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Helical Structures

Lamellar-Twisting-Induced Circular Dichroism of Chromophore Moieties in Banded Spherulites with Evolution of Homochirality**

*Ming-Chia Li, Hsiao-Fang Wang, Chen-Hung Chiang, Yu-Der Lee, and Rong-Ming Ho**

Abstract: *Banded spherulites are formed by crystallization of a chiral polymer that is end-capped with chromophore. Induced circular dichroism (ICD) of the chromophore can be found in the crystallized chiral polymers, giving exclusive optical response of the ICD. The ICD signals are presumed to be driven by the lamellar twisting in the crystalline spherulites, and the exclusive optical activity is attributed to the chirality transfer from molecular level to macroscopic level. To verify the suggested mechanism, the sense of the lamellar twisting in the crystalline spherulite is determined using PLM for the comparison with the ICD signals of the chromophore in the electron circular dichroism spectrum. The conformational chirality of the chiral polymer is determined by the vibrational circular dichroism spectrum. On the basis of the chiroptical results, evolution of homochirality from helical polymer chains (conformational chirality) to lamellar twisting in the banded spherulite (hierachical chirality) is suggested.*

Among self-assembled architectures, the helical morphology is probably the most fascinating texture in nature. By introducing the chirality into synthetic molecules, helical textures in different length scales can be obtained from self-assembly through interplay of non-covalent interactions.[1] The chirality effect on supramolecular self-assembly in chiral polymers possessing chiral entities has been systematically examined.[2] Helical superstructures and phases can be formed by the self-assembly of those chiral polymers owing to the steric hindrance effect, and helical morphologies with exclusive handedness might be acquired through chirality transfer from molecular level.[3] With non-covalent association, a series of achiral dynamic chiral polymers having functional groups capable of interacting with optically active small molecules may adopt predominantly one-handed helical conformation through induced chirality so that helical assemblies can be formed from the self-assembly of the induced chiral polymers.[4] Among the varieties of helical morphologies, a banded spherulite (that is, the presence of spherulitic crystalline morphology with extinction rings under polarized light microscope (PLM) observations) is commonly found in polymeric crystallites.[5] The formation of the banded spherulite is attributed to lamellar twisting along the radial growth direction.[6] However, the origins of the crystalline lamellar twisting are still controversial. For chiral polymers with regular configuration (that is, tacticity) but flexible chains (for example isotactic or syndiotactic C–C single bonds), the lamellar twisting appears to result from the imbalanced stress at opposite folding surfaces owing to different fold structures or conformations at the fold surfaces.[7]

Herein, banded spherulites were found to form by crystallization of chiral polylactides (poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA)) end-capped with a chromophore. Induced circular dichroism (ICD) of the chromophore can be found in the crystallized PLLA and PDLA, giving an exclusive optical response of the ICD. We speculate that the ICD signals are driven by the lamellar twisting in the crystalline spherulites, and the exclusive optical activity is attributed to the chirality transfer from molecular level to macroscopic level. To verify the suggested mechanism, the sense of the lamellar twisting in the crystalline spherulite is determined using PLM for the comparison with the ICD signals of the chromophore in electron circular dichroism (ECD) spectrum. The conformational chirality of the chiral polylactide is determined by vibrational circular dichroism (VCD) spectrum. On the basis of the VCD results of the chiral polylactides and the ECD results of the chromophore labeled at the chain end of the helical polymer, evolution of homochirality from the helical polymer chain (conformational chirality) to the lamellar twisting in the banded spherulite (hierachical chirality) is suggested.

Table 1 summarizes the characterization of the pyrene-labeled chiral polylactides examined in this study. To develop the lamellar twisting in the crystallized PLLA and PDLA, isothermal crystallization was conducted and the corresponding crystallization kinetics were examined by differential scanning calorimetry (DSC). The peak of exothermic crystallization can be observed when isothermal crystallization temperature is higher than the glass transition temperature (T_g) of the pyrene-labeled PLLA but is lower than 130 °C. Note that the peak time of crystallization, which is approximately proportional to the reciprocal of the crystallization rate, gradually decreases with increasing the crystallization temperature and experience a minimum value at approximately 90 °C.[8] Subsequently, the peak time of crystallization gradually increases with increasing the crystallization temperature until 120 °C. Consistent with the DSC results, banded spherulite can be found in isothermally crystallized pyrene-labeled PLLA while the crystallization temperature is over

