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Macroscopic Ordering of Liquid-Crystalline Polymers with Discotic Mesogens

B. Hüser, T. Pakula, and H. W. Spiess*

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, West Germany.

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ABSTRACT: The morphology of liquid-crystalline polymers containing disklike mesogenic groups has been studied by X-ray diffraction. Two polymers were investigated: a polymer containing disklike groups in the main chain (MCP) and a polymer with disklike groups attached to a polymer chain via a flexible spacer (SGP). The macroscopic alignment of the columnar structures, obtained by cold drawing of films or by drawing of fibers from the melt, is demonstrated for both polymers and compared with the order generated by an external magnetic field. The dependence of the nature of alignment on the polymer structure is established.

Introduction

The structure of liquid-crystalline phases formed by disk-shaped molecules has been intensively studied during the last few years. In most cases, columnar ordering has been observed in which the disklike molecules are stacked into columns with long-range intercolumnar positional order constituting various two-dimensional lattices.[1] Such structures were initially found in pure systems of disklike molecules.[2,3] Recently, however, they have also been observed in polymers containing the disk-shaped mesogens incorporated periodically into a polymer chain.[4-6] The polymer chain offers additional possibilities to exploit the tendency of self-organization of the discotic mesogens in order to generate highly oriented macroscopic structures. This order is frozen in the glassy state and results in highly anisotropic optical, mechanical, and electrical properties. In this paper, we report on X-ray studies of the mesophase structures formed in two polymers: (1) containing disklike groups in the main chain and (2) with disklike groups attached to a polymer chain via a flexible spacer. The synthesis of these compounds is described elsewhere.[4,5,7]

In order to extract information from X-ray diffraction patterns, oriented samples have to be prepared. In the case of low molecular weight discotic compounds, several alignment techniques have been used including rotating magnetic fields,[8,9] various surface treatments,[10,11] and strand suspension.[12] Orientation in polymeric samples has been obtained by stretching of films above the glass transition of the polymer.[13] Applying magnetic fields results in a comparatively high degree of alignment in the low molecular weight systems.[9] This technique, however, is less effective for polymers because of their high viscosity.[7,14]

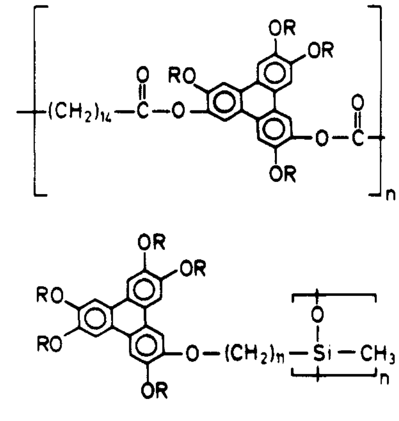
Here we report results for samples oriented by two techniques: drawing of fibers from the melt and cold drawing of films. Special attention is paid to the questions to what extent is the order increased by annealing and does the orientation process order primarily the discotic domains or the polymer chain. Results for the polymers are compared with the structure of dimer samples for which the alignment was obtained in a magnetic field.

Experimental Section

The chemical structures, the phase behavior, and the molecular weight of the dimer and the two polymers studied are shown in Table I. All compounds contain triphenylene derivatives as the magnetic group. Depending on whether the groups are incorporated into the main chain or laterally fixed to a polymer backbone, the samples are assigned as main-chain polymer (MCP) or side-group polymer (SGP), respectively.

Drawing of Fibers. The fibers were drawn from the melt surface into air at room temperature at a rate of about 1 m/s. Approximately 1-m-long fibers of thickness of several micrometers could be obtained.

Table I
Molecular Structure, Phase Transitions, and Weight-Average Molecular Weights ($\bar{M}_w$) of the Systems Studied



$R = CH_2-CH_2-CH_2-CH_2-CH_3$

system	R	*n*	$\bar{M}_w$, g mol^{-1}	phase transitions, K[a]
dimer	C_5H_{11}	0	1600	d 420 i
MCP	$COCH_3$	59	51000	g 330, d 416 i
SCP		50	45000	g 238 [d 318],[b] d 348 i

[a] g, glassy; d, discotic; i, isotropic. [b] Found only in the first heating run.

