

polymer papers

Smectic-spherulitic – a new morphology

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The phase behaviour of poly(ester imide)s (PEI) based on long aliphatic diols and aminobenzoic acid trimellitimide or aminocinnamic acid trimellitimide, respectively, was investigated by means of X-ray scattering. Whereas PEI with shorter spacers form smectic LC-phases which transform into higher ordered smectic phases upon further cooling, PEI with long spacers undergo a direct phase transition from the isotropic melt into a higher ordered solid smectic phase, which is also named smectic-crystalline owing to the lateral interactions of the mesogens. This process involves a nucleation followed by the growth of a three-dimensional spherulitic superstructure. This new morphology of spherulites with internal smectic order is named smectic-spherulitic. Moreover, the spherulites consist of stacks of crystalline and lower-ordered lamellae giving rise to a small angle X-ray reflection with a long period of 150–400 Å. The crystalline lamellae in their part consist of smectic layers. In spite of the crystallinity, the system exhibits a remarkable mobility. Upon heating and cooling the lamellae expand and shrink reversibly. This polymer system combines features of semi-crystalline polymers with the meso-phase character of smectic LC-polymers. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polymers consisting of regular sequences of rigid polar mesogens and non-polar flexible spacers tend to form smectic layer structures in a process of microphase separation. The periodic arrangement of the smectic layers gives rise to a middle angle X-ray reflection in the angular region of $2\theta = 2^\circ\text{--}6^\circ$ depending on the lengths of spacer and mesogen¹. These smectic phases can be either liquid-crystalline or true-crystalline in the solid state. *Figure 1* represents schematically the arrangement of the mesogens in a smectic LC-phase (A) and a higher ordered smectic-crystalline phase (B). While the direction of the mesogens in the LC-phase varies about the director, the mesogens in the smectic-crystalline phase undergo lateral interactions giving rise to WAXS reflections. Of course, the spacers are partly disordered even in the latter phase which, thus, can also be named condiscrystal according to Wunderlich².

The nature of the layer structure and the phase transition between different phases depend strongly on the chemical structure, i.e. the length of the spacer in relation to the mesogen^{3–8}. Poly(ester imide)s (PEI) based on α,ω dihydroxyalkanes and aminobenzoic acid (formula **1**) or aminocinnamic acid (formula **2**) were first synthesized by Kricheldorf and coworkers^{3–5,8}. They have recently attracted more interest, because they can form a large variety of smectic phases depending on spacer length and thermal history^{4,7,8}. It was found that the PEI **1** with spacers up to 12 CH₂-groups form monotropic smectic LC-phases which crystallize upon further cooling. The metastability of such monotropic LC-phases has been described very early^{9,10} and recently also for LC-polymers¹¹. Furthermore, investigations by means of wide angle X-ray scattering reveal that the positions of the crystal reflections differ totally for PEI **1** ($n < 11$), while they become independent for PEI **1** ($n > 11$). Obviously, in PEI with long spacers,

only two-dimensional crystals exist with the mesogen layer, because the unit cell does not cover the spacer layer.

New syntheses yielded analogous PEI with spacers of $n = 16$ and $n = 22$ and copolymers with $n = 12 + 22$. The question arises, how the extension of the spacer length influences phase transitions and morphology.

In a previous paper¹², DSC measurements of an isomeric class of PEI **3** indicated that PEI with long spacers crystallize directly from the isotropic melt, because only one exotherm was observed during a cooling trace. In those cases a very short-lived LC-phase is often discussed⁵ which is not resolved in DSC. The investigation reported in this paper was focused on elucidating this direct formation of the smectic-crystalline phase for the PEI of structure **1** and **2**.