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[*] Dr. M.-C. Li, H.-F. Wang, C.-H. Chiang, Prof. Y.-D. Lee, Prof. R.-M. Ho
Department of Chemical Engineering
National Tsing Hua University
101, Section 2, Kuang-Fu Road, Taiwan, 30013 (ROC)
E-mail: rmho@mx.nthu.edu.tw
Homepage: http://www2.che.nthu.edu.tw/HO_LAB/

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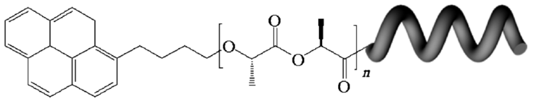
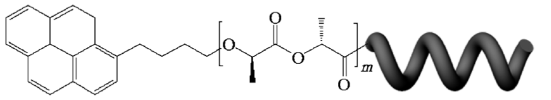
Table 1: Characterization of pyrene-labeled chiral polymers.



(I)



(II)

Sample code	M_n[a] [g mol^{-1}]	M_n/M_w[b]	T_g [°C][c]	T_m [°C][c]
Pyrene-labeled PLLA (I)	16600	1.48	45.0	148.0
Pyrene-labeled PDLA (II)	17300	1.45	56.5	153.3

[a] M_n was determined by ^{1}H NMR. [b] Determined by GPC. [c] T_m and T_g of the pyrene-labeled polymers isothermally crystallized at 120 °C measured by DSC at a heating rate of 10 °C min^{-1}.

the T_g of PLLA (Supporting Information, Figure S1a). Also, the corresponding band spacing of the banded spherulite increases with increasing crystallization temperature (Figure S1b), indicating that the increase in crystallization temperature results in the reduction of twisting power.[9] Similar results can also be found in pyrene-labeled PDLA isothermally crystallized at different crystallization temperatures from the melt state.

To identify the sense of lamellar twisting in the banded spherulite, a home-made goniometer was introduced in the microscope stage to hold the sample, and the sample was rotated along the Y-axis. By analogy between a twisted lamellae and a screw, a twisted lamellae rotated in the sense of its own twist leads to a descent of the corresponding extinction rings because a right-handed positive rotation applied to a right-handed screw conducts to a visual descent of the apparent screw thread. By contrast, a right-handed positive rotation of a left-handed screw leads to a visual raise of the apparent screw thread so that opposite effect (that is, a raise of the corresponding extinction rings) will be observed.[6b,10] Figure 1 a and b show the PLM images of pyrene-labeled PLLA and pyrene-labeled PDLA isothermally crystallized at 110 °C with the use of gypsum plate. Figure 1 c and d show the PLM images of the central vertical slices of the banded spherulites of pyrene-labeled PLLA (Figure 1 a) and pyrene-labeled PDLA (Figure 1 b) subjected to a right-handed rotation. In the case of pyrene-labeled PLLA (Figure 1 c), a descent of the extinction rings can be clearly seen, underlined with the AA′ and BB′ lines, suggesting that the screw goes in the same sense with the applied rotation. Accordingly, the twisted lamellae appear to be left-handed. By contrast, in the case of pyrene-labeled PDLA (Figure 1 d), the inverse behavior is observed, underlined with the CC′ and DD′ lines. As a result, the sense of twisting of the lamellae is opposite to the sense of rotation, suggesting that the twisted lamellae are right-handed. Moreover, both banded spherulites appear as negative birefringence texture (that is, the first and third quadrants of spherulite appear yellow but the second and fourth quadrants appear blue); namely, the orientation of the polymer chain in the helical

