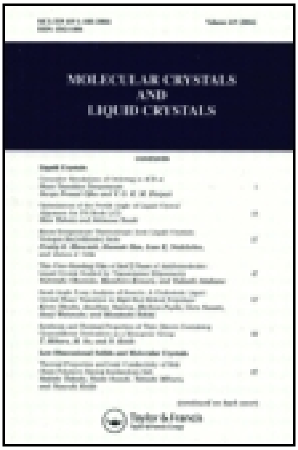

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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CRYSTAL AND PSEUDO-CRYSTAL PHASES IN MAIN CHAIN MESOGENIC HOMO- AND COPOLYMERS WITH FLEXIBLE SPACERS

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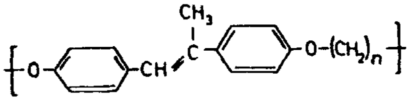
Abstract Some packing principles of polymers containing rigid and flexible segments are presented, as revealed by X-ray diffraction of crystal phases. Two types of conformationally disordered crystal states are recognized: (a) with "layered" disorder (quasi-2-dimensional) and (b) with "occluded" disorder (3-dimensional). In both cases the flexible spacer is non-crystalline, which is ascribed to the mismatch in cross-sectional areas of the spacer and the mesogen. The relative ease of crystallization of random copolymers containing spacers of varying length is attributed to their miscibility in the disordered layers.

INTRODUCTION

While the nature of long range order in crystal phases of mesogenic compounds can provide clues about molecular short range ordering in the mesophases, studying crystalline phases may be of considerable interest in its own right. It is felt that neither the conformational disorder associated with the flexible parts of the molecule, nor the question of the true dimensionality of such crystals, have received adequate attention. In this paper we report on some novel features of molecular arrangement and disorder in crystals of main chain mesogenic polyethers with flexible alkylene spacers.

EXPERIMENTAL

Polyethers of α,ω-dibromoalkanes and 4,4'-dihydroxy- α -methylstilbene, with the structural formula:



were prepared by V. Percec and T.D. Shaffer of Case Western Reserve University. The polymers (polyhydroxymethylstilbenes) are denoted PHMS-n, where n is the number of CH groups in the alkylene spacers. Homopolymers with n=5, 7, 9 and 11 were studied, as well as a random copolymer containing spacers 5 and 7 in 1:1 molar ratio (denoted PHMS-5/7). All polymers, except for some very low molecular weight ones, display the nematic phase above the crystal melting point [1,2].

Fibres for X-ray diffraction were prepared by, first, extruding the nematic melt and quenching it as a moderately well oriented glass at room temperature. This was then followed by drawing somewhat above the glass transition temperature (T_g), which is in the range 10 - 30°C, to obtain a well oriented stress crystallized sample.

X-ray diffraction patterns were recorded in vacuo with a high-temperature flat plate camera.

Experimental [3,4] and calculated [5] values for bond parameters of compounds closely related to the PHMS polymers were employed for molecular modelling.

RESULTS AND DISCUSSION

Models of two lowest energy extended conformations of the isolated PHMS-5 molecule (three monomer units) are shown in Figure 1. The two-monomer repeat distances for the most extended conformation of PHMS homopolymers, assuming an all-trans spacer conformation, are listed in Table 1 (second column).