EXPERIMENTAL

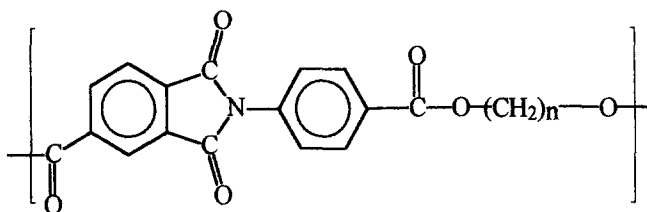
Time resolved X-ray scattering was performed employing synchrotron radiation at HASYLAB/DESY at a wavelength of $\lambda = 1.54$ Å and a one-dimensional position-sensitive detector.

Micrographs were taken between crossed polars with an Olympus BH-2 optical microscope on Agfa Pan 400 film.

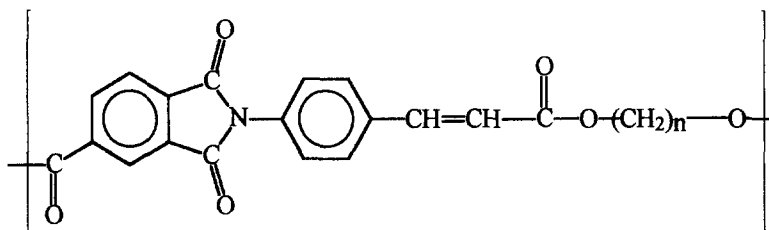
RESULTS AND DISCUSSION

The formation of certain smectic phases was identified by simultaneous measurement of middle angle X-ray scattering (MAXS) and wide angle X-ray scattering (WAXS).

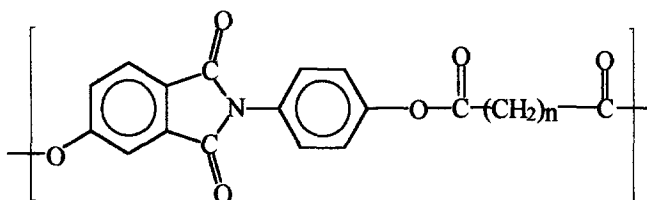
The PEI **1** form a monotropic smectic-A phase up to spacer length of $n = 12$, whereas the formation of the LC-phase in PEI **2** is extended up to $n = 16$ owing to the prolongation of the imide group by the double bond and the resulting improvement of the mesogenic character. *Figure 2* shows the change of MAXS (A) and WAXS (B) of PEI **2**



PEI 1 ($n = 12, 16, 22$)



PEI 2 ($n = 12, 16, 22$)



PEI 3 ($n = 12, 20$)

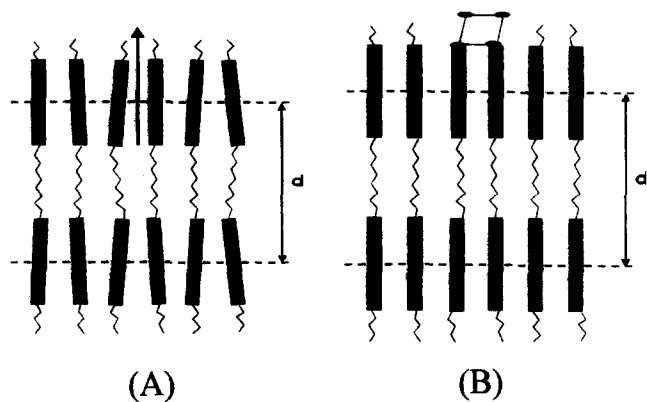


Figure 1 Schematic representation of a smectic LC-phase (A) and a higher ordered smectic phase (B)

($n = 12$) during heating and cooling at $10^\circ\text{C min}^{-1}$. During heating, the smectic-crystalline phase melts at 165°C and the broader MAXS reflection vanishes. While the smectic LC-phase indicated by the MAXS reflection occurs during cooling at 154°C , at which temperature the amorphous halo of the WAXS becomes a little bit narrower, the weak crystal reflections in the WAXS pattern do not develop until 113°C is reached. In this case, the phase transition of the smectic LC-phase into the smectic-crystalline phase coincides with a reorientation of the mesogens. The shift of the MAXS reflection to smaller angles at 113°C indicates a widening of the layer structure due to erection of the mesogens being tilted in the LC-phase (S_C). A similar behaviour was found for PEI 2 ($n = 16$).

