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Materials Chemistry of Chiral Macromolecules. 2. Solid-State Structures

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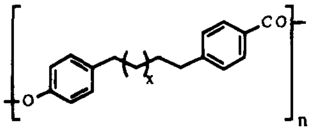
ABSTRACT: Molecular organization in the solid state of a homologous series of chiral and achiral polymers was studied by electron microscopy and electron diffraction. All polymers of the series had periodic molecular backbones and some contained a stereocenter substituted by nitrile groups every 16 or 17 atoms along the chain. An aliphatic unit served as a spacer between aromatic units and was part of the repeats in all polymers. This spacer contained either an even or odd number of carbons in order to generate a preference for extended or nonextended conformers, respectively. Enantiomeric enrichment of chains resulted in the formation of crystals but diastereomeric chains with even spacer formed a phase of intermediate order and those with odd spacer formed an amorphous material. Enantiomerically enriched chains are also board-shaped and organize edge-to-edge, a feature definitely not observed in one of the two unsubstituted (achiral) homologous chains studied here. The global conformational traits of chains determined if extended-chain or folded-chain crystals formed.

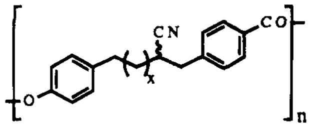
Introduction

An understanding of relationships between the covalent structure of macromolecules and their three-dimensional organization is an extremely important objective of materials chemistry. It is this organization and the consequent nano- and micron-size morphology that determine their solid-state properties. In this context, we know relatively little about the direct impact of chirality on physical structure and morphology of polymeric materials. Most previous work on chiral polymers has addressed primarily questions about their conformation in solution[1–4] and not about the role of chirality on molecular interactions in condensed states. In the extracellular matrices of biological systems chiral forces among stereogenic centers can dictate conformations of polymers and thus impact on their three-dimensional organization and microscopic morphology. This type of stereochemical control of solid-state structure is potentially very useful in establishing structure–property relations in synthetic materials.

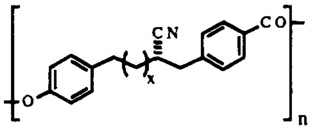
We reported in the first paper of this series on the synthesis and phase transitions of a new family of chiral macromolecules which contained the dipolar cyano group in the only stereogenic center of their chemical repeats.[5] The phase transitions were analyzed in this paper by both optical microscopy and differential scanning calorimetry. These polymers (**2a,b,** and **3a,b**) and their structural analogues without a stereogenic center have average degrees of polymerization of approximately 50 and their chemical structures are as shown. Thus, the structural variations randomize the handedness of the highly dipolar stereocenter or simply remove it from the backbone producing an achiral chain. The homologous structures also differ in the even vs odd number of methylene units in the repeat's aliphatic spacer between aryl rings. Using differential scanning calorimetry and optical microscopy, our previous work suggested that in the absence of preferred handedness the dipole moment at the stereocenters led to amorphous or less ordered condensed phases relative to those of the achiral chains. Our previous results also suggested that provided the aliphatic spacers were even the stereocenters with or without preferred handedness favored organization into layered structures. In the present work we have analyzed the three-dimensional organization of these macromolecules by electron diffraction and also their morphology by electron microscopy.



x = 3 **1a**
x = 4 **1b**



x = 3 **2a**
x = 4 **2b**



x = 3 **3a**
x = 4 **3b**

Experimental Section

The polymers used in this investigation were synthesized in our laboratory using procedures described in a previous publication.[5] Thin oriented films were prepared by shearing polymers between two microscope slides at a temperature of approximately 270 °C for polymers **1a** and **3a**, 260 °C for polymer **2a**, and 160 °C for polymers **1b**, **2b**, and **3b**. After shearing, the polymer films were slowly cooled to room temperature at a rate of approximately 3 °C/min. The sheared films on the microscope slides were detached from the glass substrate using a 1% HF aqueous solution, rinsed several times in distilled water, and then placed on 3 mm copper grids for examination by electron diffraction and electron microscopy. Crystals of **1a** were prepared using a hot solution of tetrachloroethane (0.1% by weight) deposited on a microscope slide maintained at approximately 200 °C for several hours

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Table 1. Crystallographic Data of Parent Polymer 1a (Even Spacer)

interplanar spacing d (Å)	Miller indices, $hk0$	
	hexagonal lattice	orthorhombic lattice
4.42	200, 020, $\bar{2}20$, $\bar{2}00$, $0\bar{2}0$, $2\bar{2}0$	200, 110, $\bar{1}10$, $\bar{2}00$, $\bar{1}\bar{1}0$, $1\bar{1}0$
3.34	210, 120, $\bar{1}30$, $\bar{2}30$, $\bar{3}20$, $\bar{3}10$ $\bar{2}\bar{1}0$, $\bar{1}\bar{2}0$, $1\bar{3}0$, $2\bar{3}0$, $3\bar{2}0$, $3\bar{1}0$	210, $2\bar{1}0$, $\bar{2}10$, $\bar{2}\bar{1}0$
2.55	220, $\bar{2}40$, $\bar{4}20$, $\bar{2}\bar{2}0$, $2\bar{4}0$, $4\bar{2}0$	020, $0\bar{2}0$, 310, $3\bar{1}0$, $\bar{3}10$, $\bar{3}\bar{1}0$
2.21	400, 040, $\bar{4}40$, $\bar{4}00$, $0\bar{4}0$, $4\bar{4}0$	400, $\bar{4}00$, $2\bar{2}0$, $\bar{2}20$, $\bar{2}\bar{2}0$, 220

until the solvent evaporated. The resulting thin film formed on the microscope slide was slowly cooled to room temperature at a rate of approximately 2 °C/min.

Electron microscopy and diffraction of the thin polymer films utilized a Philips EM 420 electron microscope operated at 100 kV. The camera length was calibrated using TlCl evaporated onto the thin films, and some samples for electron microscopy were shadowed with Pt−C to enhance contrast. Samples of model compounds **4** and **5** were prepared by melting and pressing these materials between a microscope slide and a cover glass and then cooling slowly to room temperature. The samples were examined in a Reichert polarizing optical microscope.

Results and Discussion

Figure 1a (top) is a selected-area electron diffraction pattern of a thin film of **1a** obtained by the solution-casting technique described above. Given the absence of the dipolar stereocenter in the repeats of this polymer, we refer to this material as the parent polymer. Geometrically, this pattern shows a hexagonal a^*b^* reciprocal lattice plane. However, the crystal lacks hexagonal symmetry because the six innermost reflections have different intensities and cannot be indexed using hexagonal unit cell parameters as 100, 010, $\bar{1}10$, $\bar{1}00$, $0\bar{1}0$, and $1\bar{1}0$ in order to index the whole pattern. The electron diffraction pattern can be interpreted as three orthorhombic reciprocal lattices differing in orientation. In these lattices $b^* = \sqrt{3}a^*$ and they are related to one another by rotations of ±60° about the c axis as shown in Figure 2a. It is clear from Figure 2a that the resulting reciprocal lattice has hexagonal geometry (Figure 2b). Because the distribution of diffraction spots in the pattern of Figure 1a has hexagonal geometry, the pattern can be indexed at first according to the hexagonal reciprocal lattice shown in Figure 2b and then the corresponding indices of orthorhombic lattices can be easily found by comparing Figures 2b and 2a. The observed d spacings and their indices (according to the hexagonal and orthorhombic lattices) of this macromolecular compound are listed in Table 1. According to Table 1 the orthorhombic unit cell parameters are a = 8.84 Å, b = 5.10 Å, and γ = 90°.

