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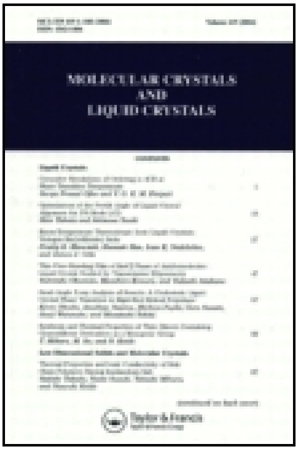

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Nanofibrillar Structures in Thermotropic Polyesters with Y-Shaped Mesogenes

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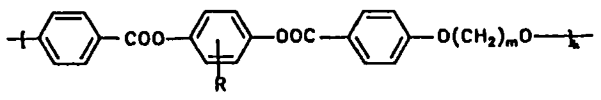
Liquid crystalline main chain polyesters containing Y-shaped mesogenes with flexible lateral substituents of different length have been investigated by X-ray diffraction and DSC experiments. The X-ray patterns of the polymers with lateral substituents longer as the methoxy group show beside the reflections at the wide angle range also small angle equatorial reflections. This is suggesting a nanofibrillar structure. The position of these reflections depends on the length of the substituent. In contrast to sanidic phases, these nematic melts are uniaxial. X-ray and DSC measurements reveal a phase transition between the "normal" nematic and the fibrillar nematic phase.

Keywords: main chain liquid crystalline polyesters, lateral groups, X-ray diffraction, fibrillar structures

INTRODUCTION

The phase structure of polymeric liquid crystals depends on the molecular architecture of the monomers as constructing parts. The study of this relationship has become an extending field of scientific and technical interest, because the microstructure affects the physical properties essentially. For this reason, macromolecules with mesogenic units arranged in different positions concerning the polymer non-mesogenic framework have been synthesized. Recently we could prepare a series of liquid crystalline main-chain polymers with Y-shaped mesogenic moieties.[1] Structure investigations of these polyesters claimed interest because the stiff side branching of the mesogenes should have consequences for the chain packing. Preliminary X-ray studies[2] provided hints to a low temperature fibrillar nematic phase. With rising temperature, this fibrillar structure undergoes an order-disorder transition into a normal nematic phase.

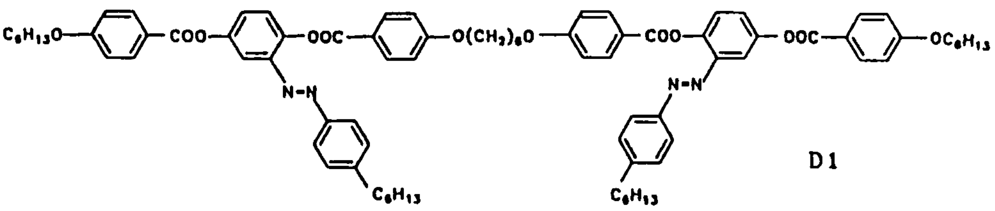
The purpose of our further investigations was to support this structure model by systematic X-ray diffraction experiments using polyesters with different lateral groups. The results will be compared with the structural peculiarities of sanidic phases published in the literature. The polyesters have the following basic structure:



P1–P13

n = 1,4,6,8,12,14 m = 6,12

Furthermore, polyesters with varying proportions of substituted and unsubstituted hydroquinone have been used. Finally as a reference compound for comparing X-ray studies the dimer **D1**

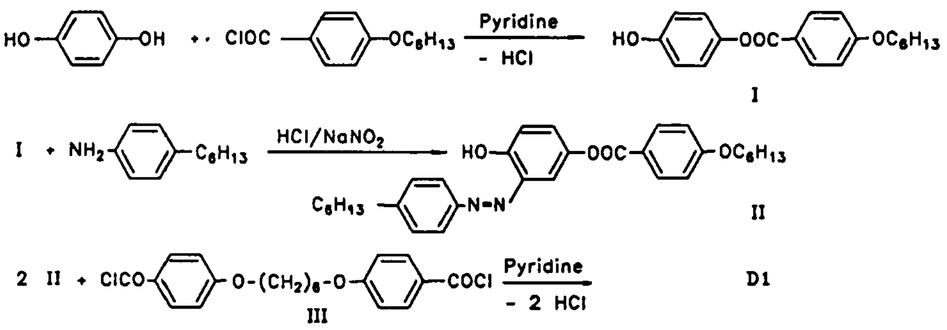


was also synthesized.

