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Double Twist in Helical Polymer "Soft" Crystals

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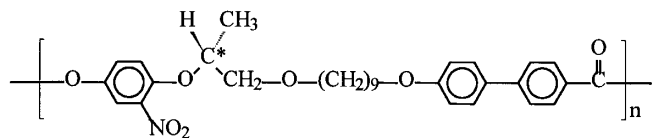
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In natural and synthetic materials having non-racemic chiral centers, chirality and structural ordering each play a distinct role in the formation of ordered states. Configurational chirality can be extended to morphological chirality when the phase structures possess low liquid crystalline order. In the crystalline states the crystallization process suppresses the chiral helical morphology due to strong ordering interactions. In this Letter, we report the first observation of helical single lamellar crystals of synthetic non-racemic chiral polymers. Experimental evidence shows that the molecular chains twist along both the long and short axes of the helical lamellar crystals, which is the first time a double-twist molecular orientation in a helical crystal has been observed.

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Biological materials and their fascinating functions in the human genome have been extensively explored and continue to stimulate new research directions in materials science. Synthetic polymers are similar to proteins and deoxyribonucleic acids (DNA) with respect to their long chain nature, but synthesizing polymers which possess properties similar to biomaterials require, at the very least, an introduction of chirality. The chirality effect on the material properties and structures of small molecular liquid crystals indicates that a series of new phases exist through the introduction of chiral centers which have interesting electro-optical behaviors [1–5]. A helical morphology with a pitch length of several micrometers is typical of chiral liquid crystalline (LC) phases, but exists only in low ordered LC phases. In highly ordered smectic crystal phases, the helical morphology is suppressed by the crystallization process, leading to the traditional parallel close packing scheme in three-dimensional space [1]. We expect that by directionally connecting small LC molecules with covalent bonds to form main-chain non-racemic chiral LC polymers will lead to an enhancement of the conformational chirality strength. The chirality strength should be strong enough to compete with the parallel close packing scheme during crystallization and stabilize the helical morphology in a crystalline state.

The material studied is a main-chain chiral polyester synthesized from (*R*)-(-)-4'-[ω-[2-(*p*-hydroxy-*o*-nitrophenyloxy)-1-propyloxy]-1-nonyloxy]-4-biphenyl carboxylic acid. The polymer has a spacer of nine methylene units, and is abbreviated as PET(*R*^{*})-9,



This polymer was specifically synthesized by an *A-B* type of condensation to ensure strict head-to-tail connections between adjacent repeating units [6,7]. The polymer possesses right-handed chiral centers (*) along the main-chain backbone. The specific rotation of the monomer is -28.5° . The molecular weight of PET(*R*^{*})-9 is approximately 16 000 g/mol with a polydispersity of 2 after fractionation, as measured by gel permeation chromatography based on polystyrene standards.

Polymer thin films (approximate thickness of 50–100 nm) were prepared by casting a 0.05 (wt) % tetrahydrofuran solution on carbon surfaces. After the solvent was evaporated, the films were heated above its highest endothermic transition temperature (189 °C) and were subsequently quenched to preset temperatures and held isothermally for various times ranging from several minutes to a few days. The samples were then quenched in liquid nitrogen and allowed to equilibrate to room temperature, which is below the glass transition temperature of the polymer ($T_g = 37^\circ\text{C}$). The thin films were shadowed by Pt and coated with carbon for transmission electron microscopy (TEM) morphological observations. Shadowing was not applied to the films used for dark field (DF) images. The TEM experiments were carried out using a JEOL (1200 EX II) TEM with an accelerating voltage of 120 kV. Electron diffraction (ED) patterns

of the samples having different zones were also obtained using a TEM tilting stage. Calibration of the ED spacing was done using T1C1 in a d -spacing range smaller than 0.384 nm, which is the largest spacing for T1C1.