On the other hand, a prolongation of the spacer or copolymerization with longer spacers result in different

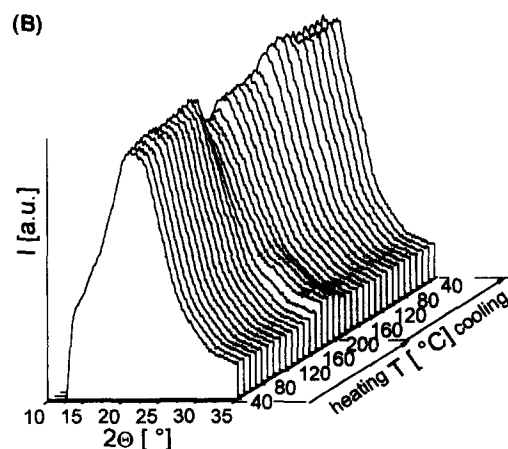
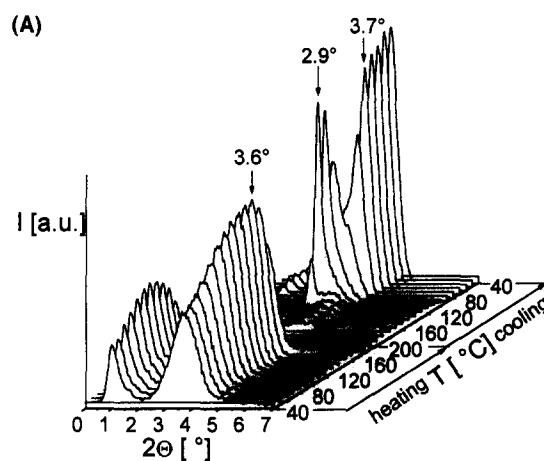


Figure 2 MAXS (A) and WAXS (B) of PEI 2 ($n = 12$) during heating and cooling at $10^\circ\text{C min}^{-1}$

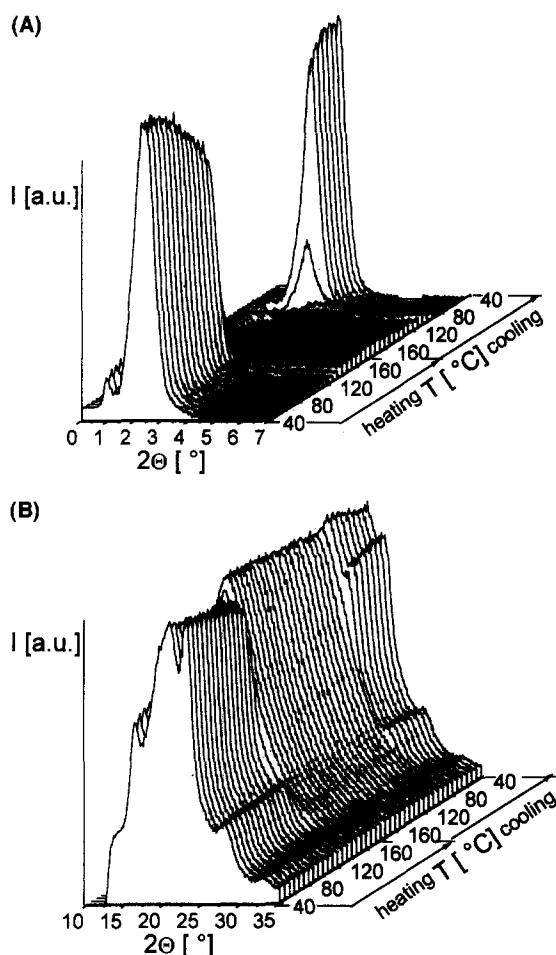


Figure 3 MAXS (A) and WAXS (B) of co-PEI 1 ($n = 12/22$) during cooling at $10^\circ\text{C min}^{-1}$