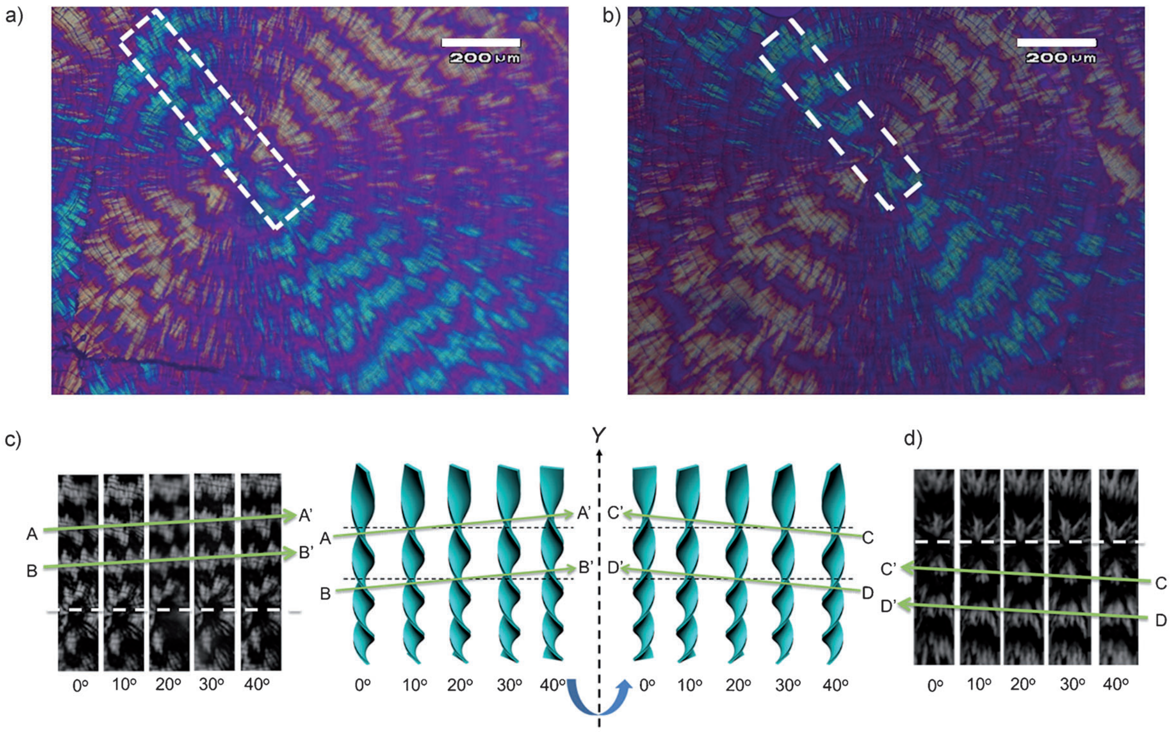


Figure 1. PLM images of a) pyrene-labeled PLLA and b) pyrene-labeled PDLA isothermally crystallized at 110 °C with the use of gypsum plate. The delimited areas in (a) and (b) represent the observed slices during the rotation experiment. Vertical sections of c) pyrene-labeled PLLA and d) pyrene-labeled PDLA spherulites observed by polarized optical microscopy during the rotation. The value at the bottom represents the angle of twist around the Y axis in the right-handed positive sense. Scale bars: 200 µm.

lamellar crystals is perpendicular to the radial (growth) direction of banded spherulite (see below for details).

To further investigate the lamellar twisting in the banded spherulite of the chiral polylactide, the pyrene moiety in the chiral polylactide was used as a molecular probe. Figure 2 shows the CD and corresponding absorption spectra of the pyrene-labeled chiral polymers isothermally crystallized at different temperatures from the melt state. As observed from the spectra, an induced negative split-type Cotton effect with negative Cotton effect at 345 nm followed by positive Cotton effect at 337 nm, attributed to the characteristic absorption band along the long axis in the molecular plane of pyrene moiety between 300–350 nm,[4h,11] can be clearly identified when the isothermal crystallization of the pyrene-labeled PLLA is carried out at 110 °C. Namely, banded spherulites with preferentially left-handed character can be formed. By contrast, for amorphous pyrene-labeled PLLA (that is, rapidly cooled sample from the melt state to 25 °C), the CD spectrum is silent. These results suggest that the pyrene moiety at the chain end of the chiral polylactide is cryptochiral.[12] For the banded spherulites of pyrene-labeled PDLA with preferentially right-handed character, a mirror-image of the ICD spectrum of pyrene-labeled PLLA can be found. Note that the CD signals might result from the anisotropic arrangement of the polymeric crystalline, which gives significant LD signals resulting in artificial CD signals. To clarify the origins of the CD signals, LD measurements were performed (Supporting Information, Figure S2). No significant LD signal in the range of 300 to 500 nm can be found. Similar results can be observed in the pyrene-labeled PDLA. Accordingly, there is no anisotropic effect on spectroscopic measurements. As a result, those results suggest that the ICD signals of the pyrene chromophore at the chain end of polylactide-containing chiral polymer are indeed driven by the crystallization of the chiral polylactides. Most interestingly, the induced optical activity of the pyrene moiety in the crystallized chiral polymers can be defined by the helicity of chiral entity in the chiral polymers and is in line with the hierarchical chirality of the banded spherulite.