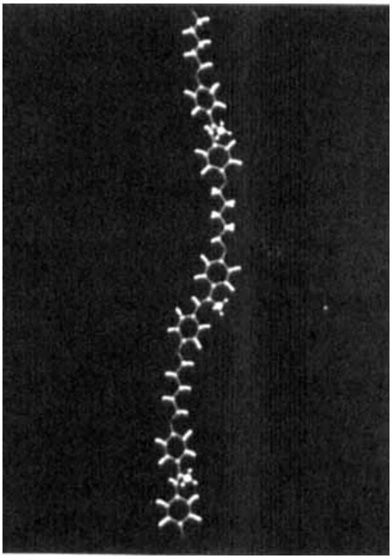
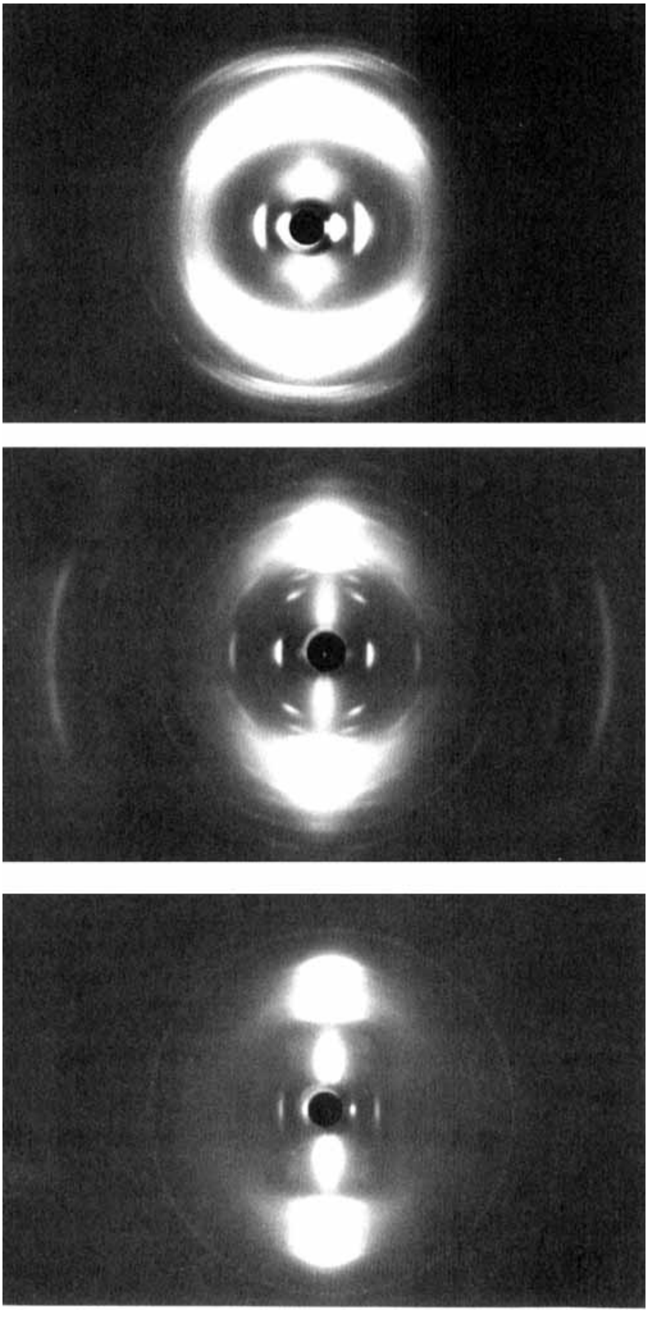


FIGURE 1. *Extended conformation* of the isolated PHMS-5 chain

A number of polymorphic forms are observed below the melting temperature of all homopolymers. Fig. 2 shows a typical sequence of X-ray fibre patterns with increasing temperature for the homopolymer PHMS-7. The polymorphic transitions are irreversible, i.e. Forms III and II do not convert into Forms II and I, respectively, upon cooling. The behaviour of PHMS-5 is essentially the same. In PHMS-9 Forms I and II are not observed and Form III appears to be stable at all temperatures below the melting point. The polymer with the longest spacer, PHMS-11, displays an altogether different phase behaviour, all modifications having layer normals highly inclined to the fibre axis. Metastable tilted forms are also observed with PHMS-9. Only one crystal form (Form III) was ever observed with the copolymer PHMS-5/7.



a) Form I

b) Form II

c) Form III

FIGURE 2. X-ray diffraction patterns of the three crystal forms of PHMS - 7 (fibre axis vertical)

TABLE 1. 2-Monomer repeat distance and density of the Layered form III

Spacer length (C-atoms)	5	7	9
calc. extended conformation (nm)	3.79	4.30	4.81
observed (nm)	3.78	3.78	4.20
contraction w.r. extd. conform. (nm)	0.01	0.52	0.61
spacer conformation (extended, contracted)	extd.	contr.	contr.
overal unit cell density (g/cm^3) increases by spacer contraction from:	(1.07)	1.03	1.01
to:	(1.07)	1.17	1.16