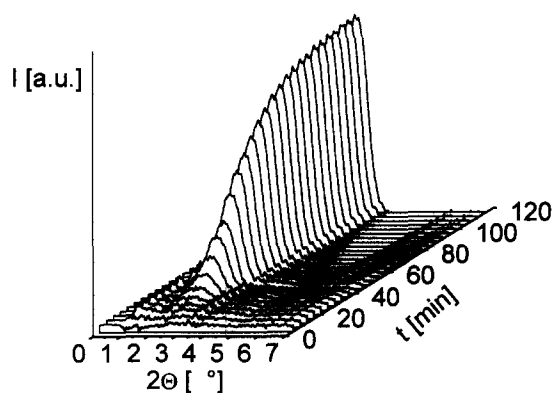


Figure 4 Development of MAXS reflection of co-PEI 1 ($n = 12/22$) at 122°C

behaviour. For PEI 1 ($n = 16, 22$), for PEI 2 ($n = 22$) and for a copolymer 1 containing different spacers of length $n = 12$ and $n = 22$ statistically, WAXS and MAXS reflections occur simultaneously upon cooling, indicating a formation of the smectic-crystalline phase directly from the isotropic melt. As an example, *Figure 3* exhibits the change of MAXS (A) and WAXS (B) during heating and cooling of co-PEI 1 ($n = 12/22$) at $10^\circ\text{C min}^{-1}$. Both MAXS and WAXS reflections develop below 92°C .

While the formation of the smectic LC-phase is a spontaneous process and the following crystallization occurs very fast, the direct crystallization of the PEI with long spacers was found to develop much more slowly. Thus,

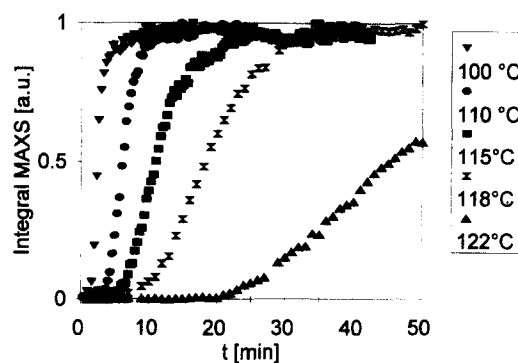


Figure 5 Integral MAXS intensity as a function of time for co-PEI 1 ($n = 12/22$) at different temperatures

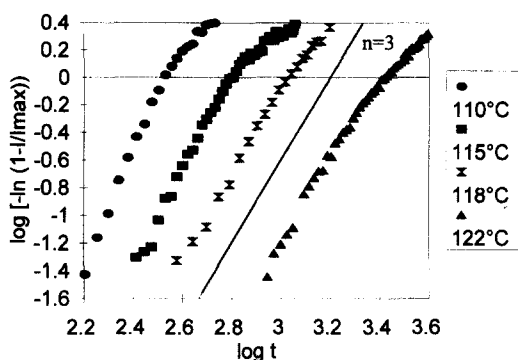


Figure 6 Avrami plot of the change of integral MAXS intensity for co-PEI 1 ($n = 12/22$) at different temperatures

it was possible to investigate the kinetics of crystallization from the melt during an isothermal process. *Figure 4* represents the development of the MAXS reflection of the co-PEI 1 ($n = 12/22$) at 122°C , as an example. It is obvious that the crystallization needs several minutes. For a more precise evaluation the change of the integral MAXS intensity as a function of time is depicted in *Figure 5* for different temperatures. Obviously, the isothermal crystallization depends strongly on the temperature, indicating a high activation energy for this process. The formation of the smectic-crystalline phase becomes faster with higher supercooling below the melting temperature. The curves of the crystallization rate calculated from the WAXS exhibit an identical sigmoidal course. The Avrami evaluation of the crystallization kinetic results in Avrami exponents close to $n = 3$ (*Figure 6*). This result is surprising at first glance, because the crystals can grow only two-dimensionally within each mesogen layer. Hence, the observations propose the formation of a three-dimensional superstructure growing from nuclei.

