, actually, that the LC reflection vanishes at 140°C and another MAXS peak develops at $2\theta = 3.2°$ corresponding to 27 Å *d*-spacing, while the reflection at $2\theta = 3.6°$ (24 Å) only forms a shoulder which grows at lower temperatures than the main peak. Assuming again that the shifting of the MAXS is caused by tilting a radial scattering angle of $2\theta = 3.2°$ corresponds to a tilt angle of $\beta = 32°$.

Hence, two different layer structures coexist below 150°C, namely S_{H1} ($d = 24$ Å) and S_{H2} ($d = 27$ Å), the fractions and growth rates of which depend on the thermal conditions. The temperature dependence can be estimated more precisely by isothermal experiments. The PEI ($n = 12$) was heated up to the isotropic melt, cooled rapidly to different temperatures T_i at which the LC phase is formed immediately and kept isothermally. The

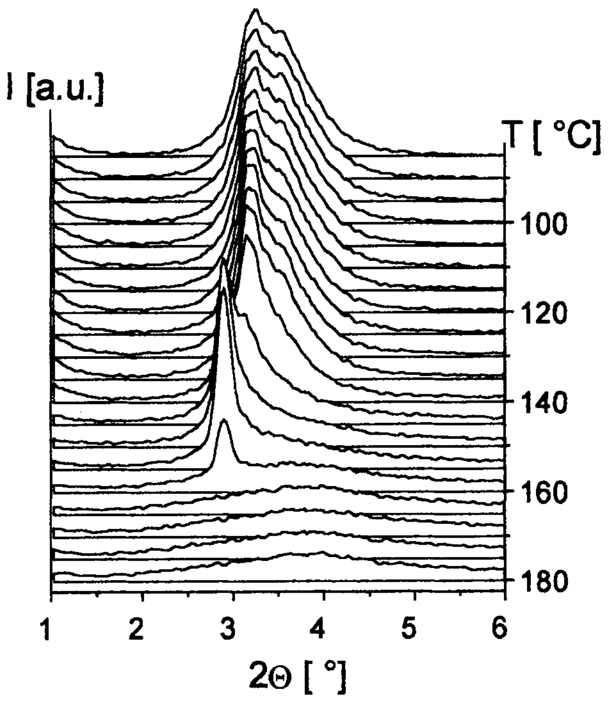
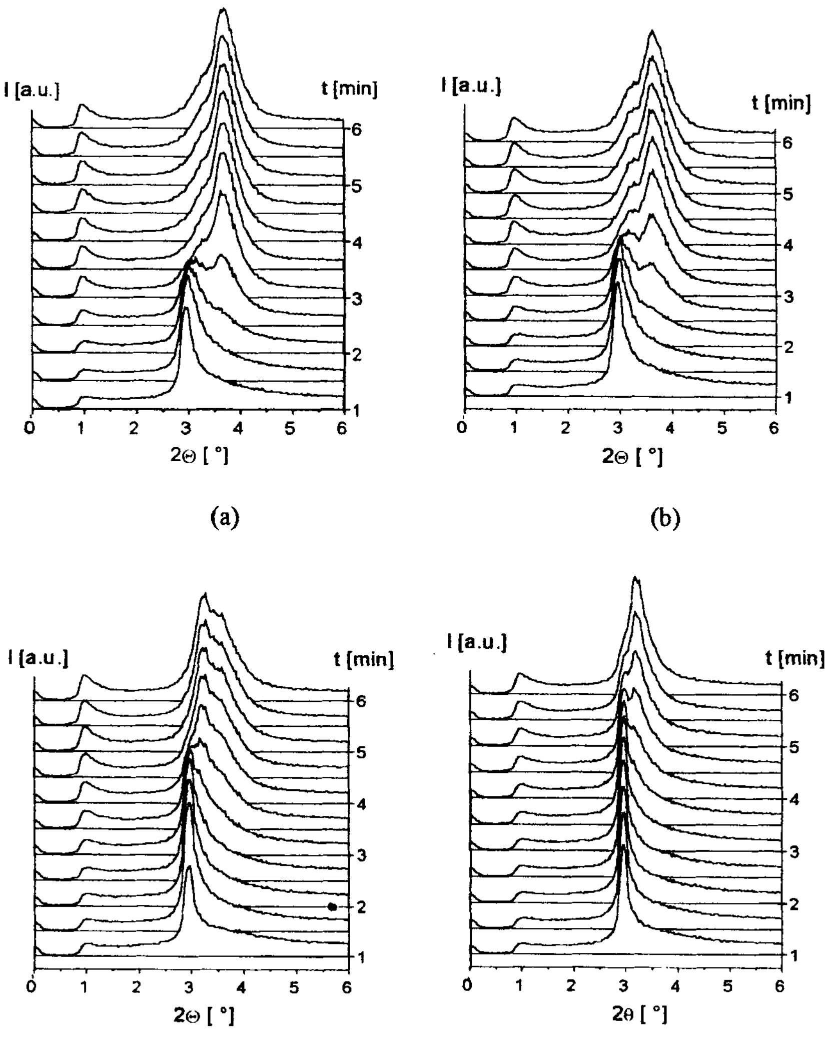


