

Left or Right, It Is a Matter of One Methylene Unit

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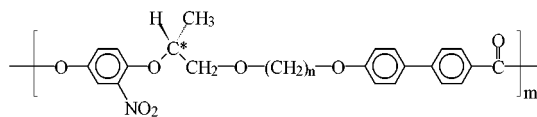
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The concept of chirality plays an increasingly important role in almost all length scales of our recent scientific life with the developments of new asymmetrical syntheses.¹ Intrigued by the helical structures of proteins and DNA in living systems, many research works have focused on the helical conformation in synthetic macromolecules (right-handed, P, or left-handed, M). By tuning the chirality of the residues, repeating units, side chains, or initiators between *dextro* and *levo*, one may obtain a specific handedness in a helical conformation, but not the other.² Helical handedness can also be controlled via external environments including achiral stimuli such as pH, solvent, temperature, light, and salt concentration.³ Of interest is that certain macromolecules can change their chain conformation between P and M, a so-called helix-helix transition, by only changing temperature.⁴

Research in chirality has also brought many insights into other important fields such as chiral liquid crystals and chiral amphiphilic self-assemblies and crystals, all of which deal with helical appearance in different-length scales. Self-assembled helical morphologies have been reported for decades.⁵ Similar to the helix-helix transition of macromolecular conformation, morphological helical handedness changes with temperature in the cholesteric and smectic C* (S_C*) phase have also been found.⁶ The helical morphology in monolayers and bilayers is often considered to be in some ways (intrinsic bending force, effective interaction potential between the two adjacent chiral centers) related to the molecular chiral centers in smaller-length scales.⁷

To investigate these transfers between chirality in different-length scales, we recently designed a main-chain chiral liquid crystalline (LC) polyester, abbreviated as PET(R*-9) (see scheme below).⁸ The covalent bonding connections of these chiral LC repeating units enhanced the chiral strength, and unique helical

single crystals have been observed via isothermal crystallization from LC states. These helical crystals possess an orthorhombic unit cell although three-dimensional translational symmetry is broken due to the helical morphology.⁹ As a result, it becomes a true crystal only in Riemannian space,¹⁰ in which a conversion of the curved crystal in the Euclidean space can be carried out to form a flat crystal having linear and parallel edges. Dark-field images from transmission electron microscopy (TEM) show that these helical crystals possess two twist axes in regard to the molecular orientation and packing, which has also been observed in chromosomes.¹¹ The chiral center in the configurational level was right-handed (R*), and all of the helical crystals observed were also right-handed. To better understand this helical assembly (crystallization) process, we tried to tune the chemical structure first, by changing the handedness of the chiral center from right-handed (R*) to left-handed (L*). The sample was thus abbreviated as PET(L*-9). Second, one or two more methylene units were added into the repeat unit of PET(R*-9), and the new polyesters are abbreviated as PET(R*-10 or 11). Their chemical structures are



The molecular weights of PET(L*-9) and PET(R*-9, 10 and 11) are approximately 10 000–20 000 g/mol, and the polydispersities are approximately 2 after fractionation, as measured by gel permeation chromatography based on polystyrene standards. The thin film sample preparation, crystallization, and TEM experimental procedures are identical to those previously reported.

Figure 1a shows a TEM micrograph of PET(R*-9) helical crystals, which are right-handed. It is expected that the PET(L*-9) helical crystal should possess an opposite handed helicity since the chiral centers in the macromolecules have opposite handedness. Figure 1b is a TEM micrograph of PET(L*-9) helical crystals crystallized at 145 °C for 1 day, and it exhibits a left-handed helicity. This indicates that configurational chirality does alter the morphological chirality. On the basis of this type of analysis, we may expect that PET(R*-10) should also grow a right-handed helical single lamellar crystal. However, it is surprising that Figure 1c shows left-handed PET(R*-10) helical crystals, even though the chiral centers of these PET(R*-9 and -10) on the configurational level are identical. Furthermore, the helical crystal handedness changes back to become right-handed with a morphology similar to Figure 1a when we added one more methylene unit [PET(R*-11)]. This observation clearly illustrates that one methylene-unit difference completely changes the handedness of the helical crystals. This is possible because a different number of methylene units gives rise to a different molecular conformation, leading to different packing schemes. The chiral center on the configurational level thus seems not to be the only dominant role in determining the handedness of the helical crystals since all PETs(R*-9, -10, and -11) possess right-handed chiral centers.

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(1) Janoschek, R. Ed., *Chirality From Weak Bosons to the α -Helix*; Springer-Verlag: Berlin, 1991.

(2) Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336–3343.

(3) (a) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. *Science* **1997**, *277*, 1793–1796. (b) Prince, R. B.; Saven, J. G.; Wolynes, P. G.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 3114–3121. (c) Blout, E. R.; Carver, J. P.; Gross, J. *J. Am. Chem. Soc.* **1963**, *85*, 644–646. (d) Yashima, E.; Maeda, Y.; Okamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8895–8896.

