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Liquid-crystalline polyesters with y-shaped mesogens: Phase structure pecularities

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SUMMARY

Liquid crystalline (LC) main-chain polyesters with y-shaped mesogenic elements have been investigated by X-ray diffraction. The X-ray pattern of the glassy nematic polyester with the largest branching shows besides the reflections in the wide angle range corresponding to the average distance between the molecules also equatorial reflections in the small angle range. This is suggesting a spontaneous formation of microfibrils. X-ray pattern of the polymer above 150 °C points to the existence of a "normal" nematic phase. The proposed order-disorder model is supported by results of calorimetric measurements and mixing experiments with a low-molecular-weight LC-compound.

INTRODUCTION

The variation of common structures of liquid crystalline polymers has become an extending field of interest. Macromolecules with an unusual arrangement of the mesogens with respect to the polymer backbone as well as combined LC-polymers are able to form a broad variety of mesophases. In last time we could synthesize a series of LC main-chain polymers with y-shaped mesogenic moieties (1). Structure investigations of these polyesters are of interest because the stiff side branching should lead to special steric conditions and therefore to a specific change of the mechanical properties.

Deviating from X-ray patterns of linear LC main-chain polyesters, the y-like branching of mesogenic building blocks can cause an unusual position of inner reflections (1). To explore the reason for this scattering behaviour, it should be desirable to study polyesters with different lateral units. Furthermore, because of some general uncertainties in evaluation and unique appointment of X-ray patterns of partially ordered states, it is necessary to support structural models by additional studies. Therefore, calorimetric measurements and mixing investigations using a compound related to the unbranched main-chain polymer have been done.

A proposal for a phase structure model including an order-disorder transition within the nematic state will be discussed.

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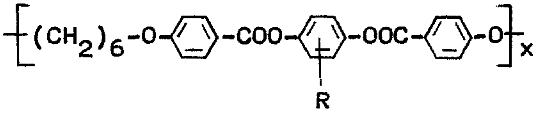
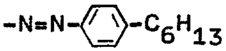
EXPERIMENTAL

Materials

The synthesis and thermal properties of the polyesters were described elsewhere (1,2). They have the following chemical structure:



No.	R	Ref.
1	H	(2)
2		(1)
3		(1)

The substance used as low-molar-mass model compound was of related structure:

4

In Table 1 the phase transition data are summarized.

Table 1: Phase transition temperatures of low and high molecular weight compounds

No.	Transition $^{a)}$ temperatures in ^{o}C						
1	P_{cr}	220	P_{s_A}	280	P_n	380	P_i
2	P_g	74	P_n	219	P_i		
3	P_g	44	P_n	183	P_i		
4	cr	124	n	212	i		

a) cr: crystalline; g: glassy; s_A: smectic A; n: nematic; i: isotropic; P: polymeric

The synthesis of compound 4 is described in (3).

Techniques

X-ray diffraction patterns were obtained using monochromatic Cu-K_α-radiation (graphite monochromator crystal) collimated by glass capillaries (diameter 0.6 mm) and a flat camera or a Guinier goniometer from Huber. The samples were prepared by drawing fibres from a nematic melt and sealing in glass capillaries. Optical texture and miscibility studies were performed with a polarizing microscope combined with a hot stage. A Perkin-Elmer DSC 1-B or DSC 7 was used for the DSC-investigations (heating and cooling rates 10 K/min). The density measurements have been carried out by means of the floating method using diluted aqueous KI solutions of known density.

RESULTS AND DISCUSSION

Throughout the X-ray patterns obtained from polyesters 1 and 2 were quite normal and as well known for smectic A and nematic phases. But the obtained X-ray pattern from a fibre of polyester 3 was somewhat unusual (Figure 1a). Besides the usual diffuse spots at the wide angle range corresponding to the average distance between adjacent chains (d = 4.7 ±0.1 Å) there are additional diffuse reflections on the equator at the small angle range (d = 24.5 ±1 Å). In contrast to this, small angle reflections of smectic phases should be observable in the same angle range but in meridional direction due to the period of electron density corresponding to the interlayer distance. In our case, there must exist two different electron density periods perpendicular to the fibre axis.