Drawing of Films. Thin films of both polymers can be easily obtained from molten layers, but they cannot be drawn to high extensions at room temperature because of their low tensile strength. Therefore, laminates of such films and thin polycarbonate films have been used which can easily be drawn to the natural ratio of polycarbonate ($\lambda = 2$). Drawing rates of 50 mm/min were used. Drawn films had a thickness of about 100 μm.

Magnetic Alignment. Samples were melted in a glass capillary and slowly cooled in a static magnetic field of strength 7 T.[14]

X-ray Diffraction. Patterns were recorded photographically by means of a Polaroid flat camera. Bundles of fibers were studied with the fiber axes aligned vertically, perpendicular to the incident beam. The diffraction patterns of the films were recorded at two positions: with the film surface perpendicular and parallel to the primary beam, respectively. In order to resolve wide-angle and small-angle reflections, diffractograms were recorded at two different sample-to-film distances (l_1 = 50 mm and l_2 = 120 mm). Wide-angle and low-angle diffractograms are shown in all figures of this paper as upper and lower pictures, respectively (two vertical line shadows appearing in some patterns are an artifact of the camera and do not influence the essential information contained in the diffractograms).

Results and Discussion

All diffraction patterns obtained can be characterized by three reflections related to different correlation periods

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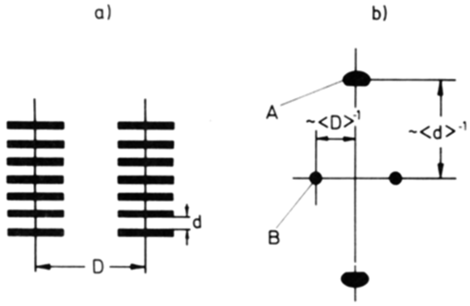

Figure 1. Schematic illustration of the relation between the structure (a) and the diffraction pattern (b) for a perfectly aligned columnar arrangement of disks.

Table II
Intracolumnar (*d*) and Intercolumnar (*D*) Distances

	system			
	(hexapentyloxy)-triphenylene[15]	dimer	MCP	SGP
d, nm	0.36	0.34	0.35	0.34
D, nm	1.88	2.05	2.04	1.85

in the structure. Our assignment to particular periods in our samples follows the proposals of Levelut,[15] cf. Figure 1, illustrating schematically the relation between the structure and the diffraction pattern for a perfectly aligned columnar arrangement of disks. The wide-angle diffraction, A, indicating periodicity of typically 0.35 nm is attributed to the periodic arrangement of the triphenylene cores within the columns, *d*. The diffuse halo observed at slightly smaller scattering angles is related to a liquidlike structure of the intercolumnar matrix consisting of the aliphatic chains of spacers and the aliphatic side chains of the mesogenic units (R groups in Table I). The maximum intensity in this halo corresponds to a spacing of about 0.42 nm. The small-angle reflections, B, are attributed to the arrangement of columns in lateral directions with respect to their axes and in this way reflect the most probable distance, *D*, between them. The assignments introduced here, A and B for wide-angle and small-angle reflections and *D* and *d* for intercolumnar and intracolumnar distances, respectively, will be used throughout this paper.

Dimer. Diffraction patterns for two dimer samples prepared in various ways are shown in Figure 2. The above-described reflections are observed for both a quenched sample and a sample aligned in a magnetic field. This indicates that the columnar structure is formed in both cases. Intracolumnar (*d*) and intercolumnar (*D*) distances determined for these samples are given in Table II. The intramolecular distances are not influenced by the differences in sample preparation and are very similar to values reported for (hexapentyloxy)triphenylene.[15] However, a slight increase is observed in intercolumnar distances, which indicates that the spacers, although only slightly longer than two aliphatic side chains, can influence the density of column packing in the dimer sample.[13] In spite of the identical parameters of local packing in the two dimer samples, considerable difference is observed in their macroscopic order. Whereas the quenched sample is macroscopically isotropic, the sample cooled in a magnetic field shows considerable macroscopic alignment of the columns in the direction perpendicular to the magnetic field. From diffractograms reported here, we cannot uniquely determine the type of intercolumnar order: however, the coincidence of intercolumnar distances observed for dimers with those of monomers suggests that hexagonally ordered domains are formed in the dimers as well. This means that domains randomly oriented in the quenched sample are partially ordered in the sample cooled in the magnetic field. Here the directors of the domains are oriented perpendicular to the direction of the magnetic field. The distribution of column axes, as studied by ^{2}H NMR,[14] is centered around a direction of 90° to the magnetic field and has a full width at half height of 27°, corresponding of an order parameter of 87%.