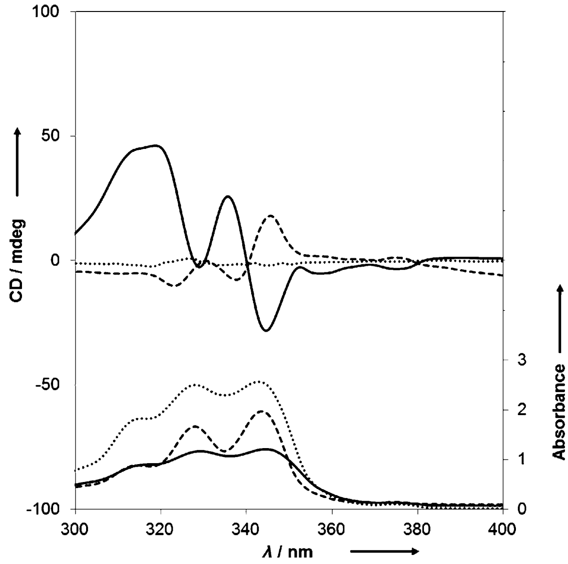


Figure 2. CD and UV/Vis spectra of banded spherulite of pyrene-labeled PLLA (——) and PDLA (-----) isothermally crystallized at 110 °C and amorphous pyrene-labeled PLLA (•••••).

To systematically examine the crystallization effect on the ICD of the pyrene moiety, the CD spectra of the pyrene-labeled PLLA isothermally crystallized at different temperatures from the melt state were acquired. Figure 3 shows the CD and corresponding UV/Vis absorption spectra of pyrene-labeled PLLA isothermally crystallized at different temperatures from the melt state. Consistently, an induced negative split-type Cotton effect of the pyrene moiety can be clearly observed once banded spherulites were formed. Also, an induced negative Cotton effect of the pyrene moiety, attributed to the characteristic absorption band along the short axis in the molecular plane of the pyrene moiety between 260–290 nm,[4h] can be clearly observed. Most interestingly, the ICD signals of the pyrene moiety will increase with increasing the crystallization temperature. By contrast, no ICD signals at the absorption bands of the pyrene moiety can be found when the chiral polylactides are in the amorphous state, reflecting that the ICD signals of the pyrene moiety are truly attributed to the formation of banded spherulite. Also, as shown in the UV/Vis absorption spectra, the characteristic absorption bands of the pyrene moiety between 300 to 350 nm gradually shift toward longer wavelength (that is, bathochromical shift) with the increase in crystallization temperature, suggesting that increasing crystallization temperature will give rise to the formation of a slipped π–π stacked J aggregation in banded spherulite and further decrease in the intermolecular distance between pyrene moieties, giving the split-type ICD signals with the enhancement of the ICD signals as the CD couplet intensity is inversely proportional to the square of the inter-chromophoric distance.[13]

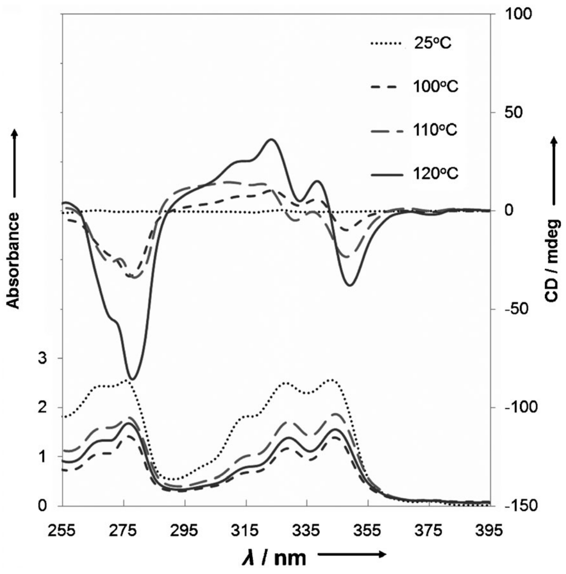


Figure 3. CD and corresponding UV/Vis absorption spectra of pyrene-labeled PLLA isothermally crystallized at different temperatures.