EXPERIMENTAL

The polyesters and copolyesters **P1–P13** have been prepared as described.[1] Details of the chemical composition and the transition temperatures are given in Table I.

The synthetic route of dimer **D1** is given in the following Scheme.



SCHEME 1

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TABLE I

Chemical composition and phase transitions

Code	m	R (%)	Phase transition (°C)
P1	6	-H (100)	P_c 220 P_{sA} 280 P_n 380 P_i
P2	6	-N=N-Ph-OCH_3 (100)	P_g 74 P_n 219 P_i
P3	6	-N=N-Ph-OC_4H_9 (100)	P_g 58 P_{fn} 70 P_n 192 P_i
P4	6	-N=N-Ph-OC_6H_{13} (100)	P_g 44 P_{fn} 119 P_n 195 P_i
P5	6	-N=N-Ph-OC_8H_{17} (100)	P_g 43 P_{fn} 142 P_n 201 P_i
P6	6	-N=N-Ph-$OC_{12}H_{25}$ (100)	P_g 45 P_{fn} 152 P_n 192 P_i
P7	6	-N=N-Ph-$OC_{14}H_{29}$ (100)	P_g 46 P_{fn} 155 P_n 186 P_i
P8	12	-N=N-Ph-OC_8H_{17} (100)	P_g 27 P_{fn} 55 P_n 136 P_i
P9	12	-N=N-Ph-$OC_{14}H_{29}$ (100)	P_g 25 P_{fn} 73 P_n 128 P_i
P10	6	-H(20),-N=N-Ph-$OC_{14}H_{29}$ (80)	P_g 30 P_{fn} 110 P_n 152 P_i
P11	6	-H(40),-N=N-Ph-$OC_{14}H_{29}$ (60)	P_g 30 P_{fn}^{1} P_n 150^{2} P_i
P12	6	-H(60),-N=N-Ph-$OC_{14}H_{29}$ (40)	P_g 30 P_{fn}^{1} P_n 120^{2} P_i
P13	6	-H(80);-N=N-Ph-$OC_{14}H_{29}$ (20)	P_n 130^{2} P_i

(c: crystalline; g: glassy; s_A: smectic A; n: nematic; fn: fibrillar nematic; i: isotropic; P: polymeric)

1) detected only by x-ray investigation, 2) found only by polarization microscopy

4-Hydroxyphenyl-hexyloxybenzoate (I) was synthesized according to a procedure described by Weißflog.[3]

2-Hydroxy-5-(4-hexyloxybenzoyloxy)-4′-*n*-hexyl-azobenzene (II): 7 g (22 mmol) of **I** are dissolved in 175 ml of ethanol. After adding a diazonium salt solution consisting of 4 g (22 mmol) 4-*n*-hexylaniline, a mixture of 20 ml water and concentrated HCl (2:1) and 1.6 g (23 mmol) $NaNO_2$ the reaction solution was slightly alkalized by adding of 20 ml of an aqueous solution of Na_2CO_3 (25%). The precipitate was filtered after 24 hrs., washed with water and ethanol and dried in vacuum after recrystallization from acetic acid. Yield 45%, m.p. 81–82°C.

Using 4.4′-hexylenedioxydibenzoylchloride[1] **(III)**, **D1** was synthesized following the Einhorn procedure. The product was recrystallized from *n*-heptane/toluene (5:1), yield: 60%, phase behavior: crystalline 123°C liquid crystalline 137°C isotropic.

elementary analysis: $C_{82}H_{94}O_{12}N_4$	cal.:	C: 74.18% H: 7.14% N: 4.22%
	found:	C: 73.50% H: 7.09% N: 4.15%