Figure 7 exhibits micrographs between crossed polarizers of PEI 1 ($n = 16$) (A), ($n = 22$) (B) and PEI 2 ($n = 22$) (C). In fact, one can see clearly birefringent spherulites of some micrometres in diameter. The novel outstanding feature of these spherulites is their internal smectic-crystalline order. Hence, this new morphology can be named smectic-spherulitic. Up to now, to our best knowledge, only spherulites with a nematic order have been observed¹³.

Moreover, the observed superstructure proves the existence of a second process for the formation of a smectic-crystalline phase. While the crystallization from the LC-phase only involves local reorientations of the mesogens and, therefore, does not change the texture, the direct crystallization from the isotropic melt originates from nuclei

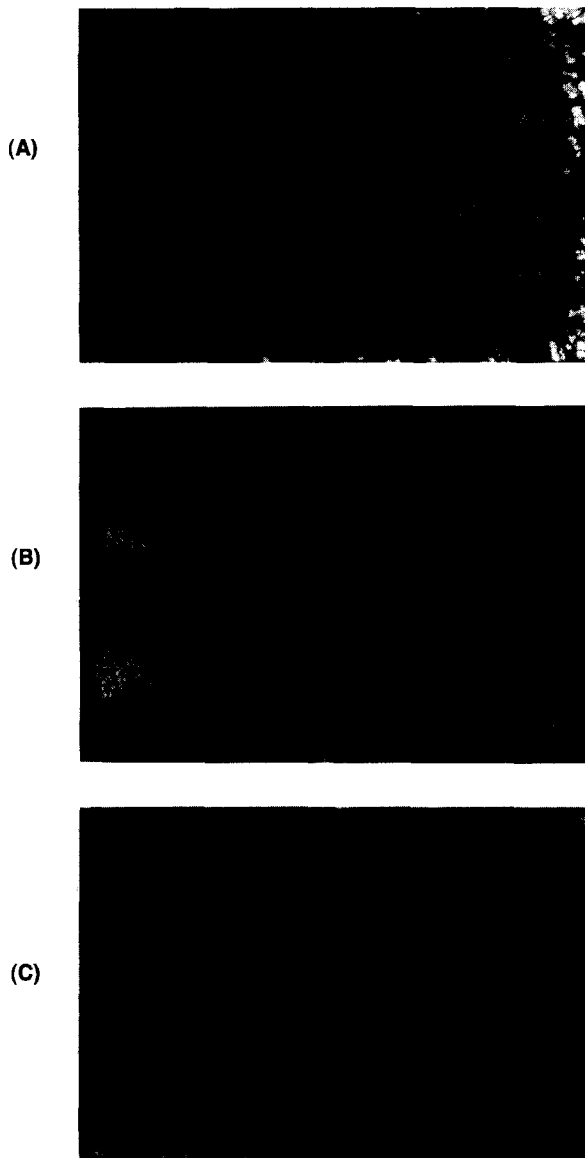


Figure 7 Micrographs between crossed polars of PEI 1 ($n = 16$) after 25 min at 145°C (A), PEI 1 ($n = 22$) after 120 min at 150°C (B), and PEI 2 ($n = 22$) after 50 min at 180°C (C)

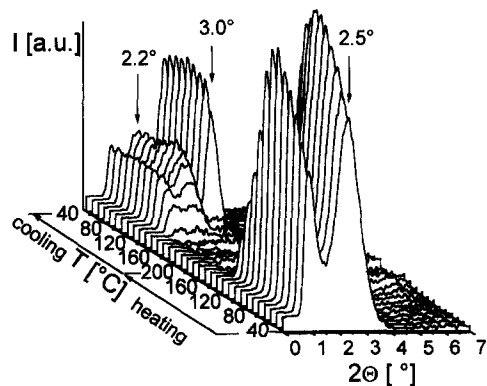


Figure 8 Change of MAXS of PEI 2 ($n = 22$) during heating and cooling at 10°C min⁻¹

growing into a spherulitic superstructure. Consequently, the formation of an ever-so-short-lived LC-phase prior to the crystallization can be excluded for the PEI with long spacers, because it would dominate the texture.