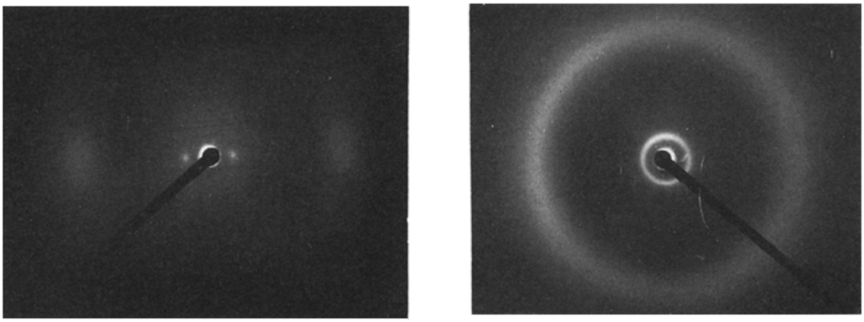

(a) (b)

Figure 1: X-ray diffraction patterns of a fibre of polyester 3 at room temperatures: (a) X-ray beam perpendicular to the fibre axis, (b) X-ray beam in fibre direction

The next diffraction experiment was carried out aligning the incident beam parallel to the fibre axis. The resulting pattern is shown in Figure 1b. Obviously, there is no indication of an asymmetric electron density profile perpendicular to the fibre axis. Noël et al. (4) have reported on such diffuse spots with oriented samples of a copolyester containing methylhydroquinone and pyrocatechol units. They discussed a helical arrangement of roughly parallel chain bundles without long-range order. A similar structure has been deduced for poly(di-n-hexylsilanes) from X-ray diffraction (5). Therefore, it should be reasonable to propose a packing of the chains of polymer 3 according to a fibrilar model (Figure 2). Because of the dominating interaction, the aromatic chain elements should be segregated in the fibre cores, whereas the pendant alkyl groups are mainly arranged in the outer parts of the bundles.

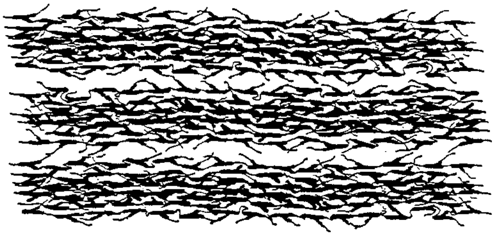


Figure 2: Model of the fibrilar packing of the chains of polymer 3

It is quite probable that this segregation depends on the temperature. Indeed, goniometer measurements do not show the small angle reflexes at 150 °C (Figure 3). Obviously, the thermal energy caused a splitting of the bundles at higher temperatures.

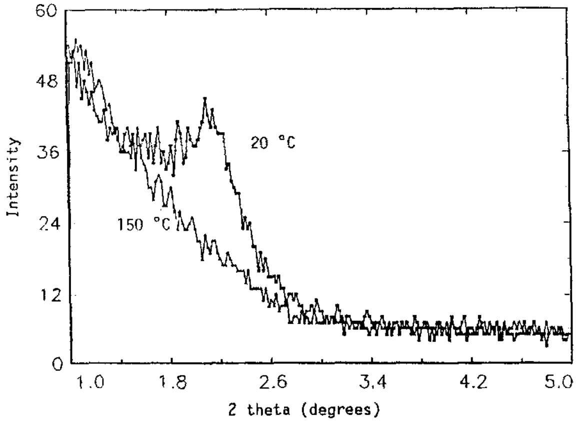
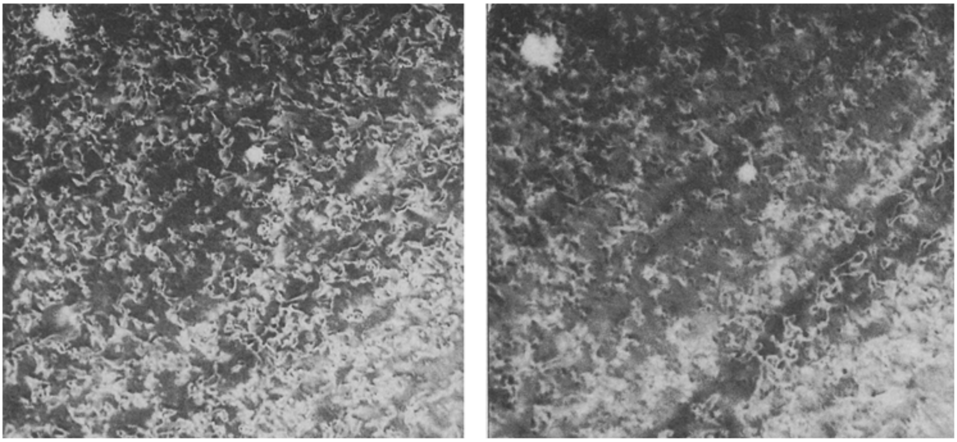