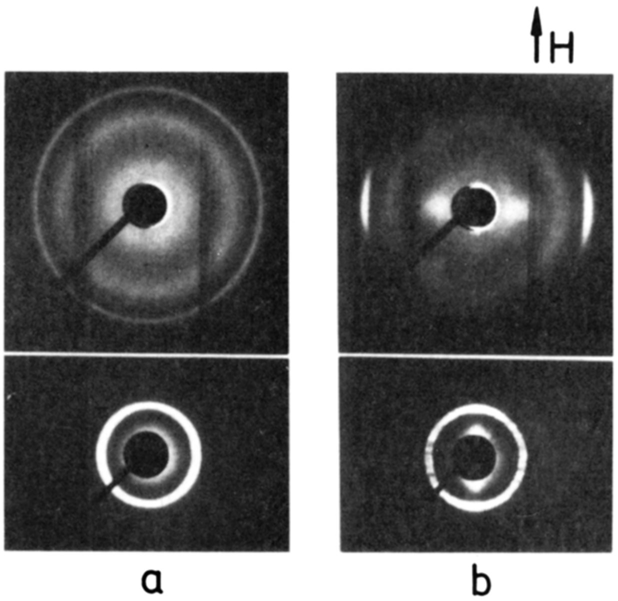

Figure 2. Diffraction patterns for dimer samples: (a) quenched sample and (b) sample aligned in a magnetic field (H).

Main-Chain Polymer. The main-chain polymer, because of its relatively high glass temperature, can easily be obtained in a nonordered form when quenched from the melt in ice–water. The diffractograms from such a sample (Figure 3a) do not show wide-angle reflections of type A; diffuse small-angle reflections, however, are observed. The latter even show up in diffractograms of the melt (460 K). Thus, we conclude that the quenched sample does not contain well-developed columnar structures. The diffuse small-angle reflections could then be attributed to correlations between the discotic units along a given polymer chain rather than to intercolumnar spacings. If such quenched films are cold drawn, chain orientation in the drawing direction takes place which manifests itself in a high optical anisotropy of the samples. If the ordering procedure primarily orders the polymer chain, it can generate correlations of disks along the drawing direction. This is in fact observed in the diffraction patterns as an increase of the low-angle diffraction intensity in the direction of drawing as demonstrated by the diffractogram in Figure 3b, which was recorded for a film drawn at room temperature. The wide-angle reflections (A), related to intracolumnar correlations, are absent in this diffractogram, and only the diffuse amorphous halo from aliphatic chains is observed with the maximum intensity in equatorial directions. This also shows that the drawing results in chain orientation. Similarly for fibers drawn from the melt, high optical anisotropy indicating chain orientation has been determined, but no order of discotic columns has been observed as the diffraction patterns in Figure 3e indicate. This means that fibers drawn from the melt into air at room temperature are quenched in their macroscopically oriented but not columnar ordered state. The structure of such films and fibers changes drastically when they are annelated at a temperature just below the isotropic phase transition. The diffractograms shown in

