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Controlled Handedness of Twisted Lamellae in Banded Spherulites of Isotactic Poly(2-vinylpyridine) as Induced by Chiral Dopants

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Abstract: *Herein, we suggest a unique approach to control the handedness of twisted lamellae in banded spherulites of a stereoregular polymer, isotactic poly(2-vinylpyridine) (iP2VP). When (R)- or (S)-hexahydromandelic acid (HMA), which can associate with iP2VP, was introduced as a chiral dopant, mirror-image CD spectra in the complex systems showed induced circular dichroism (ICD) of the iP2VP by chiral HMA. Banded spherulites resulting from lamellar twisting due to the imbalanced stresses at the opposite folding surfaces could be formed by crystallization of the iP2VP/HMA complexes, which had a crystalline structure similar to that of neat iP2VP. A preferential sense of the twisted crystalline lamellae was found in the iP2VP/HMA complex, thus suggesting homochiral evolution from conformational to hierarchical chirality.*

Chirality at the molecular scale is vital for driving the formation of helical structures with different length scales. In polymers, a stereogenic center could be introduced in either the backbone or side chains. Such chirality usually leads to a helical conformation of the polymer owing to steric hindrance from intramolecular chiral interactions. By taking advantage of ordering through self-assembly, those helical chains can be collectively packed as hierarchical helical superstructures as a result of intermolecular chiral interactions.[1] Owing to the effect of steric hindrance, it may be possible to generate helical morphologies and superstructures with exclusive handedness through chirality transfer from the molecular level.[2] Helical polymers can be classified into two types: static and dynamic, depending on the nature of the helical conformation. A static helical polymer possesses a stable helical conformation with optical activity, whereas a dynamic helical polymer may adopt an alternating sequence of left- and right-handed helices separated by helical reversals. For a dynamic helical polymer, the formation of a stable helical conformation might be possible by the complexation of chiral dopants. This effect is known as induced circular dichroism (ICD).[3] Most dynamic helical polymers with ICD have conjugated or peptide-based backbones, and the rigidity of the main chain stabilizes the forming helical conformation.[3c] Examples of polyolefins and vinyl polymers with induced chirality are rare. Recently, stereoregular vinyl polymers with backbones composed of C–C bonds were successfully used for the association of a variety of chiral guest molecules with functional side chains to give ICD signals. The ICD behaviour was found to be strongly dependent on the isotacticity of the poly(2-vinylpyridine) polymers and the acidity and bulkiness of chiral acids used as guests.[4]

In this study, we used stereoregular isotactic poly(2-vinylpyridine) (iP2VP) for self-assembly with ICD and crystallization as banded spherulites, and observed concentric rings or extinction bands by polarized-light microscopy (PLM) of the resulting crystals. The formation of iP2VP banded spherulites is attributed to the twisting of crystalline lamellae as a result of the imbalanced stresses at the opposite folding surfaces. By the introduction of chiral dopants, the crystallization of iP2VP with ICD could be used as a model system to examine the feasibility of controlling the handedness of the twisted lamellae. Specifically, we examined homochiral evolution through the self-assembly of stereoregular polymers, as directed by the associated chiral dopants. This approach may provide a new mechanism for homochiral evolution through self-assembly, which is critical for key molecular processes and relies on a delicate balance between molecular and hierarchical chirality. A preferential chain helicity can be induced by complexation with chiral HMA for homochiral evolution from molecular to conformational chirality (Figure 1). The crystallized iP2VP with complexed HMA showed twisted lamellae with controlled handedness but without a change in its intrinsic crystalline structure. Thus, banded spherulites with specific optical activity could be formed by collective growth of the twisted lamellae to enable homochiral evolution from conformational to hierarchical chirality.