^{1}H-NMR ($CDCl_3$): 8.17 ppm (H-arom, q., 8H) 7.65 ppm (H-arom, t., 6H), 7.38 (H-arom, s., 4H), 7.24 ppm (H-arom, d., 4H), 6.89 ppm (H-arom, q., 8H), 4.02 ppm ($O—\underline{CH_2}$, t., 12H), 2.59 ppm ($O—CH_2—\underline{CH_2}$, t., 12H), 1.87 ppm ($\underline{CH_2}$, m, 12H), 1.34 ppm ($\underline{CH_2}$, t, 8H), 1.26 ppm ($\underline{CH_2}—CH_3$, t., 8H), 0.85 ppm (CH_3, q., 12H)

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Characterization Methods

The phase behavior of the polyesters was investigated by means of polarizing microscopy and differential scanning calorimetry (DSC 7, Perkin-Elmer). The DSC scan rate was 10 K/min. X-ray diffraction studies were performed with Cu-K_a-radiation monochromized by a graphite monochromator crystal and a collimation using glass capillaries (diameter 0.6 mm). The detection device used was a flat film camera or a Guinier goniometer from HUBER, Rimsting, Germany. The samples used have been sealed in glass capillaries or hand drawn fibers. Optical transformation experiments have been carried out using a standard equipment.[4] The mask represented the proposed structure model.

RESULTS AND DISCUSSION

Generally, depending on temperature and the length of the lateral pendent alkyl groups three different types of X-ray patterns have been obtained:

(i) The X-ray fiber patterns of the crystalline or glassy mesophases of the polyesters **P1** and **P2** are quite normal and as known for smectic A and nematic phases, respectively.

(ii) Glassy mesophases of samples **P3–P12** yielded unusual scattering diagrams (Figure 1a). Beside the normal diffuse spots at the wide angle range cor-

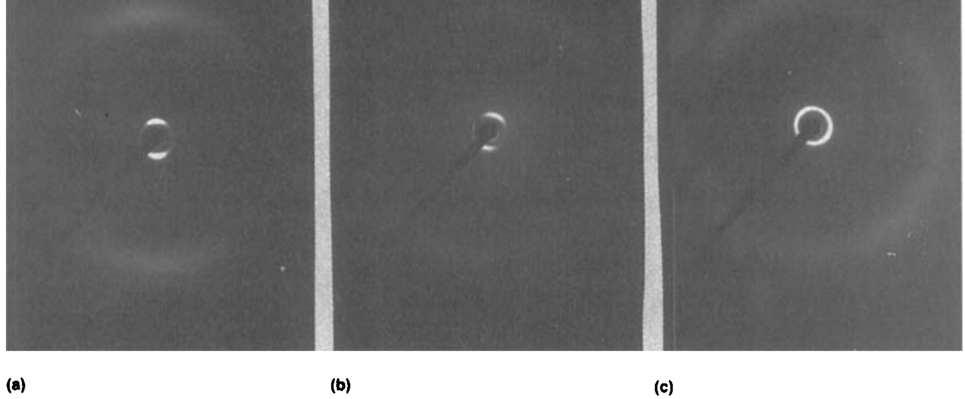

FIGURE 1 X-ray diffraction photographs of a shear oriented sample of polymer **P6**, first arrow indicates shear direction, second arrow or sign indicates direction of investigation, a) X-ray beam perpendicular to the shear direction (25°C), b) X-ray beam perpendicular to the shear direction and perpendicular to the previous experiment (25°C) and c) X-ray beam in shear direction (25°C).

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responding to the average lateral distance between the molecules (d = 4.7 ± 0.1 Å) there are additional more or less diffuse reflections also on the equator at the small angle range (d = 23–33.5 ± 1 Å) observable.

(iii) Above a transition to a high temperature mesophase, the small angle reflections of the polyesters **P3–P12** disappeared.

In contrast to the small angle reflections of smectic phases indicating a layered packing, the equatorial reflections must be attributed to two different electron densities perpendicular to the fiber axis.

To obtain more insight into details of the phase structure of **P3–P13**, further X-ray studies have been undertaken. A bidirectional flow field orientation corresponding to the method as described for the sanidic phases[5] has shown no difference between the diffraction patterns of the oriented sample **P6** in the two different lateral directions with respect to the main chain (compare Figure 1a and 1b). If the investigation direction (direction of the X-ray beam) was identical with the shear field, a diffraction pattern showing two rings has been observed (see Figure 1c).