The MAXS of PEI 2 ($n = 22$) exhibits a peculiarity. In

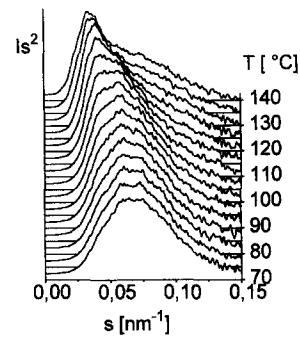


Figure 9 Change of SAXS of PEI 1 ($n = 22$) during heating at 10°C min⁻¹

Figure 8 a broad MAXS reflection at $2\theta = 2.5^\circ$ is detectable in the crude polymer. Upon cooling from the melt, however, two reflections occur, an intensive sharp one at $2\theta = 3.0^\circ$ and a weaker broader one at $2\theta = 2.2^\circ$. While the latter corresponds to a layer distance of upright mesogens (S_E) and mainly extended spacers, the former indicates tilted mesogens (S_H). Such a coexistence of two different solid smectic phases has been observed previously in isomers based on dihydroxy-imides and dicarboxylic acids¹². However, the orientation of the mesogens with respect to the smectic layer in poly(ester imide)s will be the subject of another paper¹⁴.

Spherulites of conventional semi-crystalline polymers normally consist of lamellar stacks giving rise to a long period in the small angle X-ray scattering (SAXS). Surprisingly, the smectic-spherulitic PEI exhibit a SAXS reflection as well. Figure 9 shows the development of the SAXS during heating of PEI 1 ($n = 22$) at 10°C min⁻¹. With increasing temperature the SAXS increases and shifts to smaller angles. This SAXS reflection indicates periodic fluctuations of the electron density with correlation length of a few hundred Å.

In summary, the PEI with long spacers yield reflections in the WAXS, MAXS and SAXS. Based on these observations, a model for the smectic-spherulitic morphology can be derived, which is represented in Figure 10. The spherulites are built up by two types of lamella, a disordered one with lower electron density and a crystalline lamella which within its structure consists of an integral number of smectic layers. The nature of the other lamella is still ambiguous. It could be amorphous owing to entanglements or frozen liquid-crystalline. With respect to the observed high difference in electron density between the two lamellae the former possibility seems to be more likely.

Contrary to semi-crystalline polymers this smectic-lamellar system is still mobile even in the crystalline state. Figure 11 shows the change of SAXS during cooling of PEI 2 ($n = 22$) at 10°C min⁻¹ after entire isothermal crystallization. The SAXS reflection shifts back to larger angles upon cooling. This implies a reversible, temperature dependent shrinking and expansion of the crystalline lamellae. The long period changes from 150 Å to 400 Å corresponding to 4 up to 10 smectic layers each with a thickness of 38 Å, as calculated from the MAXS reflection. The mobility is evident also from the change of WAXS and MAXS. Figure 12 represents the WAXS of PEI 2 ($n = 22$) during cooling at 10°C min⁻¹. The intensity of the WAXS reflections increases during cooling proving that the smectic-crystalline lamellae expand. A position shift cannot be determined with absolute accuracy, because the amorphous halo shifts with temperature.