The interpretation of three identical orthorhombic reciprocal lattices with $b^* = \sqrt{3}a^*$ related to one another by rotations of ±60° about the c axis requires the six innermost reflection spots to have the same intensity. This structure could prevail at the temperature of sample preparation (200 °C) and could then freeze in at room temperature. This suggestion is supported by previous experiments on main chain and side chain liquid crystalline polymers.[6−8] For example, the orthorhombic crystalline phases of the 95/5 copolymer of p-hydroxybenzoic acid/m-hydroxybenzoic acid transform to this phase at 350 °C.[6,8] In another

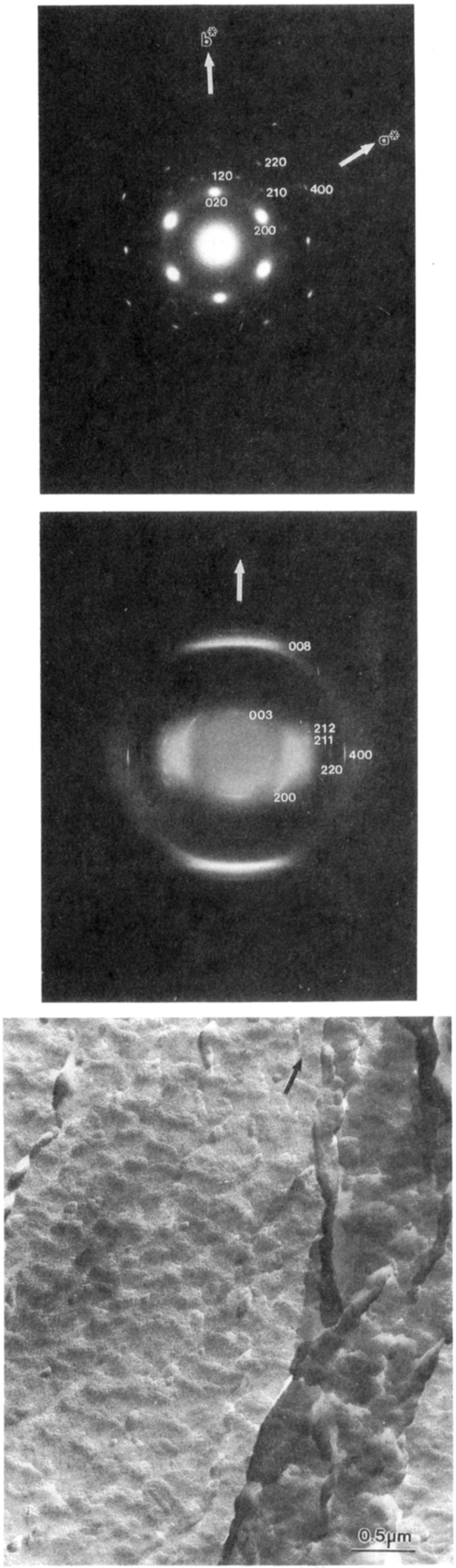


Figure 1. (a) Selected-area electron diffraction pattern of a thin film of **1a**, indexed according to the hexagonal reciprocal lattice in Figure 2b. (b) Electron diffraction pattern of a sheared film of **1a**. The equatorial reflections are indexed according to the hexagonal reciprocal lattice in Figure 2b. (c) Electron micrograph of the sheared film of **1a**.

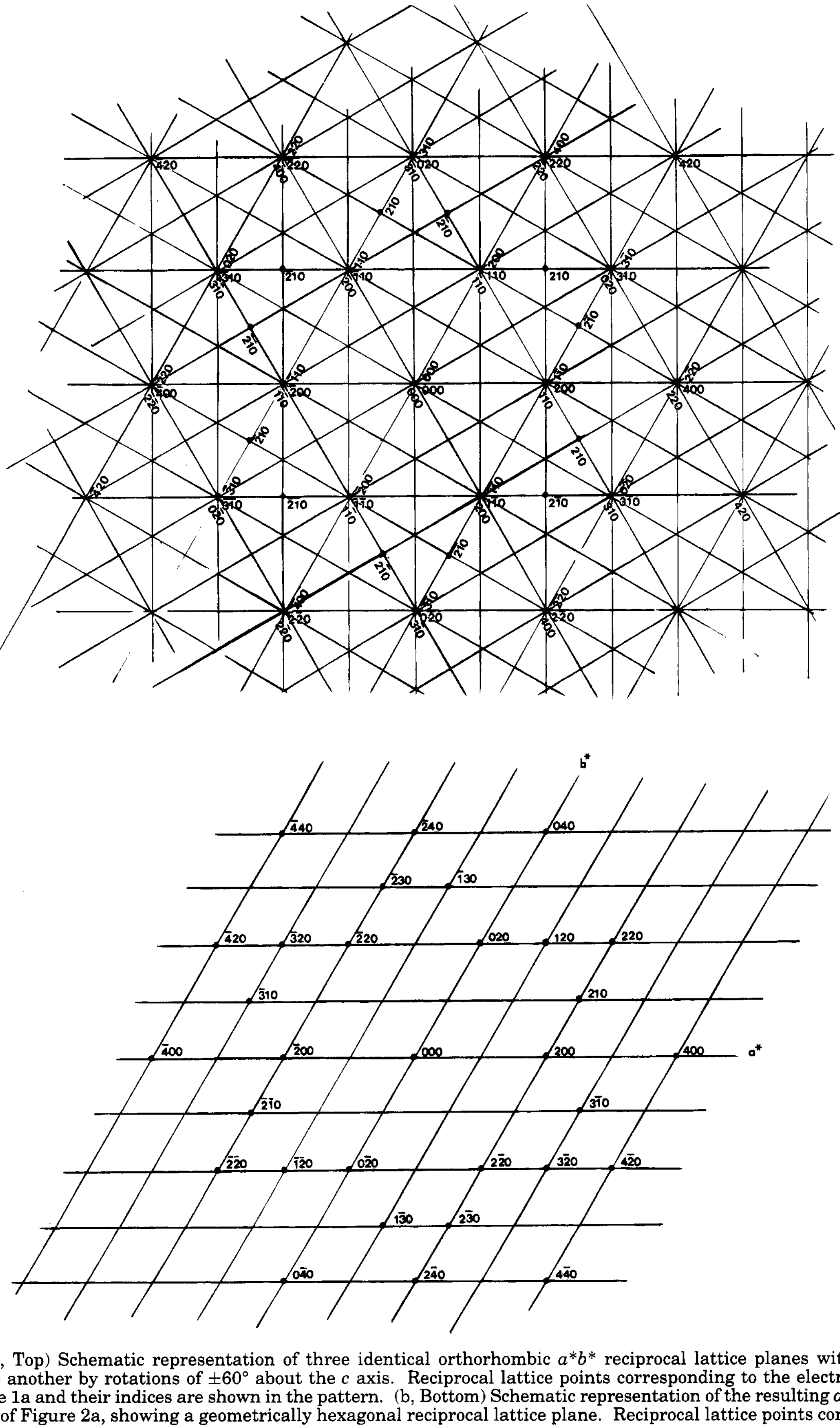


Figure 2. (a, Top) Schematic representation of three identical orthorhombic a^*b^* reciprocal lattice planes with $b^* = \sqrt{3}a^*$ related to one another by rotations of ±60° about the c axis. Reciprocal lattice points corresponding to the electron diffraction spots in Figure 1a and their indices are shown in the pattern. (b, Bottom) Schematic representation of the resulting a^*b^* reciprocal lattice planes of Figure 2a, showing a geometrically hexagonal reciprocal lattice plane. Reciprocal lattice points corresponding to the electron diffraction spots in Figure 1a and their indices are shown in the pattern.