Also diffraction pattern of the supercooled mesophase of the synthesized dimer **D1** shows the equatorial reflection as observed in the case of the polymers **P3–P12** (see Figure 2). These observation points to an uniaxial structure like a bundle of threads. Every thread should consist of a certain number of molecules. A model of the assumed fibrillar structure is shown in Figure 3.

The observed small angle reflections correspond to the mean distance between bundles of roughly parallel chains. In our model, the core of bundles is described as being formed of extended backbones of the polyesters surrounded by the lateral aliphatic chains.

The tendency to segregate chemically different parts of macromolecules forming fibrillar or bundled structures has been assumed to explain the X-ray diagrams also in other cases. Noel *et al.*[6] investigated polyesters substituted with lateral methyl groups and found also equatorial reflections in the small angle range. The origin

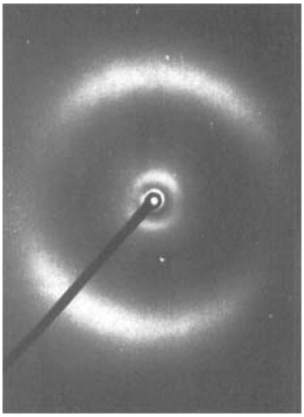

FIGURE 2 X-ray diffraction photographs, X-ray beam perpendicular to a fiber of dimer **D1** (25°C).

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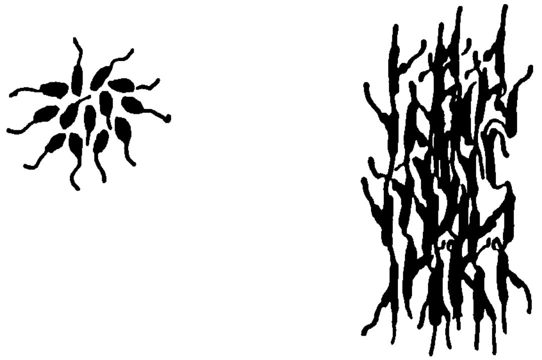

FIGURE 3 Model of the fibrillar packing in the nematic phase. a) in fibrillar direction, b) perpendicular to fibrillar direction.

has been attributed to roughly parallel bundled chains or strings of main chains.[6] Azaroff and coworkers[7] published X-ray data of copolyesters substituted with large arylsulfonyl substituents in lateral position with respect to the main chain. Modeling of possible structures led to a disturbed hexagonal packing where all side chains are arranged in the middle of the hexagonal cell. Similar investigations and interpretations using other copolyesters showing also such X-ray reflections in the small angle range have been published by Blackwell *et al.*[8] and Fischer *et al.*[9] Further, the structure of mesophases formed by poly(di-*n*-alkylsilanes) has been described as two dimensional hexagonal packing of columns consisting of straight polymer backbones surrounded by alkyl chains in a disordered conformation.[10]

Structural studies of a wholly aromatic polyamide with a rigid pendent group by scanning tunnelling microscopy enabled to conclude the existence of multimolecular strands built up by several single chains.[11]

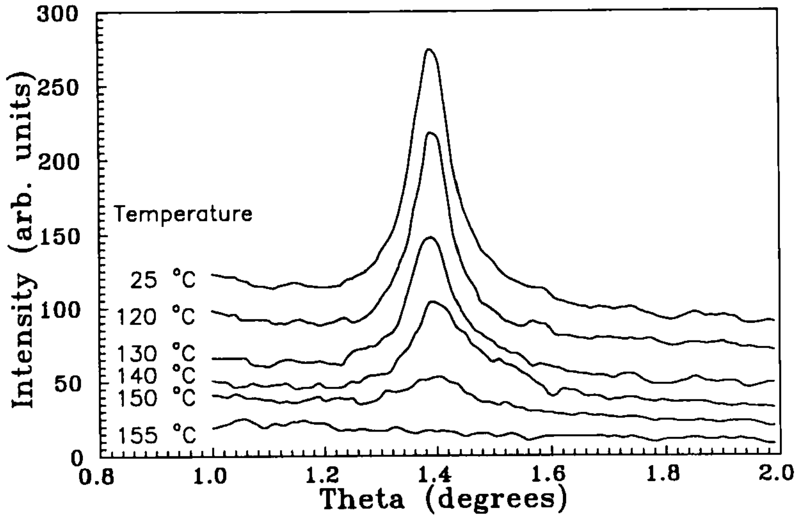

FIGURE 4 Dependence of the intensity of the small angle reflection of the polyester **P6** on the sample temperature.