(4) (a) Watanabe, J.; Okamoto, S.; Satoh, K.; Sakajiri, K.; Furuya, H. *Macromolecules* **1996**, *29*, 7084–7088. (b) Cheon, K. S.; Selinger, J. V.; Green, M. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1482–1485.

(5) (a) Rybnikar, F.; Geil, P. H. *Biopolymers* **1972**, *11*, 271–278. (b) Keller, A.; Wills, H. H. *J. Polym. Sci.* **1959**, *39*, 151–173. (c) Saupé, A. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 97–112. (d) Goodby, J. W.; Waugh, M. A.; Stein, S. M.; Chin, E.; Pindak, R.; Patel, J. S. *Nature* **1989**, *337*, 449–452.

(6) Kaspar, M.; Gorecka, E.; Sverenyak, H.; Hamplova, V.; Glogarova, M.; Pakhomov, S. A. *Liq. Cryst.* **1995**, *19*(5), 589–594.

(7) (a) Fuhrhop, J. H.; Helfrich, W. *Chem. Rev.* **1993**, *93*, 1565–1582 and references therein. (b) Sakurai, I.; Karvamura, T.; Dakurai, A.; Kegami, A.; Setoi, T. *Mol. Cryst. Liq. Cryst.* **1985**, *130*, 203–222. (c) Nandi, N.; Bagchi, B. *J. Am. Chem. Soc.* **1996**, *118*, 11208–11216. (d) Nandi, N.; Bagchi, B. *J. Phys. Chem. A* **1997**, *101*, 1343–1351. (e) Kruger, P.; Losche, M. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2000**, *62*, 7031–7043.

(8) Bai, F.; Chien, L. C.; Li, C. Y.; Cheng, S. Z. D.; Percheck, R. *Chem. Mater.* **1999**, *11*, 1666–1671.

(9) (a) Li, C. Y.; Yan, D.; Cheng, S. Z. D.; Bai, F.; Ge, J. J.; He, T.; Chien, L. C.; Harris, F. W.; Lotz, B. *Phys. Rev. B* **1999**, *60*, 12675–12680. (b) Li, C. Y.; Yan, D.; Cheng, S. Z. D.; Bai, F.; Ge, J. J.; He, T.; Chien, L. C.; Harris, F. W.; Lotz, B. *Macromolecules* **1999**, *32*, 524–527. (c) Li, C. Y.; Cheng, S. Z. D.; Ge, J. J.; Bai, F.; Zhang, J. Z.; Mann, I. K.; Harris, F. W.; Chien, L. C.; Yan, D.; He, T.; Lotz, B. *Phys. Rev. Lett.* **1999**, *83*, 4558–4561. (d) Li, C. Y.; Cheng, S. Z. D.; Ge, J. J.; Bai, F.; Zhang, J. Z.; Mann, I. K.; Chien, L. C.; Harris, F. W.; Lotz, B. *J. Am. Chem. Soc.* **2000**, *122*, 72–79.

(10) Kleman, M. *Adv. Phys.* **1989**, *38*, 605–667.

(11) (a) Kleman, M. *Rep. Prog. Phys.* **1989**, *52*, 555–654. (b) Livolant, F.; Bouligand, Y. *J. Phys.* **1986**, *47*, 1813–654.

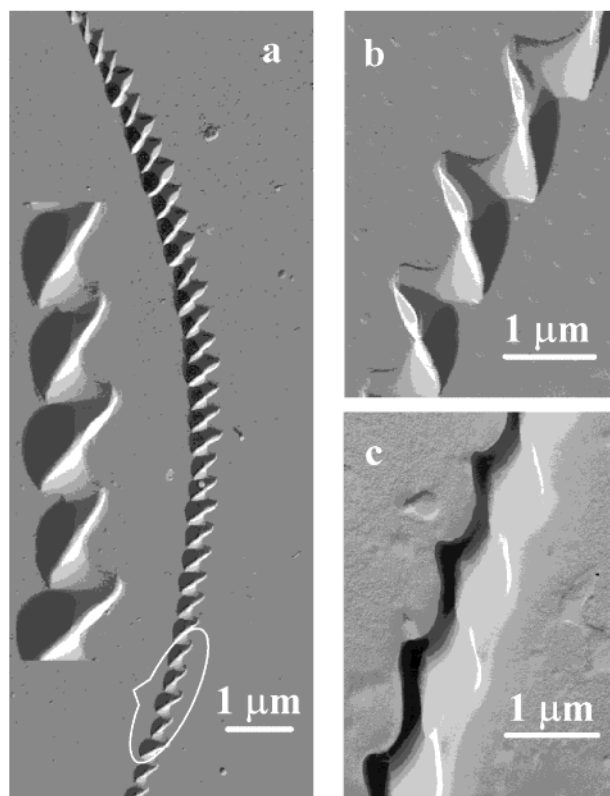


Figure 1. TEM micrograph of PET(R*-9) right-handed helical single crystal crystallized at 145 °C for 1 day (a), PET(L*-9) right-handed helical single crystal crystallized at 145 °C for 1 day (b), and PET(R*-10) left-handed helical single crystal crystallized at 130 °C for 1 day (c).