example, the smectic E phase of a chiral comb polymer transforms to the same phase at 67 °C.[7] Furthermore, when the chiral comb polymer and the main chain copolymer are heated to 91[7] and 430 °C,[8] respectively, this phase transforms to a hexatic smectic B[9-11] phase in which chains rotate independently. Therefore the phase observed here could be considered an intermediate one between the orthorhombic crystalline phase (including the smectic E phase) and a hexatic smectic B phase. In the main chain and comb polymers mentioned above, this phase appears at elevated temperatures, but upon cooling transforms back to an orthorhombic crystalline phase or a smectic E phase. Interestingly, in the case of **1a** this phase is apparently frozen in at room temperature. The fact that the innermost six reflections do not have the same intensity could reflect the random freezing of chain rotation. Chains of **1a** probably deviate from boardlike shapes and might be instead distorted cylinders given the large angle rotations of chain segments at high temperatures.

Figure 1b (middle) is an electron diffraction pattern of a sheared film of **1a**. (The arrows in (b) and (c) indicate the shear direction.) The ratios of the reciprocal vectors of the equatorial reflections are 1:1.73:2. The off-meridional reflections appearing in the pattern indicate that this material possesses three-dimensional order. However, there are also streaks observed along the layer lines, indicating some axial shift between adjacent chains. Figure 1b is a fiber pattern with the c axis (chain axis) parallel to the fiber axis (shear direction). The three equatorial reflections are obtained from the same structure represented by the pattern of Figure 2a. However, the normal to the resulting a^*b^* reciprocal lattice plane of the three identical orthorhombic lattices is parallel to the shear direction and the a^*b^* plane is rotated about the c axis. According to the meridional reflections, the c axis is equal to 17.44 Å. The observed d spacings and their respective indices are listed in Table 2.

The electron micrograph in Figure 1c (bottom), corresponding to an oriented sample of polymer **1a**, shows crystalline entities protruding from the surface and oriented perpendicular to the shear direction. The thickness of the crystalline entities parallel to the shear direction is about 1000 Å, on average. Because the average degree of polymerization of this polymer is approximately 50, chains are most likely extended within these entities.

Figure 3a shows an electron diffraction pattern of a sheared sample of polymer **2a** revealing three sharp reflections on the equator. The ratios of reciprocal vectors of these reflections are 1:1.73:2, indicating hexagonal lateral packing of chains in this material. The meridional reflections 003, 005, 006 and 008 are more or less sharp but spread along the direction perpendicular to the meridian. In addition, there are long streaks along the layer lines, indicating some axial shift between the chains. The off-axis reflections 211 and 212 which appear in the electron diffraction pattern of polymer **1a** (Figure 1b) are no longer distinctly observed and instead there is extremely diffuse scattering in this region of the pattern. This indicates that when a CN group substitutes the aliphatic spacer with configurational disorder, three-dimensional order is lost and the sample exhibits a liquid crystalline structure which is reminiscent of the hexatic smectic B phase found in low molar mass compounds, but with some axial shift of the chains. Usually the hexatic smectic B phase is observed at high temperatures and in this phase molecules rotate independently. Therefore the structure of polymer **2a** is analogous to that of a high-temperature phase frozen in at room temperature. The observed hexagonal lateral packing of polymer molecules in this material suggests that chains have cylinder-like global shapes and within each layer there is long-range hexagonal bond orientational order. The equatorial reflections of the electron diffraction pattern can be indexed with hexagonal unit cell parameters $a = b = 5.30$ Å, and the $c = 17.35$ Å, the periodicity along the chain. The indices of the observed reflections and their corresponding d spacings are listed in Table 3. Figure 3b is an electron micrograph of an oriented sample of this polymer. The picture shows a banded or layered texture perpendicular to the shear direction. The width of the bands parallel to the shear direction is approximately 1000 Å, suggesting again the presence of extended chains within the layers.

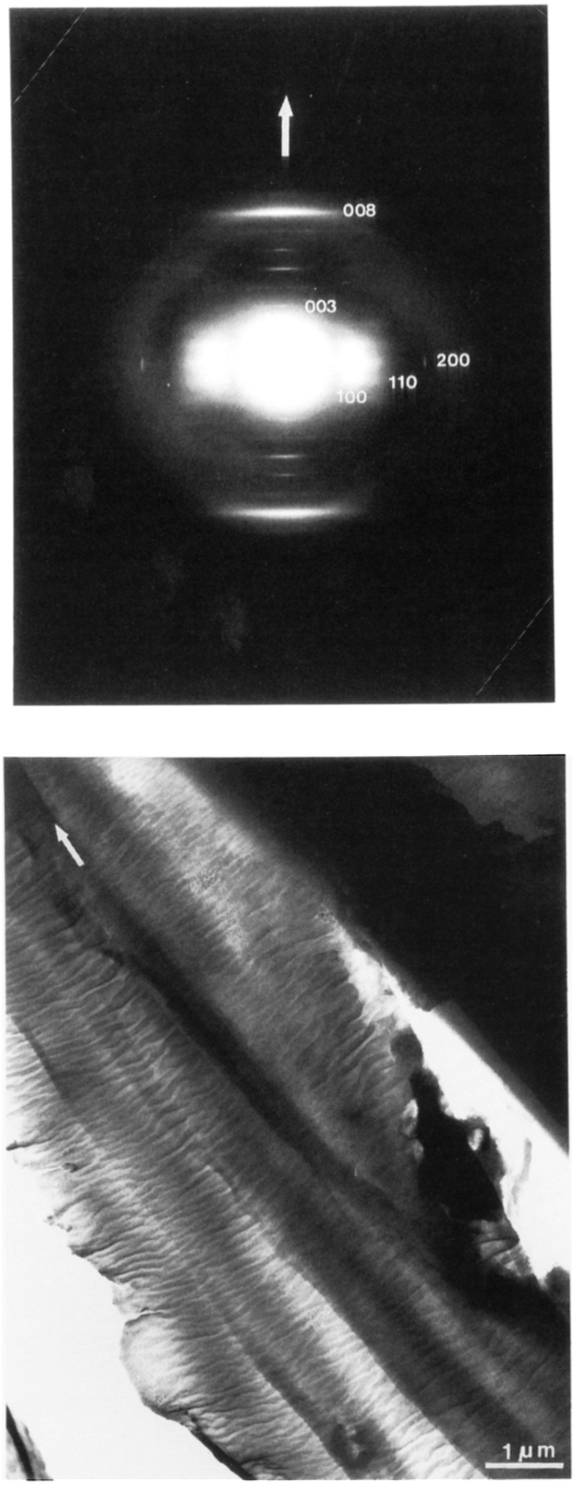


Figure 3. (a, Top) Electron diffraction pattern of a sheared film of polymer **2a**. The arrow indicates the shear direction. (b, Bottom) Electron micrograph of the sheared film of polymer **2a**. The arrow indicates the shear direction.