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A temperature dependent measurement of the small angle reflection of the polyester **P6** points to a phase transition between the fibrillar nematic and the normal nematic phase at about 152°C (Figure 4).

The transition is also observable with DSC (Figure 5) for polyesters **P3–P9**.

Obviously, with rising temperature the enhanced flexibility of pendent groups as well as the decay of the multichain aggregates favour the formation of the classical nematic state.

Figure 6 shows the phase transition temperatures in dependence on the number

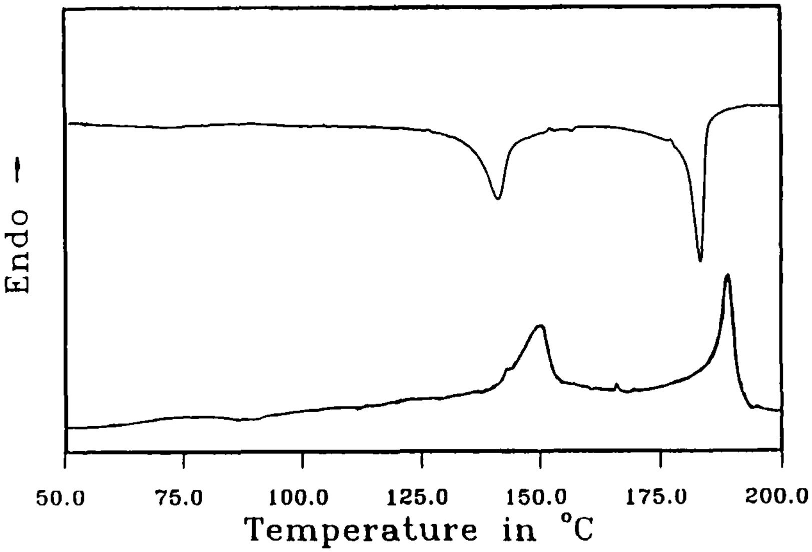

FIGURE 5 DSC scan of polyester **P6**, heating and cooling mode.

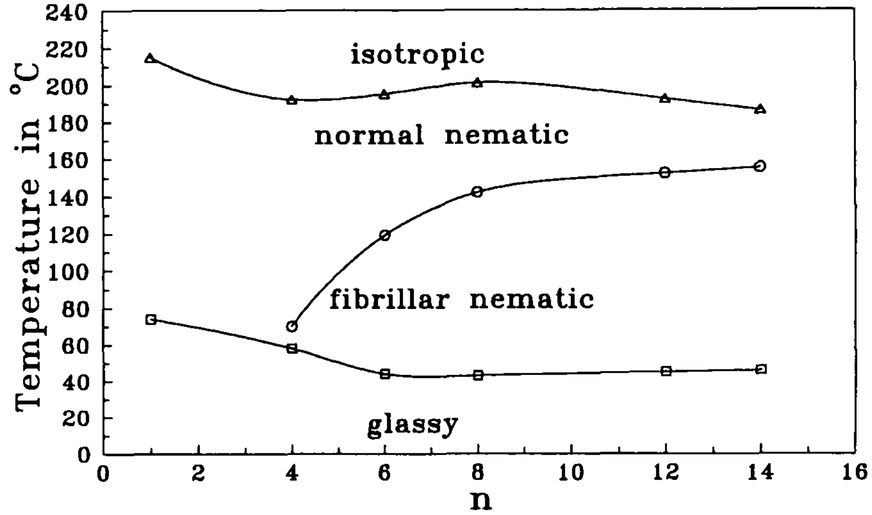

FIGURE 6 Phase behavior of the polyesters with different length of tail groups at the lateral part of mesogenic unit.

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of methylene units in the lateral group. We note that the thermal stability of the fibrillar nematic phase increases with the length of the lateral substituent.

As demonstrated for polydialkylsilanes by Weber *et al.*,[10] the squared distances between the axis of neighbouring fibrils in our polymers increased linearly with the number of methylene units in the alkyl groups (Figure 7).