Figure 3: Guinier goniometer curves of the small angle diffraction of a fibre of polymer 3 at 20 °C and 150 °C

There are further indications for the existence of different phase structures at low and elevated temperatures.



a)

b)

Figure 4: Optical polarized micrographs of the textures displayed by polyester 3 at a) 155 °C and b) 100 °C

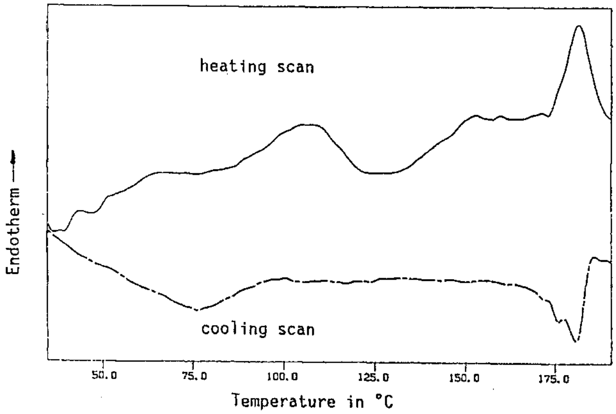


Figure 5: DSC thermograms of the polymer 3 (second cycle)

The microscopical observation shows a texture change upon cooling from the high to the low temperature nematic state (Figure 4). DSC measurements provided indications for a transition within the nematic phase range at about 105 °C in the heating mode and at about 75 °C in the cooling mode (Figure 5). Furthermore, a comparison of the isotropization enthalpies (Table 1) shows that the values for the lateral substituted polymers 2 and 3 are smaller than for the unbranched polymer 1. That can be due to the reduced interaction between the branched aromatic ester triads.

Table 1: Isotropization enthalpies (DSC 7)

Sample	ΔH (kJ/mol)
1	4.2 ±0.5
2	2.9 ±0.5
3	2.3 ±0.5

Figure 6 shows the result of miscibility studies in the binary system 3-4. The low-molecular weight compound 4 and the polyester 3 form nematic mixtures in the entire concentration range. In order to explore the influence of the low-molar-mass material on the fibrilar ordered polymer, X-ray studies of the mixture with a content of 70 mol-% polyester were carried out. The obtained pattern did not show any reflection at small angles. That means that the chain bundles have been dissolved in the nematic mixture.

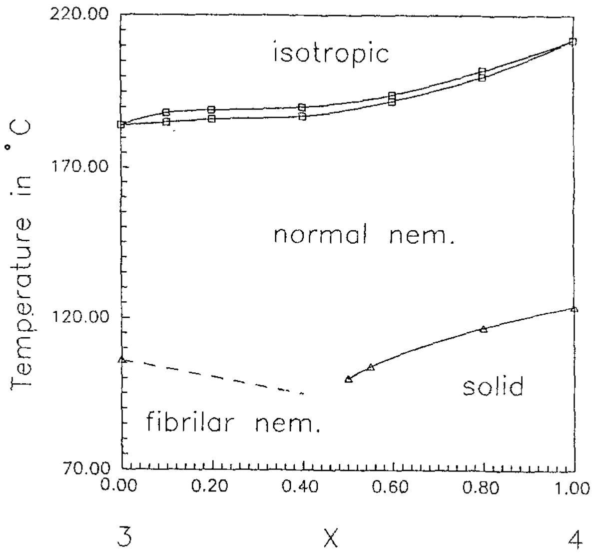


Figure 6: Phase diagram for binary mixtures of polyester 3 with low-molar-mass compound 4

The less efficient space filling of the y-branched polyesters in relation to the corresponding unsubstituted material 1 should be responsible for reduced densities especially in case of polyester 3. Our data together with densities of some conventional polymers (6) for comparison are listed in Table 2.

Table 2: Densities of the polyesters 1-3 and of some commercial polymers (6) at 22 °C

Sample	Density (g/cm^3)	Sample	Density (g/cm^3)
1	1.201	PETP	1.335
2	1.179	LDPE	0.925
3	1.060	PE (amorph)	0.855

The results presented in this paper suggest that LC-polymers of a branched segment architecture can exist in a low temperature fibrilar and a high temperature normal nematic phase. The fibrilar ordered phase is characterized by a dense packing of backbones surrounded by the lateral groups consisting of an aromatic core and a terminal hexyl chain. The interfibrilar space is filled by these side groups.

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