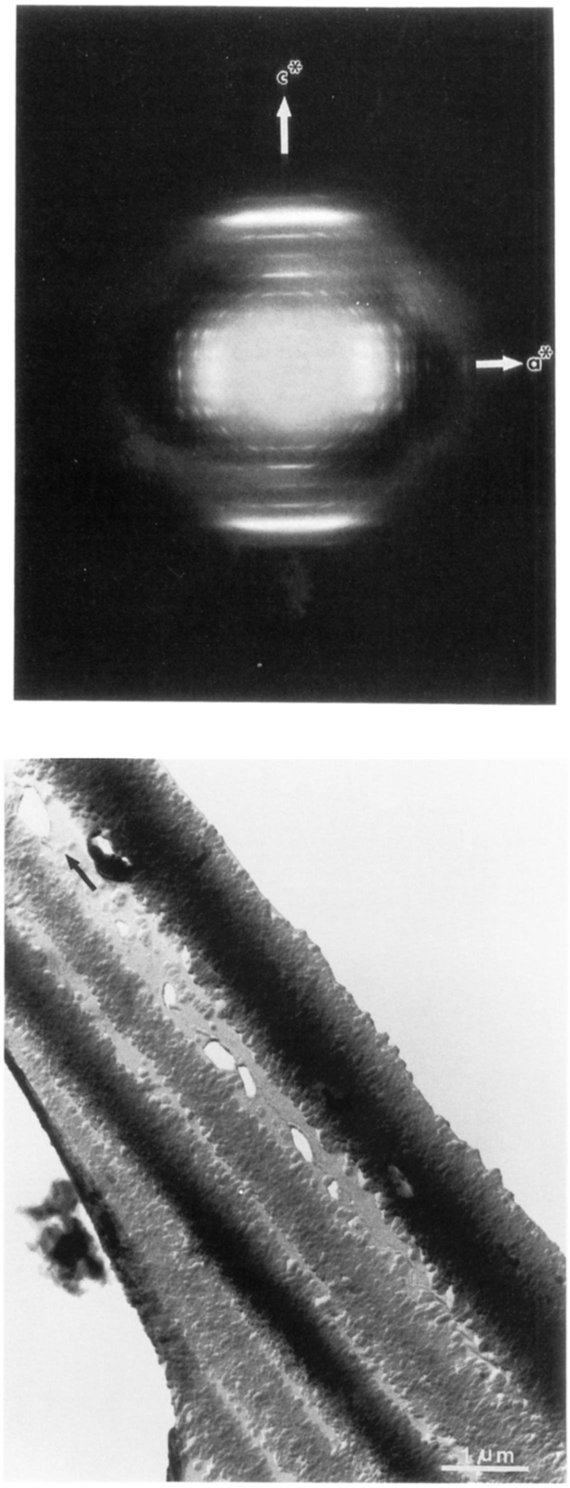


Figure 4. (a, Top) Electron diffraction pattern of a sheared film of polymer **3a**. (b, Bottom) Electron micrograph of the sheared film of polymer **3a**. The arrow indicates the shear direction.

Table 2. Crystallographic Data for a Sheared Film of Parent Polymer 1a (Even Spacer)

interplanar spacing *d* (Å)	equator Miller indices, *hk*0	
	hexagonal lattice	orthorhombic lattice
4.42	200, 020, $\bar{2}20$, $\bar{2}00$, $0\bar{2}0$, $2\bar{2}0$	200, $\bar{2}00$, 110, $\bar{1}10$, $1\bar{1}0$, $\bar{1}\bar{1}0$
2.55	220, $\bar{2}40$, $\bar{4}20$, $\bar{2}\bar{2}0$, $2\bar{4}0$, $4\bar{2}0$	020, $0\bar{2}0$, 310, $3\bar{1}0$, $\bar{3}10$, $\bar{3}\bar{1}0$
2.21	400, 040, $\bar{4}40$, $\bar{4}00$, $0\bar{4}0$, $4\bar{4}0$	400, $\bar{4}00$, 220, $2\bar{2}0$, $\bar{2}20$, $\bar{2}\bar{2}0$

interplanar spacing *d* (Å)	off-axis Miller indices, *hkl*	
	hexagonal lattice	orthorhombic lattice
3.28	211, 121, $\bar{1}31$, $\bar{2}31$, $\bar{3}21$, $\bar{3}11$ $\bar{2}\bar{1}1$, $\bar{1}\bar{2}1$, $1\bar{3}1$, $2\bar{3}1$, $3\bar{2}1$, $3\bar{1}1$	211, $2\bar{1}1$, $\bar{2}11$, $\bar{2}\bar{1}1$
2.36	212, 122, $\bar{1}32$, $\bar{2}32$, $\bar{3}22$, $\bar{3}12$ $\bar{2}\bar{1}2$, $\bar{1}\bar{2}2$, $1\bar{3}2$, $2\bar{3}2$, $3\bar{2}2$, $3\bar{1}2$	212, $2\bar{1}2$, $\bar{2}12$, $\bar{2}\bar{1}2$

interplanar spacing *d* (Å)	meridian Miller indices, 00*l*
5.81	003
2.91	006
2.18	008

Table 3. Crystallographic Data of the Configurationally Disordered Polymer 2a (Even Spacer)

interplanar spacing *d* (Å)	equator Miller indices, *hk*0	interplanar spacing *d* (Å)	meridian Miller indices, 00*l*
4.59	100, 010, $\bar{1}10$, $\bar{1}00$, $0\bar{1}0$,$1\bar{1}0$	5.78	003
2.65	110, $\bar{1}20$, $\bar{2}10$, $\bar{1}\bar{1}0$, $1\bar{2}0$, $2\bar{1}0$	3.47	005
		2.89	006
2.30	200, 020, $\bar{2}20$, $\bar{2}00$, $0\bar{2}0$, $2\bar{2}0$	2.17	008

Table 4. Crystallographic Data of the Parent Polymer 1b (Odd Spacer)

meridian		equator and off-axis	
interplanar spacing *d* (Å)	Miller indices, 00*l*	interplanar spacing *d* (Å)	Miller indices, 0*kl*
8.13	004	4.70	020
		4.62	021
		4.40	022
		4.24	023
		4.07	024
		3.91	025

Table 5. Crystallographic Data of the Configurationally Ordered Polymer 3b (Odd Spacer)

meridian		equator			
interplanar spacing *d* (Å)	Miller indices 00*l*	interplanar spacing *d* (Å)	Miller indices 0*k*0	interplanar spacing *d* (Å)	Miller indices, *h*00
8.14	004	9.80[a]	010	5.55[b]	200
5.43	006	4.89	020	3.68	300
4.07	008				
3.26	0010				

[a] Calculated according to the first row line. [b] Calculated according to the second row line.