In the case of PHMS-5 and PHMS-7 the nematic glass first crystallizes into Form I whose diffraction pattern is characterised by comparatively broad and scarce equatorial and off-equatorial hkl reflections and horizontally streaked meridional reflections which are sharp in the meridional direction. This structure will not be discussed here further, except for noting the close resemblance of the diffraction pattern to that of Form II into which it transforms on heating. It is believed that Form I is unstable but is favoured by crystallization kinetics. The periodicity of meridional reflections corresponds approximately to the length of one monomer unit.

FORM II - "INTERMESHED"

Form II appears through an exothermic solid state transformation of Form I at approx. 100°C in both PHMS-5 and PHMS-7. It is distinguished by a large number of sharp hkl reflections extending to large angles, both equatorially and meridionally. Unlike in Form I, layer lines are not well defined (cf. Fig. 2). This indicates that the fibre axis does not coincide with any of the principal axes of the real lattice. The characteristic texture of Form II is impaired by the particular mechanism of the Form I - Form II transition.

The most conspicuous feature of the diffraction pattern of Form II, when compared with Forms I and III, is the absence of odd-numbered meridional reflections. The periodicity of meridional reflections in Form II is $1/c^* = 1.04$ nm and is identical for both polymers where it is observed, i.e. PHMS-5 and PHMS-7. It corresponds closely to half the calculated extended monomer length for PHMS-5 with the alkylene group in the all-trans conformation.

The molecular packing in Form II, consistent with the halving of the fibre period, is schematically presented in Fig. 3a. The principal feature is the "intermeshing" of mesogen and spacer moieties. The fact that the fibre periodicity is independent of spacer length (1.04 nm in both PHMS-5 and PHMS-7) suggests that the structure is essentially determined by the intermolecular contact between mesogen units, while the spacers only fill the voids between them. In order to account for the observed fibre repeat distance it must be assumed that the spacer in PHMS-5 is nearly fully extended to span the gap between two consecutive mesogens. On the contrary, in PHMS-7 the spacers appears to adopt a contracted form, most likely involving dynamic conformational disorder.

In PHMS-9 Form II is not observed, suggesting that the $-(CH_2)_9-$ spacer is too large to fit into the interstices between the mesogens.

FORM III - "LAYERED"

Around 130°C the "Intermeshed" form in PHMS-5 and PHMS-7 undergoes an endothermic transition into Form III (see Fig. 2). This modification is also found in PHMS-9 and the copolymer PHMS-5/7, in both cases apparently being the only stable crystal form. Its unit cell is orthorhombic, with the lateral dimensions a = 0.761±0.002 nm and b = 0.637±0.005 nm. The fibre periodicities c are listed in Table 1 (3rd column). The space group was determined as Pnam. There are four monomer units in the cell, situated on two nonequivalent polymer chains.

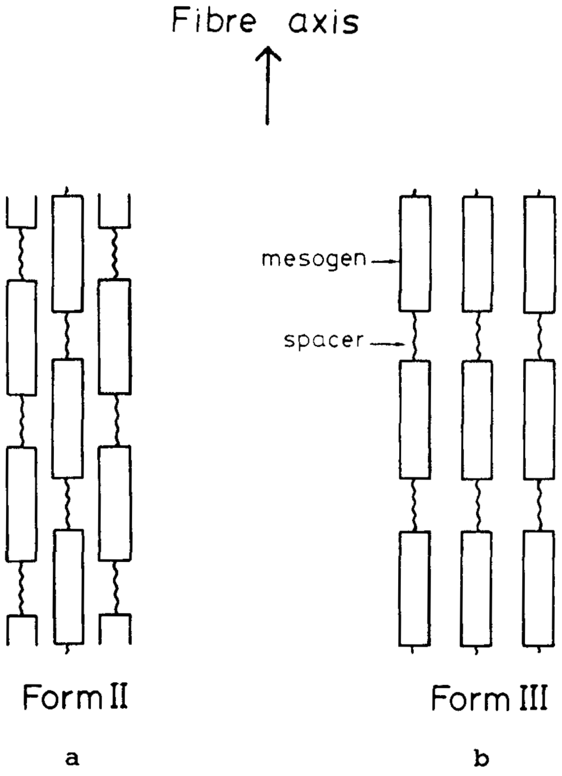


FIGURE 3. Mesogen - spacer packing in (a) Form II (Intermeshed) and (b) Form III (Layered)

The essential packing arrangement in Form III is schematically shown in Fig. 3b. The mesogens and the spacers are located in alternating layers which are normal to the chain axis.