To systematically investigate the chirality effect on the formation of banded spherulite and corresponding chirality transfer, the chiralities in various length scales are detected by chiroptical methods. According to our previous studies,[3d] the molecular chirality in the chiral polylactides can be identified by CD; a positive CD signal from L-lactic acid and a negative one from D-lactic acid at 210 nm are found, and the characteristic absorption band is attributed to the n→π* transition of carboxylate chromophore in the lactic acid. By contrast, the solution of D,L-lactic acid yields no CD signal. However, for chiral polymers with chiral entities on their polymer backbone (main-chain chirality), such as polylactides, the handedness of the helical conformation cannot be simply determined from the CD results because the n→π* transition is relatively delocalized so that the CD results might be significantly affected by the neighboring chiral centers on the corresponding absorptions. Notably, as compared to the electron transitions in CD, the absorptions that are attributed to molecular vibrational motions are less sensitive to the neighboring vibrational modes so that VCD can be utilized as a powerful method in determining the handedness of the helical conformation of chiral polymer with main-chain chirality.[14] Figure 4 shows the VCD and corresponding IR absorption spectra of pyrene-labeled PLLA and pyrene-labeled PDLA isothermally crystallized at different temperatures from the melt state. For amorphous pyrene-labeled PLLA, a negative split-type Cotton effect with a negative VCD band at 1750 cm^{-1} and a positive band at 1767 cm^{-1} can be found. The inflection point at 1759 cm^{-1} corresponds to the characteristic absorption of the C=O stretching motion of the ester group in polylactide with the electric transition moment perpendicular to the helical axis of the chiral polylactide. Consistently, the VCD spectrum of amorphous pyrene-labeled PDLA appears as the mirror-image of the spectrum of amorphous pyrene-labeled PLLA (Figure 4). On the basis of the coupled oscillator model and the signatures of the split-type Cotton effect in the VCD spectra,[4d,14c,15] the Cotton effect in the pyrene-labeled PLLA is identified as negative chirality whereas that in the pyrene-labeled PDLA is identified as positive chirality. Namely, the helical conformation of the pyrene-labeled PLLA is left-handed, and the pyrene-labeled PDLA therefore exhibits a right-handed helical conformation. These results suggest that the chiral polylactide indeed has a preferential one-handed helical conformation in amorphous state. Most importantly, once the crystallization occurs to give the formation of banded spherulite, the intensity in the optical activity of the conformational chirality is significantly amplified. Also, the absorption band of the C=O stretching motion undergoes hypsochromic shift, suggesting the occurrence of intramolecular interaction of C=O chromophore of the ester group in the chiral polylactide, resulting from the folding of the polymer chains into crystalline lamellae that enhances the optical activity. Most interestingly, an induced VCD signals in the absorption bands of the C-O-C vibration in the range from 1000 to 1250 cm^{-1} appear in the crystallized pyrene-labeled PLLA and pyrene-labeled PDLA. By contrast, for amorphous pyrene-labeled chiral polylactides, the VCD signals in the absorption bands of the C-O-C vibration are silent. Note that the electron transition dipoles of the C-O-C vibration are almost parallel to the helical axis of chiral polylactide. As a result, we suggest that the split-type Cotton effect of the induced VCD signals in the absorption bands of the C-O-C vibration is attributed to the occurrence of intermolecular interaction from the C-O-C stretching at which the tilted helical chains in adjacent lamellae drive the crystal twisting with preferential direction along the radial direction of spherulite, giving the formation of banded spherulite with preferential left- or right-handedness (see below for details).