Figure 4a is an electron diffraction pattern of an oriented film of polymer **3a** revealing many sharp reflections. A few reflections are those observed in structures **1a** and **2a** but most of the reflections are characteristic of the enantiomerically enriched polymer **3a**. The distribution of reflections in the pattern of Figure 4a is similar to that of an orthorhombic single crystal with *h*0*l* reflections. This indicates that both the *c* and *a* axes are oriented in the plane of the thin film and the corresponding lattice parameters are 17.58 and 17.12 Å. From the electron diffraction results it is obvious that when a CN group substitutes the aliphatic spacer between aryl units in a stereoordered fashion (enantiomerically enriched structure) the global shape of the chain is changed, from the hexagonally packed cylindrical shape of the configurationally disordered polymer to a flattened shape which packs in an orthorhombic lattice. The electron diffraction pattern shown in Figure 4a has only *h*00 reflections on the equator. This is very different from the usual fiber patterns of aromatic polymers with orthorhombic or monoclinic

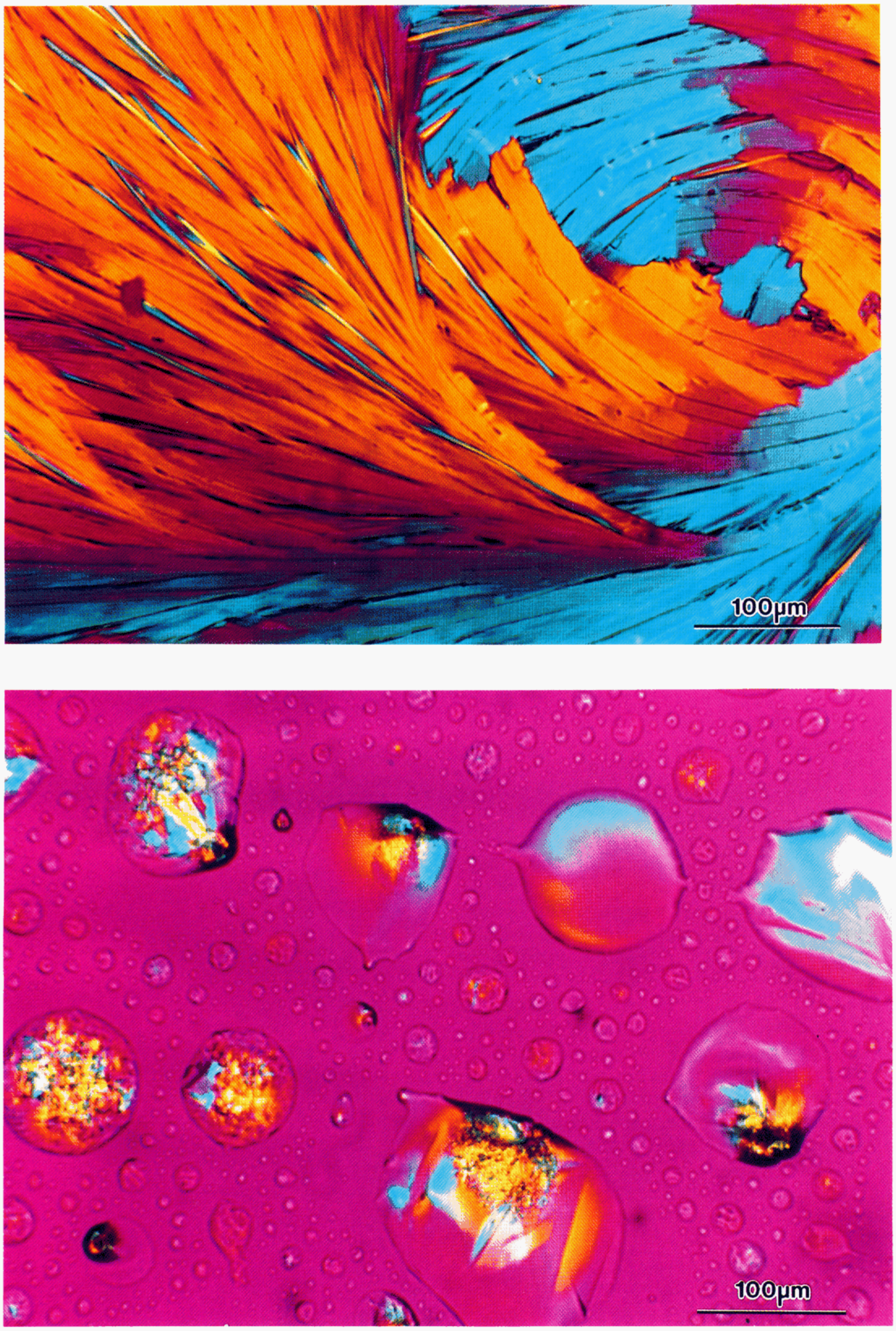
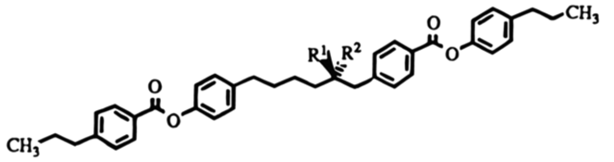


Figure 5. (a, Top) Optical micrograph of the enantiomerically enriched model compound **4** (between crossed polars), revealing a crystalline texture. (b, Bottom) Optical micrograph of racemic model compound **5** (between crossed polars), revealing birefringent frozen droplets.

crystalline structures in which there are always *h*00, 0*k*0, and *hk*0 reflections on the equator and chains are packed edge-to-face. This suggests that chains of polymer **3a** are packed edge-to-edge given that their *c* and *a* axes are oriented in the plane of the film. A single-crystal-like texture, with only *h*0*l* reflections present in the electron diffraction pattern has also been observed in an oriented thermotropic liquid crystal polyester.[12] Finally, Figure 4b shows an electron micrograph of the oriented film of polymer **3a** revealing grainlike crystalline entities measuring about 1000 Å. This observation suggests that chains are extended within these crystalline entities.

The remarkable impact of common handedness at the stereocenter on solid-state structure is revealed by optical micrographs on model compounds. The synthesis and phase transitions of the two model compounds used to obtain the micrographs had been reported by our group earlier.[5] The compounds studied have the following structure:



4 $R^1 = -H$, $R^2 = -CN$
5 $R^1, R^2 = -CN \Leftrightarrow -H$

Compounds **4** and **5** are dimeric model compounds for polymers **3a** and **2a**, respectively, but have only a *single* stereocenter corresponding to one structural unit in the center of the structure. The central structural unit is flanked by half a structural unit on each side not containing any stereocenters. Figure 5 shows two optical micrographs corresponding to compounds **4** and **5**, obtained at room temperature between crossed polars. The only difference between the two model compounds is random handedness vs preferred handedness at the *single* stereocenter of the dimer. Nonetheless, remarkably different solid-state textures are observed in these two compounds which reflect structural differences found in the analogous polymers studied here. The enantiomerically enriched compound **4** has clearly a crystalline texture as does its analogous polymer **3a** whereas the racemate appears as frozen liquid droplets which are birefringent. The birefringence of the frozen droplet strongly suggests the existence of a noncrystalline mesomorphic structure, in analogy to the frozen hexatic smectic B phase discussed above in polymer **2a**.

Figure 6a is an electron diffraction pattern of a sheared film of polymer **1b**. This pattern shows an orthorhombic single-crystal-like texture with *c* and *b* axes oriented in the plane of the film. The observed *d* spacings and their indices are listed in Table 4. Based on the data summarized in Table 4, the *c* and *b* lattice parameters are 32.52 and 9.40 Å, respectively. It is interesting to see that these chains with an odd number of CH_2 units in the aliphatic spacer are also flattened in shape. The electron diffraction pattern of Figure 6a has only one 0*k*0 equatorial reflection and a series of 0*kl* off-axis reflections; this suggests that chains of polymer **1b** are probably packed face-to-face with *c* and *b* axes in the plane of the film. Figure 6b is an electron micrograph of the sheared film of polymer **1b** revealing crystalline lamellae perpendicular to the shear direction. The thickness of these lamellae is about 350 Å, roughly one-third the dimension of crystalline entities observed in **1a**. Given the average degree of polymerization of these polymers, it is likely that chains are folded in each lamella, therefore adopting antiparallel packing. It is interesting to consider that the differences observed in molecular packing and global shape between the even and odd parent polymers might be the result of chain folding.