Exclusively right-handed helical single lamellar crystals are obtained by crystallization at 145 °C from a chiral smectic-A LC phase of the polymer thin film as shown in Fig. 1(a). The crystal structure is orthorhombic with unit cell dimensions of $a = 1.07$, $b = 0.48$, and $c = 5.96$ nm, wherein the molecular chain axis is parallel to the c direction [6]. A typical ED pattern is shown in Fig. 1(b). Generally, a two-dimensional ED pattern possesses a single zone, and the reciprocal lattice axes (a^* , b^* , and c^* axes) are used as the coordination axes to index the diffraction spots. However, in this case [Fig. 1(b)], the ED pattern is attributed to multiple zones due to the lamellar twisting. Therefore, we use the nomenclature of a "horizontal" direction defined as the OO' line in Fig. 1(b) to avoid confusion. Along the horizontal OO' direction, we can clearly observe three diffraction arcs, which correspond to the (201), (205), and (206) planes based on the d -spacing calculations. The $(h1l)$ diffraction line shown is normally diffuse due to the crystal superstructure [6,7]. This ED pattern comprises at least three different zones. The DF image obtained from these three diffraction arcs is shown in Fig. 2. Sets of bright bands are observed across the short (n_s) axis of the helical lamellar crystal. The bright bands are twisted along the long helical (n_l) axis resulting in either 5°, 25°, or 30° tilt from the substrate, since the half pitch length along the n_l axis requires a lamellar twist of 180° (see Fig. 2). Based on the relationship of the unit cell dimensions, it can be determined that the bands correspond to the (201), (205), and (206) diffractions, which are the strongest of the $(20l)$ planes [7]. The ED and DF experiments are consistent with each other.

In explaining the ED [Fig. 1(b)] and DF (Fig. 2) results, we first assume a single-twist model of chain

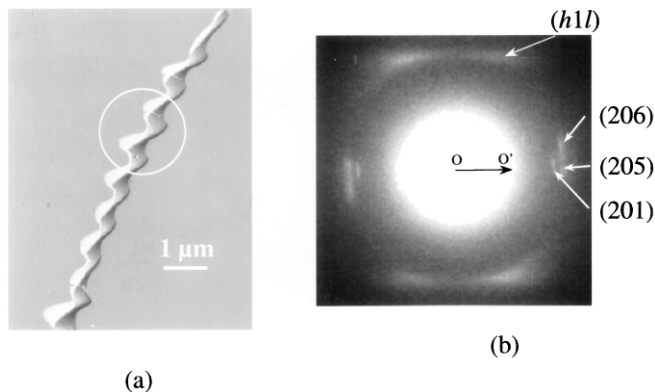


FIG. 1. (a) TEM bright image of the helical lamellar crystal; (b) ED pattern obtained from the circled area in (a).

orientation, which is the simplest way to generate a helical morphology (as is the case of a cholesteric phase). In this model, there is only one twist axis, which is along the n_l axis in Fig. 3(a) (also in Fig. 2). Chains are parallel to each other in each cross section of the crystal along the width of the cross section (the width of the cross section corresponds to the lamellar thickness, i.e., the c axis). Therefore, the chain direction is always perpendicular to both the n_l and n_s axes. Three cross sections of the helical crystal denoted as I, II, and III [white lines of Fig. 3(a)] are shown in Fig. 3(b) with a $\pm 30^\circ$ twist about the n_l axis of cross sections I and III with respect to II. Cross section II corresponds to the n_s axis parallel to the substrate with the chain direction perpendicular to the substrate. Cross sections I and III possess n_s axes which are in and out of plane of the substrate. If cross section II provides the $[00l]$ zone in the ED pattern, the cross sections I and III give rise to the $[301]$ and $[30\bar{1}]$ zones, respectively, providing a pair of (206) diffractions on the horizontal OO' direction of the registration plane [Fig. 3(c)]. However, this model does not, in fact, generate the diffraction arcs observed by the ED, suggesting that the chain orientation in the helical crystals is more complicated than a single-twist geometry. A double-twist model is therefore proposed and is shown in Fig. 3(d). The difference between the single- and double-twist models is that in the latter model, the cross section of the crystal is twisted along the n_s axis. The molecular chain direction is parallel to

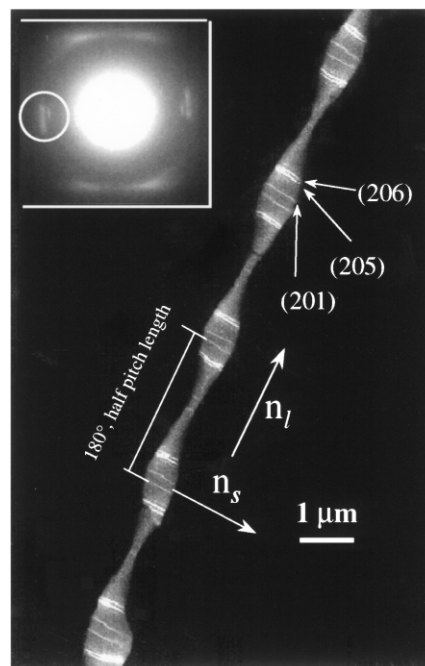


FIG. 2. TEM DF image of the helical lamellar crystal from the (201), (205), and (206) diffraction arcs which are circled in the inset ED pattern. The bright bands on the crystal correspond to these three diffractions.