It is interesting that the copolymer PHMS-5/7, which contains equal amounts of randomly distributed $-(CH_2)_5-$ and $-(CH_2)_7-$ spacers, is capable of crystallizing in Form III to a considerable extent (up to ca. 40% crystallinity). Since both spacer types cannot be accommodated in the ordered extended conformation at the same time, at least the longer spacer $-(CH_2)_7-$ must adopt a non-planar contracted form. This implies that the spacer layers are by themselves not crystalline, but rather conformationally disordered. Nevertheless, they are constituents of what would normally be considered a crystalline structure. Note that the diffraction pattern of Form III (Fig. 2) contains a number of hkl reflections (up to l=7), in addition to hk0 and 00l ones. Otherwise, the sharp and numerous hk0 reflections indicate good lateral crystalline order due to the high regularity within the mesogen layers.

As it is isomorphous with the copolymer PHMS-5/7 crystals, the "Layered" form (Form III) in homopolymers must also contain non-crystalline spacer layers.

Note that the alternating ordered-disordered layers in Form III make up an equilibrium structure. The fact that even in the homopolymers the spacer layers are non-crystalline is thought to be due to the large cross-sectional area of the mesogen compared to that of the spacer, which precludes close packing of the spacers. The measured cross-sectional area per chain in Form III is 0.242 nm^2, which results from mesogen packing. This value is considerably higher than the area in close packed alkane crystals or even in the more disordered alkane mesophases, the corresponding values being as follows [6,7]:

- ordered orthorhombic or triclinic crystal (paraffins and polyethylene): 0.186 nm^2
- "rotator" phase in n-paraffins: 0.19-0.205 nm^2
- hexagonal phase in polyethylene (1 bar): 0.21-0.225 nm^2

All these cross-sections are less than that of the mesogen in PHMS. Thus alkane spacers on adjacent

PHMS chains are held too far apart and cannot crystallize.

SPACER CONFORMATION IN FORM III

An indication of spacer conformation in the "Layered" form is obtained by comparing the measured 2-monomer repeat distance (cell parameter c) with that calculated for the extended chain (see Table 1). As seen from the Table, while the $-(CH_2)_5-$ spacer in PHMS-5 is practically fully extended, the measured c-parameter for PHMS-7 and PHMS-9 is significantly shorter than the values calculated for extended spacer. It follows that the spacer in PHMS-7 and PHMS-9 is contracted.

A possible explanation for the different conformation of spacers of different length may be sought in the optimal balance between the following three tendencies: (i) that for high density of the spacer layer, (ii) that for low intramolecular (conformational) energy and (iii) that for high conformational entropy. The first two tendencies could be satisfied simultaneously only if the spacers were allowed to crystallize, as in n-alkanes. Short of this, comparatively high density (point i) can only be achieved by abandoning the all-trans extended conformation and thereby increasing the effective spacer cross-section to match that of the mesogen. Such disordering of the spacer would also lead to favourable increase in entropy (point iii). Simple calculation shows that the density of the alkylene layer in Form III is only 0.77 g/cm^3 if the spacers are extended, as in PHMS-5. This is even less than the density of liquid n-alkanes (0.86 g/cm^3). However, in order that density be increased and the intermolecular energy lowered, unfavourable conformations must be introduced which raise the intramolecular energy (point ii above).