Figure 7a is an electron diffraction pattern of a sheared film of polymer **2b**. This pattern indicates the absence of molecular orientation in the sample, revealing only the diffuse halos characteristic of amorphous materials. Therefore, when the CN group substitutes the odd aliphatic spacer with configurational disorder, the three-dimensional order of the sample is destroyed. It is remarkable that such an ordering frustration occurs in the solid state with configurational disorder at stereocenters 17 atoms apart in an otherwise periodic polymer. This is in contrast to the configurationally disordered polymer **2a** with even spacer which does exhibit orientational and some positional order. The great difference in degree of order in the solid state must be related to their differences in global shape of the chains. Figure 7b is an electron micrograph of the sheared film of polymer **2b**. As expected, this image appears almost featureless, confirming the amorphous structure of the sample.

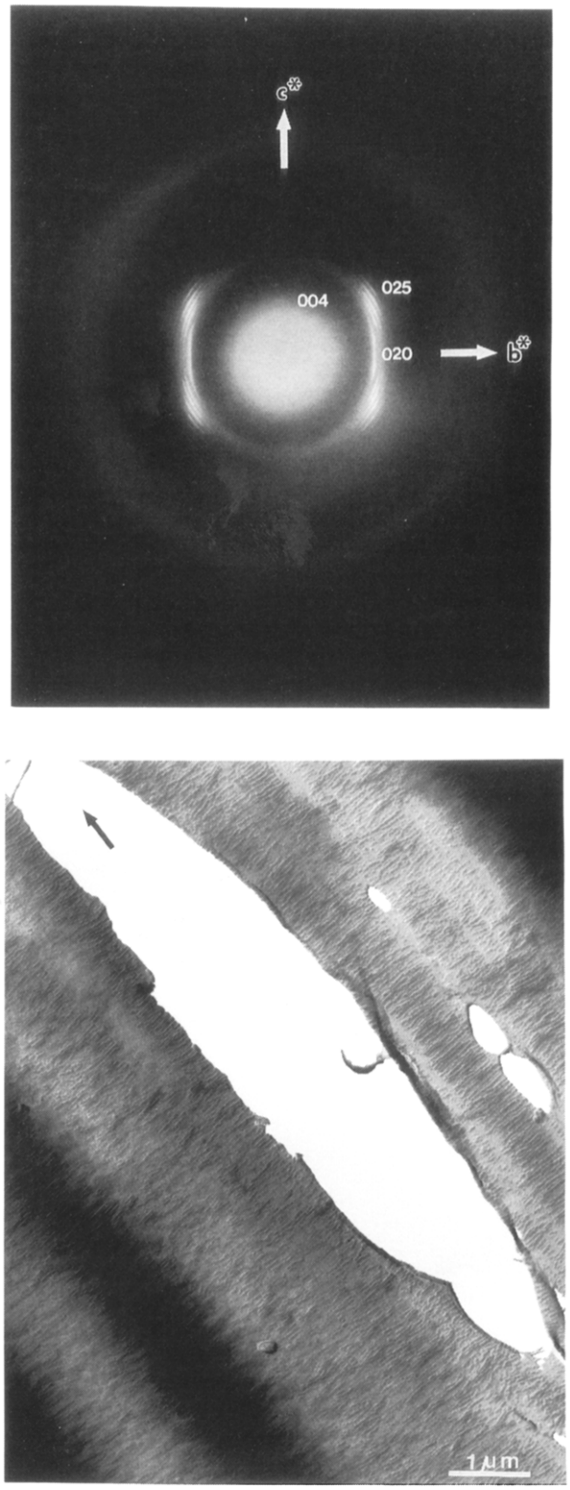


Figure 6. (a, Top) Electron diffraction pattern of a sheared film of polymer **1b**. (b, Bottom) Electron micrograph of the sheared film of polymer **1b**. The arrow indicates the shear direction.

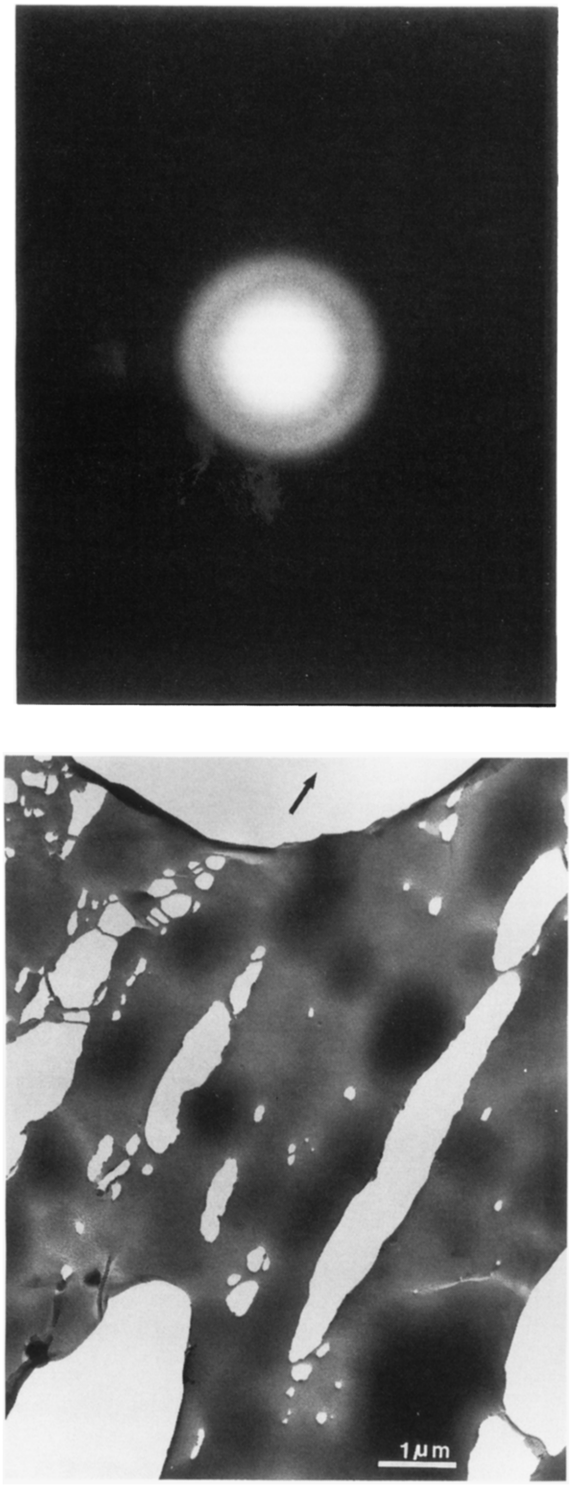


Figure 7. (a, Top) Electron diffraction pattern of a sheared film of polymer **2b**. (b, Bottom) Electron micrograph of the sheared film of polymer **2b**. The arrow indicates the shear direction.