To understand these intriguing observations, a cascade of chirality in different-length scales must be defined. On the basis of a general concept in biomacromolecules, there are at least four levels of chirality (Figure 2). The first level is related to the chiral center, originating from different chemical groups covalently connected to an atom, which have no mirror symmetry (configurational chirality). The second level of chirality is attributed to different handednesses of molecular conformations (conformational chirality). The third level is associated with the phase structures of helical monodomains or single crystals (phase chirality). Aggregation of the helical monodomains constructs a macroscopic chiral object, which belongs to the highest (the fourth) level of this chirality (object chirality). On the basis of this concept, the helical single crystals belong to the third level chirality, and a transferring mechanism between the neighboring chirality in different-length scales is essential to understand the handedness dependence of these helical single crystals. Our understanding is that it is the interaction and packing scheme instead of the lower-level chirality itself that determine the next level chirality. This point can also be proven in other examples. For example, different conformational chiralities (P or M) have been observed at different environments for the same materials. It has also been reported that a copolymer consisting of 56% (R*)- and 44% (L*)-polyisocyanates possess the same helical conformation as the R*-polyisocyanate homopolymer, indicating that the L*-enantiomer in the copolymer is forced to adopt the same

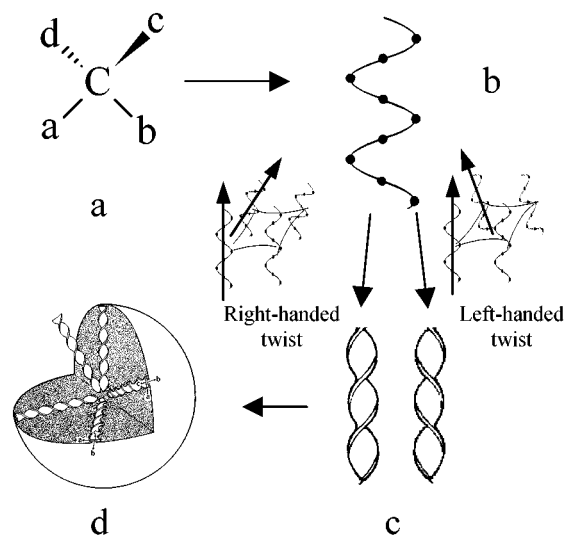


Figure 2. Chiralities in different-length scales: configurational (a), conformational (b), phase (c), and object (d) chiralities. The transfer of the conformational chirality to the phase chirality is dominated by intermolecular interactions via chain packing.

conformation as that of R-enantiomers.¹² In the present case, the helical crystals have different handednesses for PETs(R*-9 and -11) (right-handed) and PET(R*-10) (left-handed), respectively, although on the configurational level these polymers possess the identical R*-chiral center. Therefore, the intermolecular packing scheme has to be essential in the formation of third-level chiral structures, while the first-level chirality may only play roles via the conformation and packing. This argument can also be supported by the newly developed chiral LC phase from achiral banana-shaped liquid crystals.¹³ In these liquid crystals, molecules do not have chiral centers, and thus, on the level of configurational structure, they are achiral. However, helical morphology, ferroelectric properties, and the third-level (phase) chirality have been observed due to the bent mesogen cores, which gives rise to the spontaneous polar symmetry-breaking. Although the helical morphology is degenerated, banana-shaped liquid crystals provide a perfect example that the molecular packing is one of the most important steps during the formation of the third and fourth levels of chirality. In other words, the transfer of chirality from one length scale to another is neither automatic nor necessary. Attempts to relate the chiral structure in the configurational and conformational levels to the chiral structure in the phase- and object length scales in solid states without knowing the molecular packing is an incomplete practice.

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JA005805L

(12) (a) Green, M. M.; Garetz, B. A.; Munoz, B.; Chang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4181–4182. (b) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860–1866.

(13) (a) Niori, T.; Sekine, T.; Watanabe, J.; Furukawa, T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231–1233. (b) Link, D. R.; Natale, G.; Shao, R.; MacLennan, J. E.; Clark, N. A.; Korblova, E.; Walba, D. M. *Science* **1997**, *278*, 1924–1927. (c) Heppke, G.; Moro, D. *Science*, **1998**, *279*, 1872–1873.