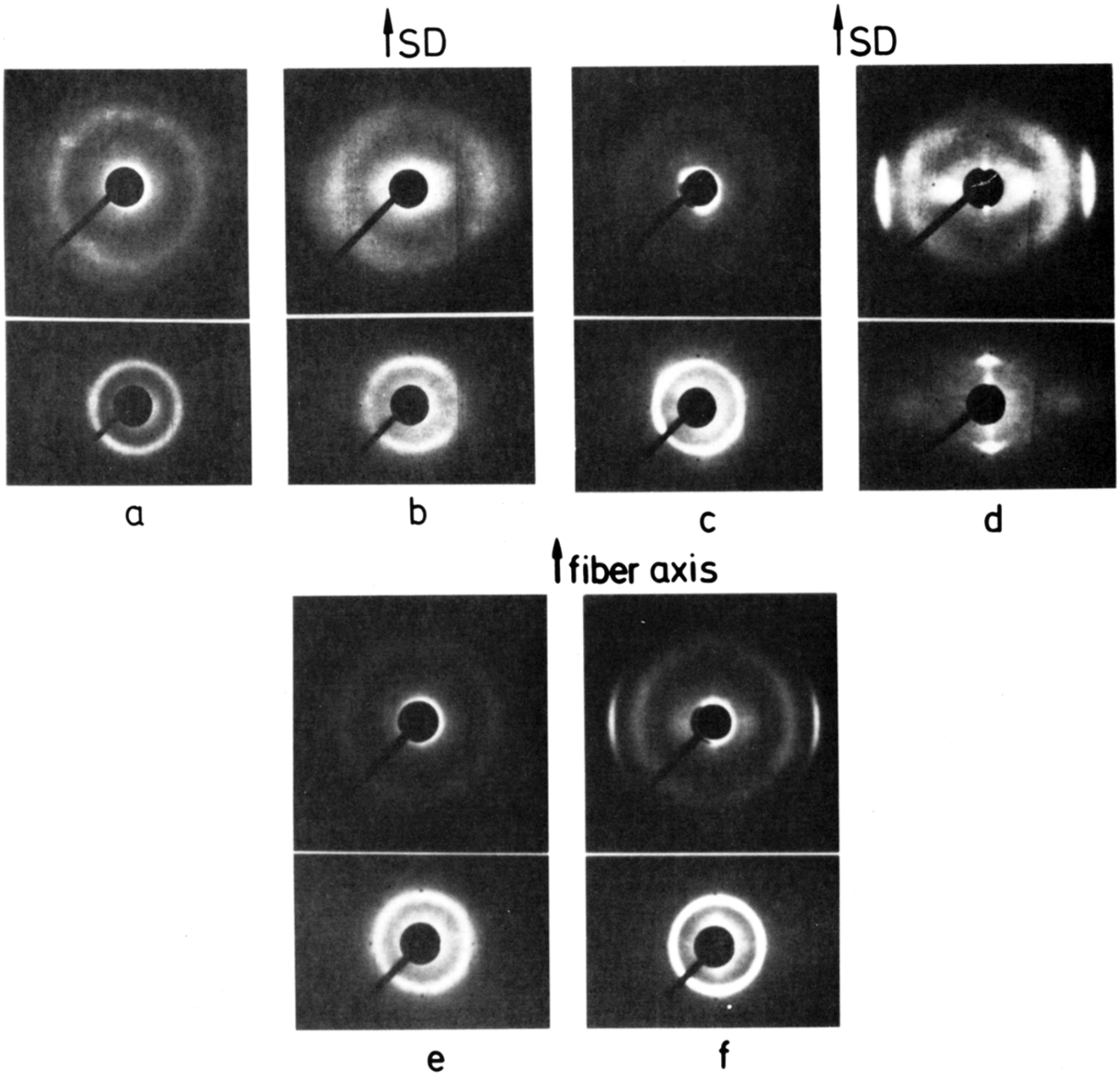

Figure 3. Diffraction patterns for MCP samples. Film: Quenched from the melt (a); quenched and subsequently cold drawn (b); oriented and annealed measured with the incident beam perpendicular (c); parallel (d) to the film surface (SD = stretching direction). Fiber: Drawn from the melt (e) and annealed (f).

Figure 3c,d,f were recorded for samples which were annealed at 408 K at constant length for half an hour. After such a thermal treatment, the films and fibers become highly ordered. In films we observe the hexagonally ordered columnar structure identical with that observed by Wendorff et al.[13] The mesogenic groups lie parallel to the film surface and form columns which are ordered in a two-dimensional hexagonal array with the directors perpendicular to the film surface. Such structural organization is deduced from patterns shown in Figure 3c,d recorded with the incident X-ray beam perpendicular to the film surface and to the film edge, respectively. With the beam perpendicular to the film surface, the small-angle diffraction (reflections B) displays hexagonal symmetry. This is somewhat difficult to recognize in the X-ray photograph reproduced in Figure 3c but has meanwhile been confirmed by use of a two-dimensional position-sensitive detector. The same sample but with the beam perpendicular to the film edge gives only zero layer reflections (Figure 3d). The wide-angle reflections (A) are observed only with the beam perpendicular to the sample edge and in equatorial positions, indicating orientation of the mesogenic units parallel to the film surface. The structure of fibers cannot be resolved in such detail because diffraction patterns in this case are recorded for bundles of fibers and artificial rotational disorder is introduced in this way. Films and fibers have the same intracolumnar and intercolumnar distances, however, which are also consistent with those of dimers.