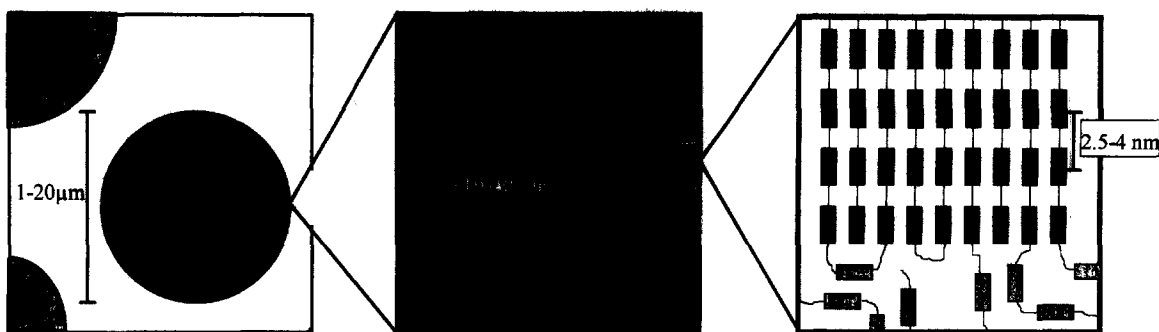


Figure 10 Schematic representation of the smectic-spherulitic morphology

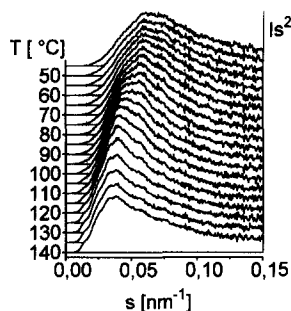


Figure 11 SAXS of PEI 2 ($n = 22$) during cooling at $10^{\circ}\text{C min}^{-1}$ after entire isothermal crystallization at 150°C

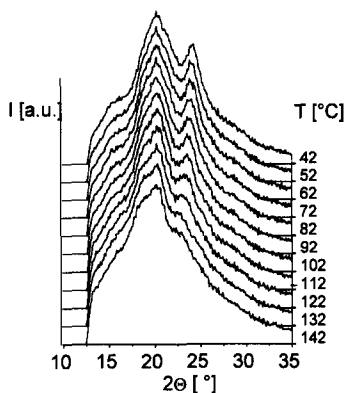


Figure 12 Change of WAXS of PEI 2 ($n = 22$) during cooling at $10^{\circ}\text{C min}^{-1}$

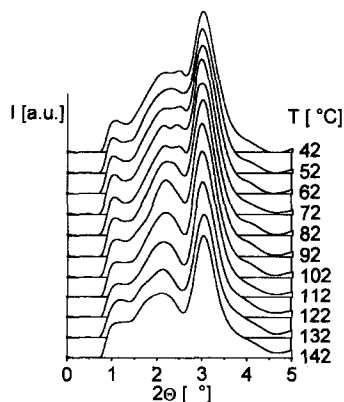


Figure 13 Change of MAXS of PEI 2 ($n = 22$) during cooling at $10^{\circ}\text{C min}^{-1}$

The change of the MAXS of PEI 2 ($n = 22$) during cooling at $10^{\circ}\text{C min}^{-1}$ represented in Figure 13 is poor, but nevertheless recognizable. At least, the weak scattering at smaller angles ($2\theta = 2^{\circ}$) changes slightly upon cooling.

Taken together, these observations indicate that the PEI with long spacers crystallize without an intermediate LC-phase, forming a spherulitic superstructure with internal smectic order and remarkable mobility in the solid state.

CONCLUSIONS

A prolongation of the spacer in the investigated class of poly(ester imide)s results in a direct phase transition from isotropic to smectic-crystalline without any intermediate LC-phase. The limit for skipping the LC-phase obviously depends on the relation between mesogen and spacer length. Contrary to the crystallization of a smectic LC-phase caused by local orientation of the mesogens, the direct formation of the smectic-crystalline phase originating from the isotropic melt is a consequence of a nucleation process followed by the growth of a three-dimensional spherulitic superstructure. This morphology can be named smectic-spherulitic, because the spherulites have an internal smectic order. Additionally, they consist of lamellar stacks with a long period of a few hundred Å. While the crystalline lamella is constructed from an integral number of smectic layers, the structure of the disordered lamella with lower density is not yet identified. In spite of the crystallinity, the system exhibits a high mobility and thus has partly kept the meso-phase character of the PEI with shorter spacers. In general, this polymer system is a borderline case between conventional semi-crystalline polymers and LC-polymers. It forms spherulites with internal crystalline-lamellar order, but is nevertheless a smectic phase which changes its structure reversibly upon heating and cooling.

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