FIGURE 7 MAXS of PEI ($n = 12$) during cooling with 5°C/min.

change of the MAXS as a function of time is represented in Figure 8a–d for $T_i = 120^\circ$, 130°C, 140°C, and 148°C (above 148°C no phase transition takes place at all), whereas at 140°C and above the peak at $2\theta = 3.2^\circ$ is predominant. In each case, the other layer reflection is present as a shoulder indicating that it is not possible to obtain pure phases.



(a)

(b)

(c)

(d)

FIGURE 8 Change of MAXS of PEI ($n = 12$) as a function of time at 120°C (a), 130°C (b), 140°C (c), and 148°C (d).

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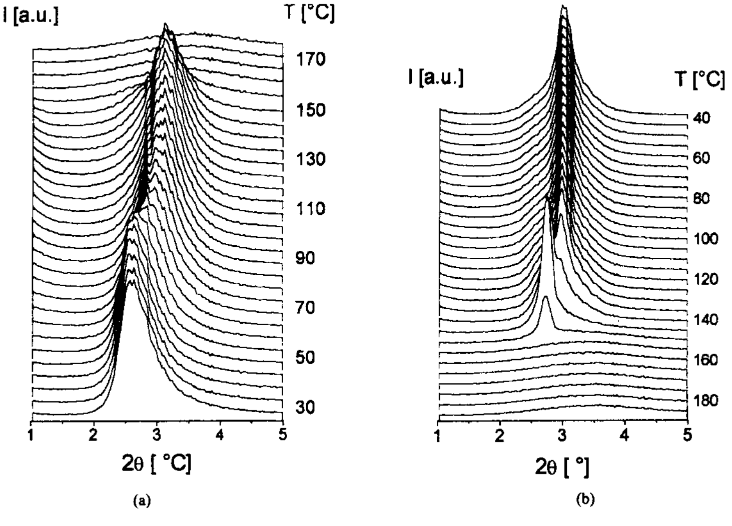
Unfortunately, the superposition and the non-gaussian profile of the reflections do not allow a precise separation by deconvolution in order to evaluate exact kinetical parameters. However, both phases seem to have an equivalent thermodynamical stability, because no transition between them is observable upon subsequent heating or cooling. Moreover, their fractions depend on their different rates of formation at the certain temperature. Both phases exhibit a temperature dependent growth rate indicating that their formation is initialized by an energy activated nucleation process.

A similar phase behavior was found for PEI ($n = 16$), but the structural changes during the phase transition are less pronounced when compared to PEI ($n = 12$). Figure 9 represents the change of the MAXS powder pattern of quenched PEI ($n = 16$) during heating (a) and cooling (b) with 10°C/min. The shift of the MAXS reflection from $2\theta = 2.6°$ to $3.1°$ during annealing above 65°C or cooling the melt below 135°C indicates, that the LC phase can be frozen in by quenching (contrary to previous suppositions [8]) and that the LC phase crystallizes involving a reorientation of the smectic layers with a decrease of the layer thickness from 33 Å to 28 Å.

The shift of the MAXS reflections is hardly recognizable in the X-ray fiber diffractograms of PEI ($n = 16$). Thus, only the pattern at 105°C is exhibited exemplary in Figure 10. The splitting of the MAXS reflection into a four point diagram indicates, again, the tilted smectic phase. The tilt angle and the layer thickness evaluated from the fiber patterns are plotted in Figure 11 as a function of temperature. Both values change only gradually



(a) (b)

FIGURE 9 MAXS of quenched PEI ($n = 16$) during heating (a) and cooling (a) with 10°C/min.