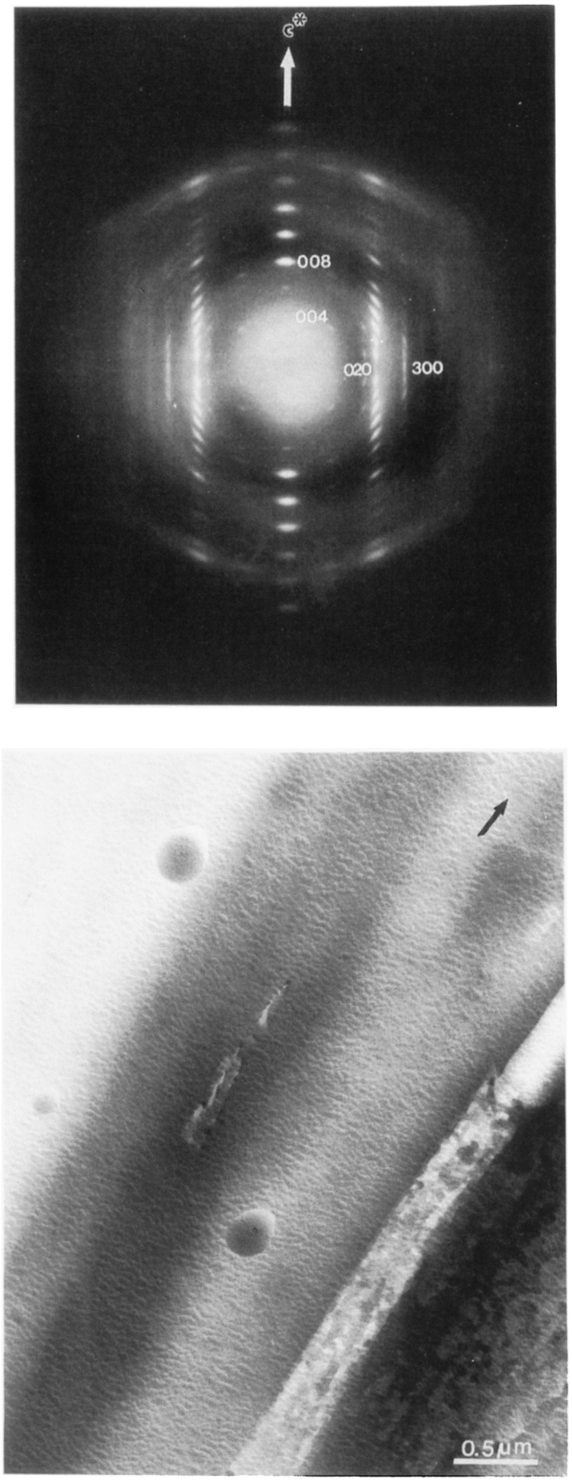


Figure 8. (a, Top) Electron diffraction pattern of a sheared film of polymer **3b**. The arrow indicates the shear direction. (b, Bottom) Electron micrograph of the sheared film of polymer **3b**. The arrow indicates the shear direction.

Figure 8a is an electron diffraction pattern of a sheared film of polymer **3b**, revealing a single-crystal-like texture with many sharp reflections. The systematic extinction of odd-order $00l$ reflections on the meridian indicates the existence of a 2_1 screw axis along the *c* axis direction. The appearance of even orders of $00l$ reflections reveals a repeating unit of 32.58 Å which contains two chemical units of the polymer. This suggests that chains acquire a 2_1-helical conformation in these films. In addition to the $00l$ reflections, there are only $h0l$ and $0kl$ off-axis reflections and $0k0$ and $h00$ equatorial reflections. This suggests that chains of polymer **3b** are probably packed edge-to-edge ($d = 11.07$ Å) and face-to-face ($d = 9.79$ Å) in the plane of the film. The edge-to-edge packing of chains is, of course, the same organization found in the even-spacer homologue. The observed *d* spacings and their indices are listed in Table 5. In a previous publication from our laboratory[13] the face-to-face and edge-to-edge packing of repeats in polymer **3b** was considered important in molecular recognition (homochiral recognition) events leading to the bulk synthesis of two-dimensional polymers. The

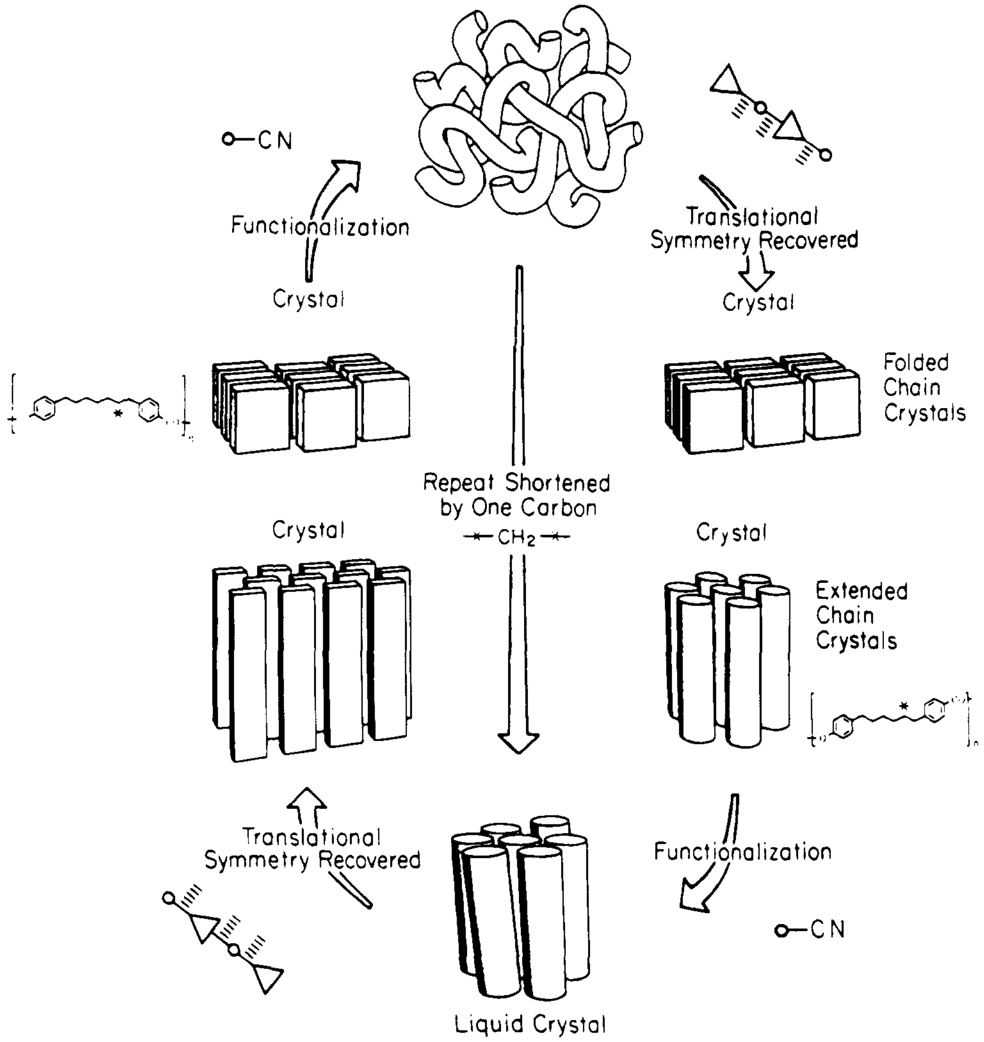


Figure 9. Schematic representation of molecular shapes and packing modes in the six homologous polymers studied here. The shorter objects at the top represent folded chains.

unit cell parameters for this polymer are $a = 11.07$ Å, $b = 9.79$ Å, $c = 32.58$ Å, and $\alpha = \beta = \gamma = 90°$. Figure 8b is an electron micrograph of a sample oriented with shear showing crystalline entities perpendicular to the shear direction. The thickness of the entities is about 350 Å, indicating again the possibility of folded chains with antiparallel packing.