Also oriented specimen of copolymers **P10–P12** show an increase of the interfibrillar distances in relation to **P7**.

Perhaps the comonomer without lateral substituent is acting like a swelling agent for the fibrils. With the copolyester **P13** a small angle reflection could not be detected. It is interesting to note that with sanidic substances a decrease in the *d-spacing* with lowering the number of lateral substituents per monomer unit has been found.[12]

Nevertheless, the question arises if the lower temperature nematic phase of our polyesters are of board-like (sanidic) structure. The lateral geometric periodicities obtained for sanidic phases are approximately the same as measured for the polyesters **P3–P7** (21–26 Å compared with 22–34 Å, see Figure 7, Table II). But it should be emphasized that our X-ray studies evidence no difference between the patterns of **P6** obtained after irradiation in two different lateral directions with respect to the orienting shear field (Figure 1a and 1b). Moreover, an investigation in shear field direction (Figure 1c) yielded two ring like diffraction pattern and no arc like as observed with sanidic polyesters and polyamides.[5] Summarizing, these

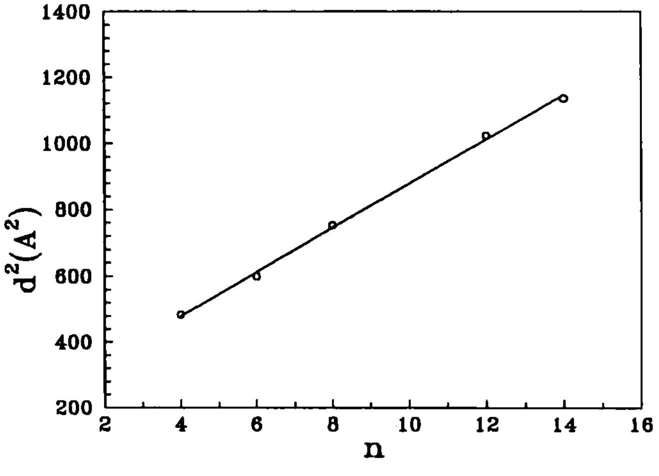

FIGURE 7 Square of the interfibrillar distances as a function of the number *n* of methylene units in the alkyl side chain at 25°C.

TABLE II

d-spacings of the inner reflections of the polymers P3–P12

Code	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
d-sp.(Å)	22.0	24.5	27.4	32.0	33.6	26.8	32.8	35.3	36.3	36.5

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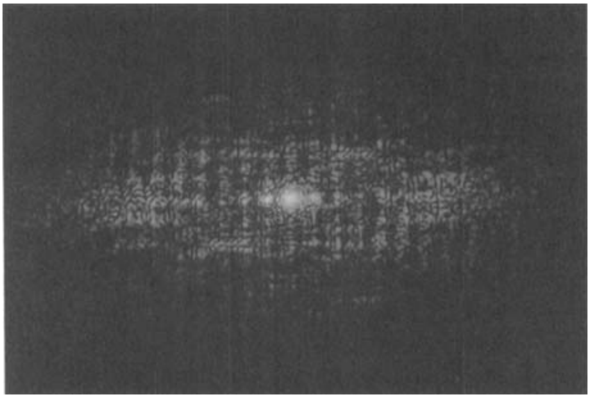

FIGURE 8 Picture of the optical transformation of a mask representing the assumed fibrillar structure.

FIGURE 9 X-ray diffraction pattern of wood, X-ray beam perpendicular to the fiber (25°C).

results illustrate the difference between the uniaxial fibrillar and the biaxial sanidic arrangement.

To support the fibrillar model some optical transformation experiments have been performed. The result shown in Figure 8 has been obtained using a mask with several bundles of lateral substituted polyester chains as sketched in Figure 3. The bundles were arranged parallel to each other. Obviously, already this simple procedure is able to simulate the small angle scattering behavior of the studied polymers.

The diffraction patterns of other natural fibrillar materials as wood or keratin do also show equatorial reflections in the small angle range.[13] For example, Figure 9 shows the x-ray pattern of wood irradiated perpendicular to the long axis. The similarity of the small angle diffraction with that of the polymers **3–7** supports additionally the postulated structural model.

Acknowledgments

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