As seen in Table 1, the polymers with longer spacers PHMS-7 and PHMS-9 opt for higher density and entropy at the expense of increased conformational energy; the reverse is true when the spacer is shorter (PHMS-5). Such trend can be rationalized qualitatively on the account of both density and entropy effects:

(a) The introduction of conformational defects is not compensated for by the concomitant, rather small, overall increase in density when the spacer is short - note that the overall unit cell density in PHMS-5 is not too low (1.07 g/cm^3) even when the spacer is extended (Table 1, 6th column). Thus the spacer in PHMS-5 remains extended. On the other hand, extended spacers in PHMS-7 and PHMS-9 would lead to a too low overall density (1.03 and 1.01 g/cm^3, respectively). Thus the spacers in PHMS-7 and PHMS-9 contract, the overall density increasing to 1.16-1.17 g/cm^3 as the result.

(b) Introduction of a defect into a long alkylene spacer increases the entropy as the defect can be located at different sites. However, if the spacer is short as in PHMS-5 this positional freedom is limited and the favourable effect of increased entropy is small.

The above concept of spacer conformation in Form III is summarized in Table 2.

TABLE 2.
Two options for minimizing spacer free energy realized in the Layered structures of PHMS

Spacer length (C-atoms)	SPACER EXTENDED + low intramolecular (conformational) energy	SPACER CONTRACTED + high density + high conform. entropy
5	o	
7		o
9		o
copol. 5/7		o

DIMENSIONALITY OF FORMS II AND III

The crystal in the "Intermeshed" form (Form II) has high long range order in all three dimensions, which is manifested in the appearance of sharp X-ray reflections with high values of all three Miller indices. The existence of high translational order, in spite of the inclusion of conformationally disordered spacers (cf. PHMS-7) is attributed to the existence of direct contact between rigid mesogen units bearing the three-dimensional structure.

A different situation can be expected in the "Layered" form (Form III), where the interaction between mesogen layers, i.e. along the fibre direction, is solely via the conformationally disordered spacers. The coupling force between the layers is therefore partially entropic and the minimum in the inter-mesogen potential in the chain direction is broad compared to that in Form II. This should lead to comparatively large fluctuations in the c repeat distance in the "Layered" form. The X-ray pattern of this form indeed reveals much fewer layer lines than that of Form II (Fig. 2). This is true in spite of the fact that Form III crystals are obtained and annealed at a higher temperature than Form II ones and, everything else being equal, the former would be expected to be larger and more perfect.

OTHER FEATURES OF THE "LAYERED" AND THE "INTERMESHED" FORM

Both Forms II and III can be classified as "condis" (conformationally disordered) crystals [8]. The type in Form II is, to our knowledge, new and can be described as having "occluded" disorder. The type in Form III has "layered" disorder and is similar in nature to that observed in alkylated perovskites [9] and phospholipids [10] and, possibly, in some other segmented mesogenic polymers [11].

A potentially important consequence of the different spacer-mesogen arrangement in the two crystal forms concerns the mechanical properties. In the "Layered" structure stiff and flexible segments are coupled in series, while in the

"Intermeshed" structure, as presently envisaged, they are coupled in parallel. The former should give a low crystal modulus, elastic up to high strains, while the latter the converse, i.e. high crystal stiffness but low elastic limit. The potential for utilising these features through appropriate design of lattices for macroscopic mechanical properties will be apparent.

CONCLUSIONS

- Two crystal types with conformational disorder are recognised: (a) the "Intermeshed" and (b) the "Layered" type, the former representing a novel mode of mesogen-spacer packing and a new condis phase, with "occluded" disorder and truly 3-dimensional.
- The orthorhombic "Layered" form is an example of a stable structure with alternating crystalline and non-crystalline layers, an arrangement arising from the mismatch in mesogen - spacer cross-section. Random copolymers containing different spacer lengths can also crystallize with this crystal type.
- Depending on spacer length, balancing of the conflicting requirements for high packing density and low conformational energy of the spacer layer is achieved either (a) by tolerating a low density layer, (b) by increasing its density through the introduction of unfavourable conformations.
- Viewing the crystals as molecular composites, the stiff (mesogen) and soft segments (spacer) are coupled in parallel in Form II ("Intermeshed") and in series in Form III ("Layered"). Dynamic mechanical studies on these systems are currently in progress.

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