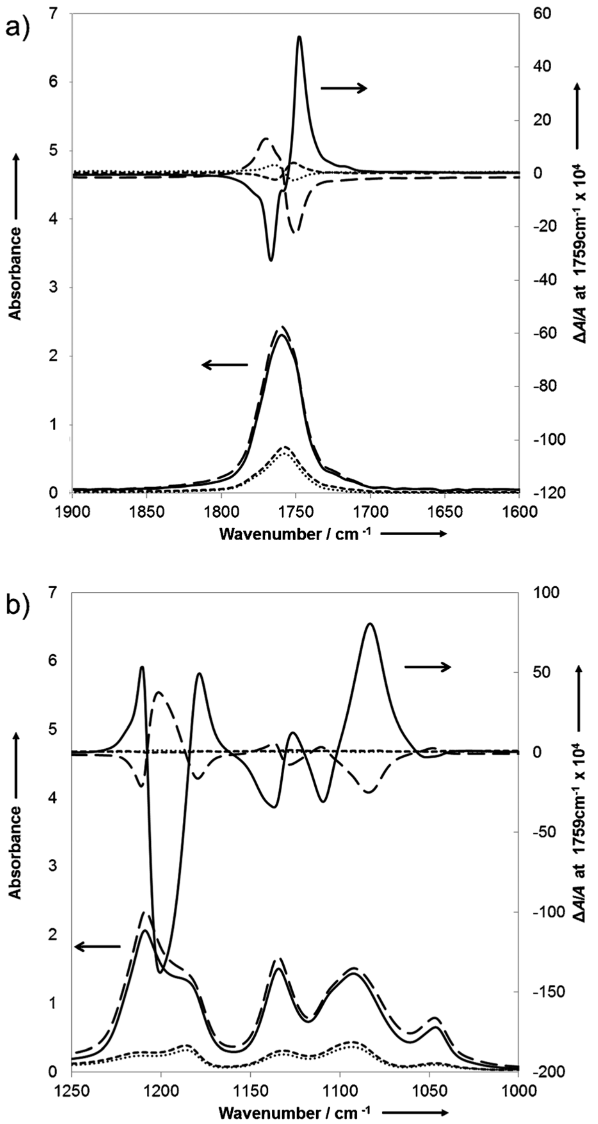
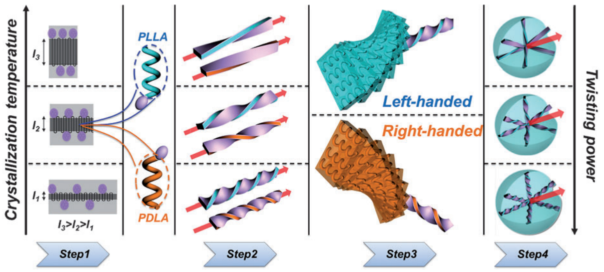


Figure 4. VCD and corresponding FTIR absorption spectra of a) C=O and b) C-O-C vibration in pyrene-labeled PLLA and PDLA in amorphous and crystallized states: ••••• amorphous PLLA, ----- amorphous PDLA, –•–• banded PLLA, —— banded PDLA.

To quantitatively examine the effect of crystallization temperature on the lamellar thickness, thermal analyses and also scattering experiments were conducted (see the Supporting Information for details). As shown in Figure S3b and S4b, the lamellar thickness is indeed strongly dependent upon the isothermal crystallization temperature and the dependence is in line with the predicted results from Lauritzen–Hoffman theory; the calculated results indicate that the lamellar thickness intrinsically increases with increasing the crystallization temperature. Note that the pyrene moieties will be excluded out from the crystallization of the polylactide and reallocated to the folding surface of the crystalline lamellae. Consequently, the average intermolecular distance of pyrene moieties on the crystalline folding surface will decrease with increasing the crystallization temperature owing to the increase in the areal density of pyrene moieties on the folding surface, resulting from the increase of crystalline lamellar thickness. As a result, the ICD signals of the pyrene moiety (Figure 3) and the excimer emission (Figure S5) will increase with increasing the crystallization temperature owing to the increase on the probability for the association of the pyrene moieties. It is also noted that the interaction between two chromophores in separate lamellae could be responsible for the induced optical activity, and the twisting within the lamellae could change with the crystallization temperature, resulting in the variations on the ICD. However, on the basis of the ICD and the SAXS results, we speculate that the effect of the interaction between two chromophores in separate lamellae is insignificant for the induced optical activity and the effect of twisting angle should not be critical on the ICD (see the Supporting Information for a detailed discussion).