Side-Group Polymer. The glass transition of the side-group polymer is about 240 K, and therefore this polymer cannot be obtained in a quenched state at room temperature. In this case, both cold drawing and fiber drawing from the melt lead to similar states in which discotic units are organized into columns highly oriented along the drawing direction or along the fiber axis, respectively. Diffraction patterns like that shown in Figure 4 are observed for both fibers and films in two directions. This pattern is very close to the schematic one shown in Figure 1. Thus, drawing in this case macroscopically aligns the column axes along a single direction as shown schematically in Figure 5b. This is in contrast to the drawn

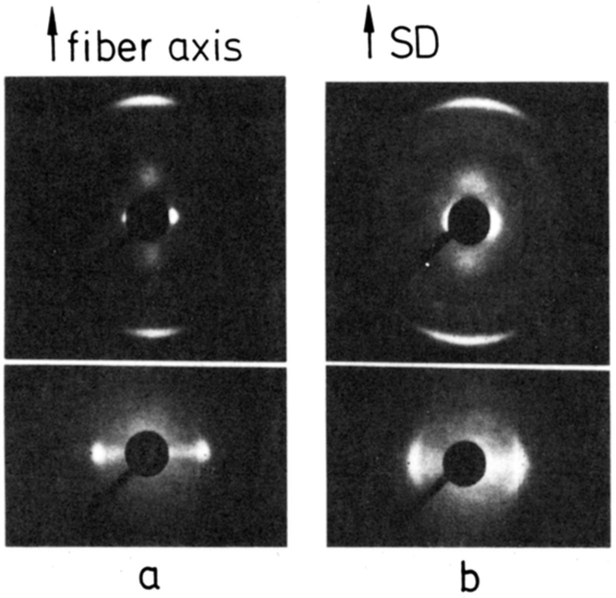

Figure 4. Diffraction patterns for SGP fiber (a) and stretched film (b) (SD = stretching direction).

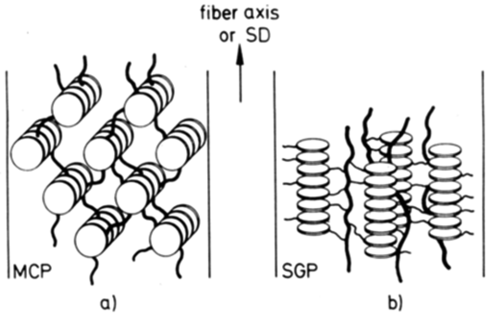

Figure 5. Schematic representation of structures obtained in fibers or stretched films (SD = stretching direction) of MCP (a) and SGP (b).

main-chain polymer, where the column axes are perpendicular to the chain orientation direction, c.f., Figure 5a. It should be noted that the orientation of columns obtained for the side-chain polymer is almost perfect, and one can suppose that continuous columns are formed along large distances.

Conclusions

The results presented here demonstrate that in polymers containing disklike mesogenic groups either in the main chain or as side groups attached to a polymer backbone a well-developed columnar structure can be formed which is analogous to that found for the corresponding low molecular weight compounds. Almost perfect macroscopic alignment of these structures can be achieved by proper mechanical and thermal treatment. Cold drawing of films and drawing of fibers primarily generate polymer chain orientation which is probably a necessary step initiating the self-organization of the disklike mesogenic groups to macroscopically aligned columnar structures. The direction of column alignment with respect to the chain direction depends on the chemical structure of the polymer. In the main-chain polymer, the columns are oriented perpendicular to the chain direction, while in the side-group polymer they are parallel to the axes of the oriented chains. Both systems are interesting objects for further investigations. Work is in progress to determine their mechanical properties and electrical conductivity, which has already been reported for the corresponding low molecular weight compounds.[16]

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Registry No. ((Hexaacetoxy)triphenylene)(hexadecanedioic acid) (copolymer), 118018-23-8.

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