Figure 2a shows the UV/Vis and CD spectra of iP2VP and the iP2VP/HMA complex in the solution state. The absorption peak at 260 nm is ascribed to the π–π* transition of the pyridine rings of iP2VP. Mirror-image CD spectra were clearly identified for the iP2VP/(*S*)-HMA and iP2VP/(*R*)-HMA complexes in 1,2-dichloroethane, whereas iP2VP without a chiral dopant was CD silent, thus suggesting ICD behavior of iP2VP. This result indicates the association of HMA with the pyridyl groups of iP2VP. Note that it is not possible to record the UV/Vis spectrum below 230 nm in solution owing to the cut-off effect of the solvent used. Similar ICD behavior

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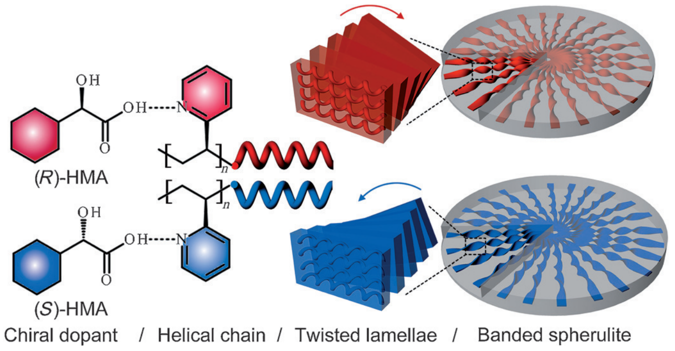

Figure 1. Schematic illustration of the controlled handedness of twisted lamellae as driven by induced chirality.

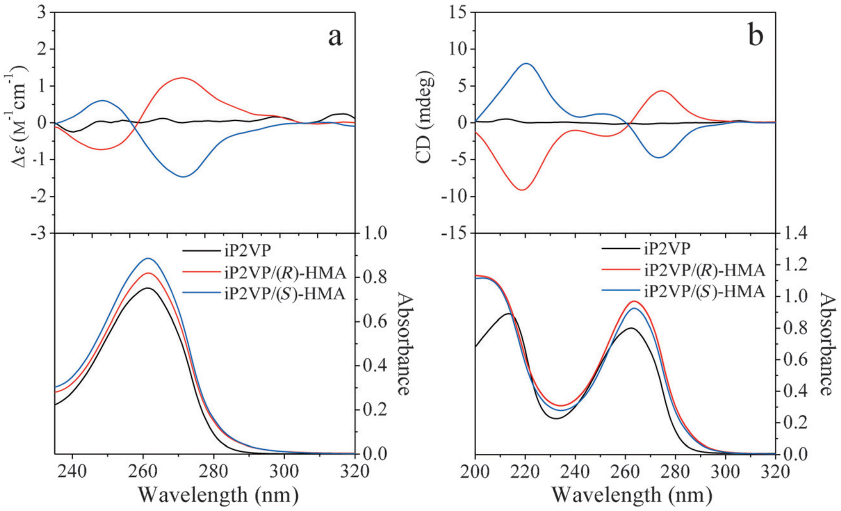

Figure 2. CD spectra of iP2VP without a dopant and iP2VP/HMA complexes a) in 1,2-dichloroethane and b) as thin films.

with mirror imaging of the CD spectra was observed for films of the iP2VP/HMA complex (Figure 2b). Moreover, the association of chiral HMA with iP2VP was further evidenced by Fourier transform infrared (FTIR) spectroscopy (see Figure S1 in the Supporting Information). In the presence of HMA, the characteristic absorption band at 1590 cm^{-1}, resulting from the C–C and C–N stretching vibrations in the pyridine rings of iP2VP,[5] broadened and shifted toward a higher wavenumber (hypsochromic shift), thus indicating the association of iP2VP and HMA owing to acid–base complexation.[4] Also, the Cotton effect was found at a shorter wavelength (ca. 220 nm; Figure 2b). In contrast to the Cotton effect of neat HMA at 210 nm (see Figure S2), we speculate that this CD signal can be attributed to the association of iP2VP and HMA. Since the CD signals could result from anisotropic texture, which gives rise to significant linear dichroism (LD) signals observed as artificial CD signals, we performed LD measurements to clarify the origin of the ICD signals (see Figure S3). No significant LD signal in the range from 200 to 320 nm was found, thus suggesting the absence of an anisotropic effect on spectroscopic measurements.