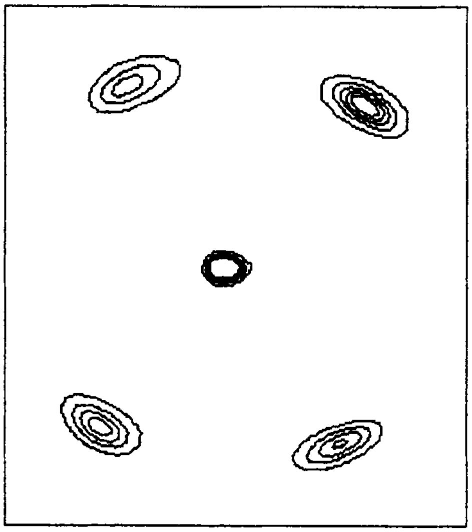


FIGURE 10 X-ray fiber pattern of PEI ($n = 16$).

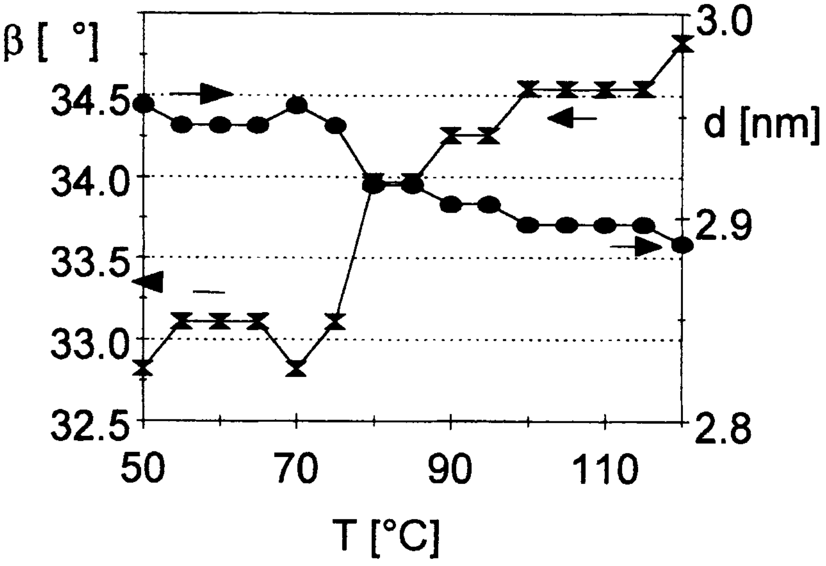


FIGURE 11 Tilt angle β and d-spacing in PEI ($n = 16$) fiber as a function of temperature.

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TABLE I Spacer length *n*, phase designation, temperature conditions, tilt angle β and normal *d*-spacing of the PEI

Spacer length n	*Phase*	$T_i[^\circ C]$	$\beta[^\circ]$	$d[\mathring{A}]$
12	S_C	> 148	23	30
12	S_{H1}	$130 < T < 148$	32	27
12	S_{H2}	$75 < T < 140$	41	24
16	S_C	$117 < T < 137$	21	33
16	S_H	$T < 117$	35	28

during the phase transition between 70°C and 90°C. While the tilt angle increases from 33° to 35° the layer thickness decreases only from 29.5 Å to 28.5 Å, indicating that drawing of the fiber in this case did not freeze in the pure LC phase. Obviously, the orientation accelerates the crystallization.

Table I summarizes the smectic phases formed by PEI ($n = 12$ and 16) with the corresponding tilt angle β and *d*-spacing.

CONCLUSIONS

Both PEI ($n = 12$ and 16) form monotropic LC phases upon cooling which can be frozen into a smectic glass by quenching. In both mesophases the chains are tilted inclining an angle of about 20° relative to the smectic layer plane (S_C). Upon cooling the LC melt or heating the glass above $T_g g$ a transition into a higher ordered smectic crystalline phase (S_H) occurs accompanied by an increase of the tilt angle 30°–40° and narrowing of the layers due to longitudinal reptations of the chains. In PEI ($n = 12$) two different smectic-H phases with different tilt angles can be formed depending of the thermal treatment. S_{H1} ($\beta = 32^\circ$) is formed preferably above 130°C, S_{H2} ($\beta = 41^\circ$) dominates below 140°C.

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