On the basis of the spectroscopic results and the PLM observations, a hypothetical mechanism for the growth of banded spherulite and the transfer of chirality from molecular chirality into hierarchical chirality in the pyrene-labeled chiral polylactide is proposed, and illustrated in Scheme 1. The chiral entity in the chiral polylactide not only leads the formation of helical conformation but also determines the handedness of the helical conformation, giving a preferential one-handed helical conformation by an intramolecular chiral interaction. As crystallization occurs, the helical polymer chains will fold into crystalline lamellae and exclude out the end-capped chromophore moieties (Step 1). The imbalanced stress at opposite folding surfaces due to different fold structures or conformations at the fold surfaces result in the twisting of cyrstalline lamellae (Step 2). Owing to the effect of specific helical steric hindrance on intermolecular packing in crystalline core and microdomain stacking, each crystalline lamella will twist toward a specific direction for the growth of the crystalline lamellae, yielding a helical superstructure with preferential handedness (Step 3). Eventually, the radial growth of the helical lamellae with the polymer chains perpendicular to the radial direction from the center of the spherulite, as evidenced in Figure 1 a and 1 b, will develop as a banded spherulite with a specific handedness (that is, a helical phase with exclusive handedness) by the transfer of homochirality (Step 4).



Scheme 1. Illustration of the formation of banded spherulite and the hypothetical mechanism of chirality transfer in the crystallized pyrene-labeled polylactides. Purple ellipses, red arrows, and *l* indicate the chromophore, the radial growth of the twist lamellae in spherulite, and lamellar thickness, respectively.

In summary, a method for systematically studying the chirality transfer in different length scales has been developed to elucidate insights into morphological evolution from the molecular level. Direct visualization of helical phases using PLM equipped with a home-made goniometer clearly reveals the formation of left- and right-handed helical superstructures (that is, twisting lamellae) in the banded spherulites of the pyrene-labeled PLLA and PDLA, respectively. VCD can be used to investigate the handedness of the helical conformation; the split-type VCD spectrum in the absorption band of C=O vibration with negative chirality suggests a preferential left-handed helical conformation of the PLLA whereas a positive chirality of the PDLA suggests a preferential right-handed helical conformation. Furthermore, the split-type induced VCD signals in the absorption bands of the C-O-C vibration indicate the tilted helical chains in adjacent lamellae with preferential direction along the radial direction of spherulite. The significant ICD, the bathochromic shift of fluorescence and the absorption results of the pyrene moiety end-capped at the chain end of the chiral polylactide driven by crystallization suggests the occurrence of twisting and shifting (that is, J aggregation) with preferential direction that is due to the imbalanced stress at opposite folding surfaces. Owing to the effect of chirality on intermolecular packing in crystalline core and lamellae stacking, the twisting and shifting mechanism thus leads to the formation of helical superstructure in the enantiomeric crystalline polylactide homopolymer from self-assembly, and also dictates the handedness of the forming banded spherulite by stacking the chiral polymer chains in a preferred direction along the growth of the crystalline lamellae, giving a preferential handedness. Accordingly, evolution of homochirality from molecular chirality into hierarchical chirality is demonstrated in the self-assembly of the enantiomeric polylactides by the twisting and shifting mechanism.

Experimental Section

The characterization of the pyrene-labeled chiral polylactides is summarized in Table 1. Pyrene-labeled polylactides (pyrene-labeled poly(L-lactide) (pyrene-labeled PLLA) and pyrene-labeled poly(D-lactide) (pyrene-labeled PDLA)) with different handedness were synthesized. The detailed procedures for the synthesis of the pyrene-labeled chiral polylactides were described in our previous studies.[16] Furthermore, sandwich-like pyrene-labeled polylactide thin-film samples were prepared by hot impression between two quartz glass at 160 °C for 30 min to eliminate the crystalline residues formed during synthetic processes, and followed by fast cooling to preset temperatures for isothermal crystallization. The thin-film samples of amorphous pyrene-labeled polylactides were prepared as described in our previous study.[16] The film thickness was 10 μm.

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