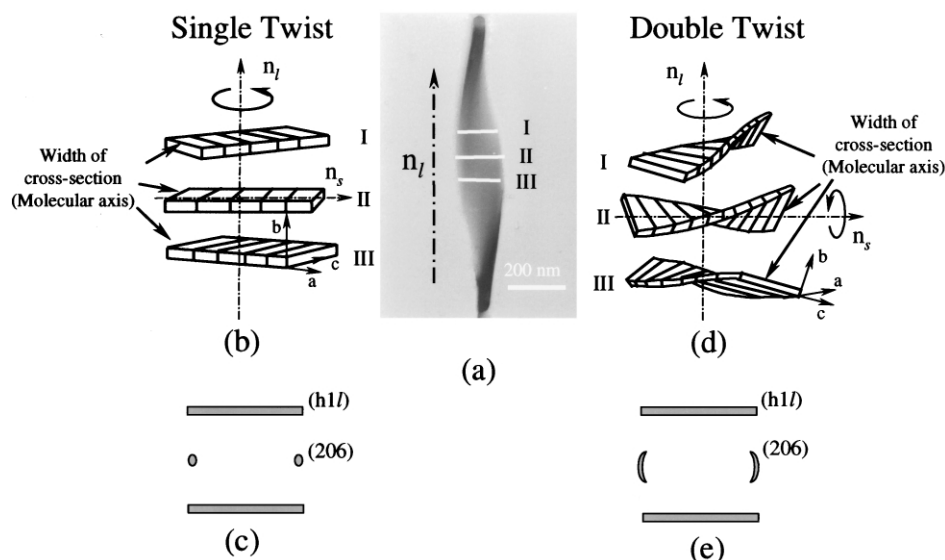


FIG. 3. Single- and double-twist models of the helical lamellar crystals. (a) Half pitch length of the crystal. I, II, and III represent three cross sections: II is parallel to the substrate, I and III are tilted $\pm 30^\circ$ with respect to the substrate. (b) Enlarged and isolated cross sections I, II, and III in the single-twist model. In each cross section, molecular chains are parallel to each other along the width of the cross section (the width of the cross section corresponds to the lamellar thickness, i.e., the c axis). There is only one helical axis (n_l) in this model. (c) The predicted ED pattern from cross sections I and III in the single-twist model. (d) Enlarged and isolated cross sections I, II, and III in the double-twist model. In each cross section, molecular chains are only locally parallel to the width of the cross section and continuously twist along the short helical axis (n_s). There are two helical axes (n_l and n_s) in this model. (e) The predicted ED pattern from cross sections I and III in the double-twist model. Note that the (206) diffraction is an arc.

the width of the cross section (as in the case for the single-twist model), but is continuously twisted along the n_s axis of the helical crystal, and thus, two twist axes, n_l and n_s , exist which are perpendicular to each other. Because of the twist along the n_s axis, the chain direction is no longer perpendicular to the n_l axis (except at the very center of the helical lamella along the n_l axis). In this case, the central portions of the cross sections I and III provide the $[301]$ and $[30\bar{1}]$ zones in the ED pattern as in the single-twist model, which gives rise to the (206) diffraction appearing on the horizontal OO' line. Moving along the n_s axis from the center to the edge within cross section I (or III), the (206) diffraction gradually deviates from the OO' line due to the twist along the n_s axis. Therefore, the (206) diffraction arcs are obtained from the entire cross section as shown in Fig. 3(e). The azimuthal angle of the arc is determined by the twisting angle of the molecular chain direction along the n_s axis. The same principle can be applied to explain the arc shape of the (201) and (205) diffractions.