Figure 9 is a schematic representation of the various molecular shapes and packing modes observed in the six homologous polymers studied here. Folded-chain crystals were observed in odd-spacer chains which should prefer nonextended conformers. In contrast, even-spacer chains organized into extended-chain ordered structures. In chiral systems, a flattened, board-like shape of chains is only observed when the stereocenters are of a preferred configuration. Furthermore, as illustrated in Figure 9, these enantiomerically enriched chains are observed to pack edge-to-edge. From our studies we do not know, of course, the solid-state conformations in terms of atomic coordinates for this family of homologous chains. The schematic representation of Figure 9 depicts simply the global shapes we believe these macromolecules have in the solid state based on the nature of the unit cells and the dimensions of the crystals. Through a systematic and subtle variation in stereochemistry, substitution, and structural unit, our work reveals interesting trends in three-dimensional organization of polymer molecules as affected by these factors.

Some of our results on these homologous macromolecules may have implications on the issue of chain folding during crystallization. For many years this has been an issue of great controversy in polymer science.[14-27] Questions which have been raised include the very occurrence of folding as the explanation for the thinness of polymeric crystals, the detailed nature of the folds, and the kinetics of folding. Whereas the prevailing view at the moment is that folding indeed occurs, the molecular basis of folding and the related question of its thermodynamic versus kinetic origin during crystallization of polymers are issues that remain open. The molecular basis of folding during crystallization has never been clearly established, perhaps because of the structural nature of polymers used in earlier work. Chain folding has been traditionally studied using polyethylene or other polyolefins in which global conformational trends are not well defined. In this context it is interesting to note that our semiflexible polymers **1b** and **3b** with an odd number of carbons in the aliphatic spacer form crystals thinner than the contour lengths of their constituent molecules. On the other hand, those with an even number of carbons in the aliphatic spacer form crystals in which the molecules appear to exist in extended conformation. As depicted in Figures 10a–c, one can expect a fundamental difference in the geometrical nature of conformers in these two groups of polymers. Those with odd spacers are prone to adopt nonextended, folded, or highly bent

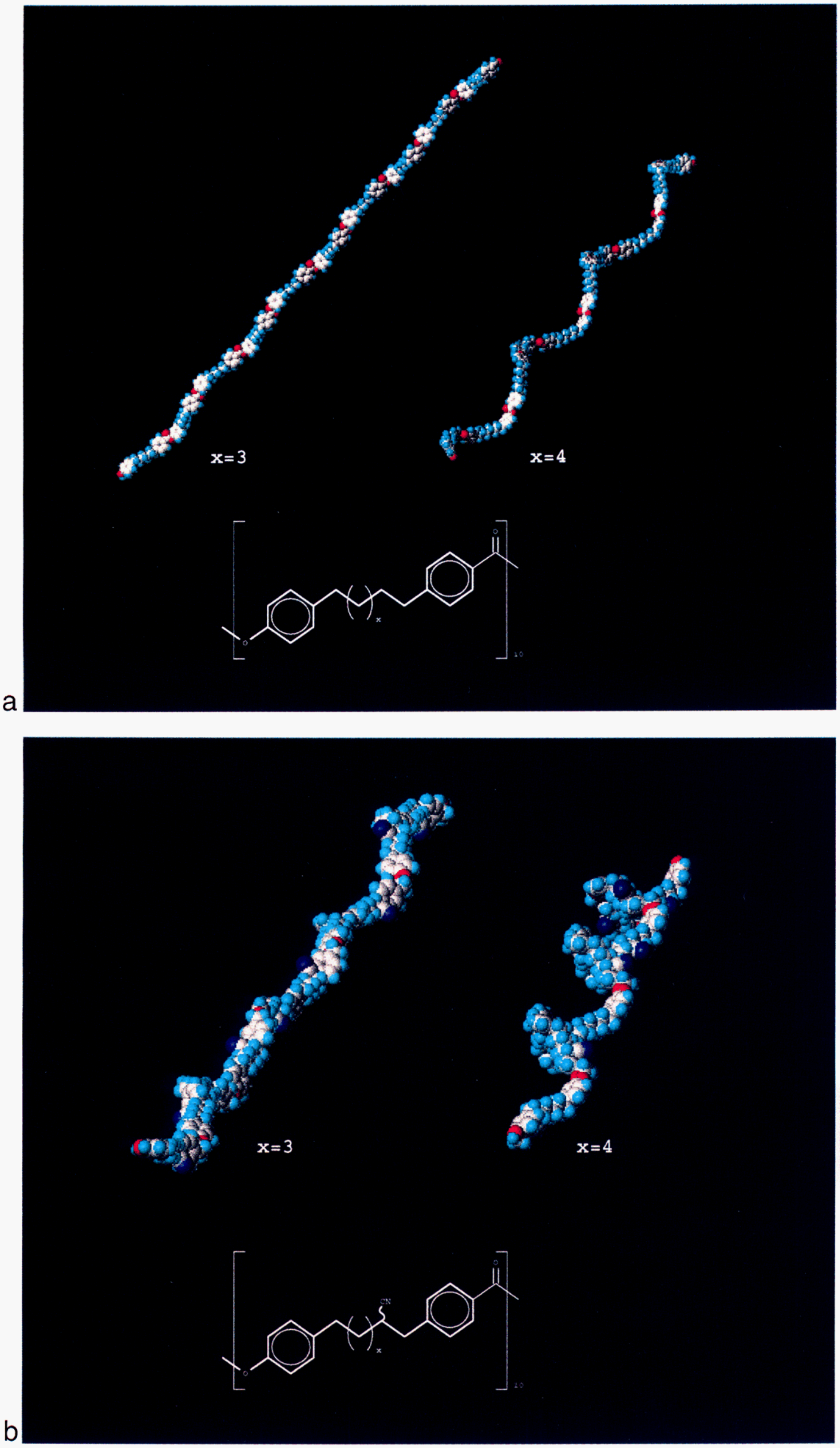

x=3
x=4
O
O
x
10
a
x=3
x=4
O
CN
O
x
10
b

Figure 10. Molecular graphics representation of the energy-minimized conformation of isolated molecules of **1a** and **1b** (a), **2a** and **2b** (b) and **3a** and **3b** (c).

conformations whereas the even-spacer chains clearly tend toward extended conformations. The implication of our findings is that conformational traits which originate in repeat unit structure may dictate if ordering in the solid state will involve formation of folded-chain as opposed to extended-chain crystals. The system's preference for one crystal or the other can of course have great impact on the physical properties of the materials obtained.

Conclusions

The global shape and three-dimensional organization of polymer molecules with a periodic backbone that contains stereocenters every 16 or 17 atoms revealed remarkable sensitivity to both their stereochemistry and global conformational traits. Enantiomeric enrichment of the chains resulted in the formation of highly crystalline solids in which board-shaped chains pack edge-to-edge, a feature definitely not observed in one of the two unsubstituted (achiral) homologous chains studied here. The global conformational traits of chains determined if extended-chain or folded-chain crystals formed.

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