In order to provide experimental evidence of the double-twist model, we have designed an experiment using partial (205) and (206) diffraction arcs to construct the DF image as shown in Fig. 4. Note that the circled area selected in the ED pattern (the inset in Fig. 4) does not include the (201) diffraction and therefore, the bright band corresponding to the (201) diffraction in Fig. 2 is not observed. More importantly, only portions of the (205)

and (206) bright bands appear along the n_s axis of the helical lamellar crystal. The azimuthal distribution of the diffraction arc corresponds quantitatively to the different positions within each bright band, implying that the chain orientation in the bright bands continuously changes as predicted by the double-twist model. Detailed analysis shows that the degree of twist for each molecular layer along the n_l axis is approximately 0.05° while the twist angle is approximately 0.01° per molecular layer along the n_s axis.

From this specifically designed experiment, we are able to examine the chain orientation of the helical lamellar crystals. PET(R^*)-9 possesses non-racemic (R) chiral centers (configurational chirality: the primary structure) along the polymer backbone, and these chiral centers lead to a left-handed helical conformation (conformational chirality: the secondary structure) of the polymer chain. The packing of these helical chains is determined by the intermolecular interactions. In right-handed helical lamellar crystals, the molecular chain orientation is double twisted (morphological chirality: the tertiary structure). This double-twist packing is similar to a stack of twisted β -sheets similar to several biopolymers [8–11]. The twisted sheets pack closely with a twist that is perpendicular to the helical axis of the sheets themselves. Many examples possessing double-twist helical packing exist in LC states. Dinoflagellate chromosomes (in *Prorocentrum micans*) in an *in vivo* arrangement serve

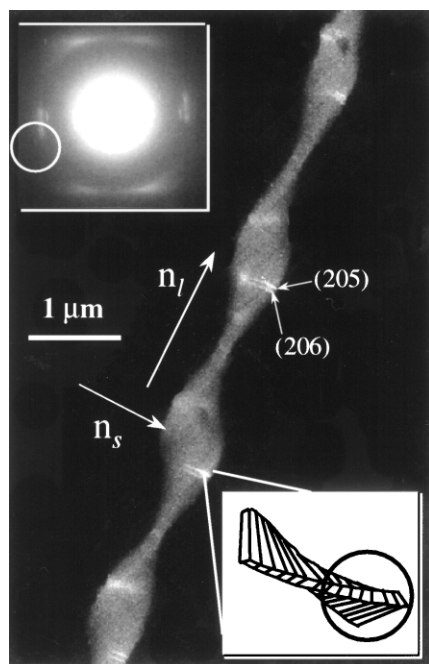


FIG. 4. TEM DF image of the helical lamellar crystal from the partial (205) and (206) diffraction arcs denoted by the circled area in the ED pattern inset. Note that the bright bands cover only a portion of the crystal cross section. The cross section inset shows that the chain orientation within the band and the circled area corresponds to the bright band.

as an example [8]. On the other hand, another form of double-twist molecular chain orientation has been described in LC blue phases in which the twisting tendency is an essential ingredient of this phase [12]. Similar structures have also been observed in DNA [13] and poly- γ -benzyl-*L*-glutamate [14,15]. Helical crystals of the β modification grown from *Bombyx mori* silk fibroin solution have been reported [9], and we believe that the chain orientation in this crystal possesses double twist. In a series of synthetic non-racemic chiral polyesters having similar chemical structures with different numbers of methylene units, we have also shown the existence of double-twisted single lamellar crystals.

This report presents for the first time, experimental evidence of single lamellar crystals with a double-twist molecular chain orientation. The formation of these helical lamellar crystals occurs through a combination of two spontaneous translational symmetry-breaking processes along the n_l and n_s axes. These are incompatible with typical crystalline structural repetition schemes, and are symmetrically “soft” rather than true crystals based on the traditional crystal definition in Euclidean space. Mathematically, they can only be true crystals in Riemannian space. Double-twist theories have been developed in describing blue phases, in which the elastic constants of twist K_2 and saddle splay K_{24} are dominant. When

$K_{24} \cong K_2 > 0$, the system has a double twist [16]. For the double-twisted molecular chain orientation in crystals, however, other factors such as the mass (electron) density modulation must also be taken into account.

The double-twist feature of the chain orientation opens new possibilities for designing materials. Since we can achieve a strong chiral strength to suppress the parallel packing scheme in crystal structures, it is likely that other ordering processes such as the formation of supramolecular phase structures may also be suppressed. Therefore, by adjusting the chiral strength, we may extend this tertiary helical structure to a nanosize scale to obtain the helical morphology in self-assembled systems.

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