For iP2VP complexed with (*R*)-HMA in the film state, a split CD spectrum with a positive Cotton effect at 275 nm followed by negative Cotton effect at 255 nm was found (Figure 2b). The inflection point at 260 nm corresponds to the maximum absorption of the π–π* transition of the pyridine rings of iP2VP that are associated with (*R*)-HMA. Consistently, the ICD spectrum of iP2VP complexed with (*S*)-HMA appeared as the mirror image of that iP2VP with (*R*)-HMA. On the basis of the exciton chirality method, the signature of the split-type Cotton effect in the ICD spectrum of the complex of iP2VP and (*S*)-HMA was thus identified as negative chirality, whereas that for the complex with (*R*)-HMA was identified as positive chirality.[6] Namely, the iP2VP chains with (*R*)-HMA and (*S*)-HMA are right-handed and left-handed, respectively, thus reflecting homochiral evolution from the molecular level (i.e., HMA) to the conformational level (i.e., iP2VP) in the solid state. A PLM image of neat iP2VP crystallized in a thin film shows banded spherulites of iP2VP (Figure 3a). The formation of the banded spherulites is attributed to lamellar twisting along the radial growth direction.[7] For helical polymers with a regular configuration but flexible chains, lamellar twisting is generally attributed to the imbalanced stresses at opposite folding surfaces owing to different fold structures or conformations at the fold surfaces.[8] As for neat iP2VP, banded spherulites were also observed in crystallized films of iP2VP in the presence of chiral HMA (Figure 3b,c).

The handedness of the twisted lamellae in the spherulites could be conveniently detected by a rotation experiment,[2c,9] for which the sample was rotated along the direction perpendicular to the light path, and a series of images were captured at different angles. The rotation of a twisted lamella in the sense of its own twist leads to a descent of the corresponding extinction rings, in the same way as a right-handed positive rotation applied to a right-handed screw leads to a visual descent of the apparent screw thread. In contrast, a right-handed positive rotation of a left-handed screw leads to a visual rising of the apparent screw thread, and by analogy, the opposite effect, that is, a rising of the corresponding extinction rings, is observed for a twisted lamella. For iP2VP crystallized with (*R*)-HMA, a descent of the extinction rings was observed (Figure 4, as underlined by the lines AA′ and BB′), thus suggesting that the screw turns in the same sense as the applied rotation (i.e., right-handed lamellae). By comparison, the inverse behavior was observed in the case of iP2VP crystallized with (*S*)-HMA (as underlined by the lines CC′ and DD′). This result indicates that the sense of twisting of the lamellae is opposite to the sense of rotation, and thus the lamellae are left-handed. The spherulites of neat iP2VP exhibited equal populations of right-handed and left-handed twisted lamellae, as expected. By contrast, the spherulites of iP2VP crystallized with one enantiomer of HMA exhibited a preferred handedness, which depended on the chirality of the dopant. On the basis of the morphological observations, the twisting direction of lamellae is expected to be controlled

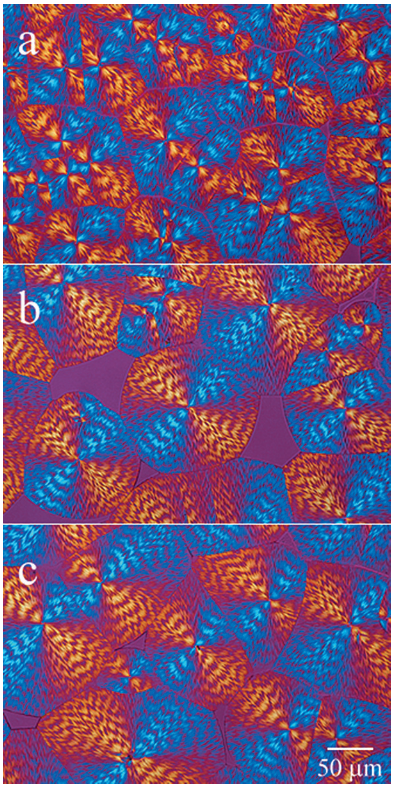

Figure 3. PLM images of iP2VP crystallized isothermally at 120 °C a) without a dopant, b) with (*R*)-HMA, and c) with (*S*)-HMA.

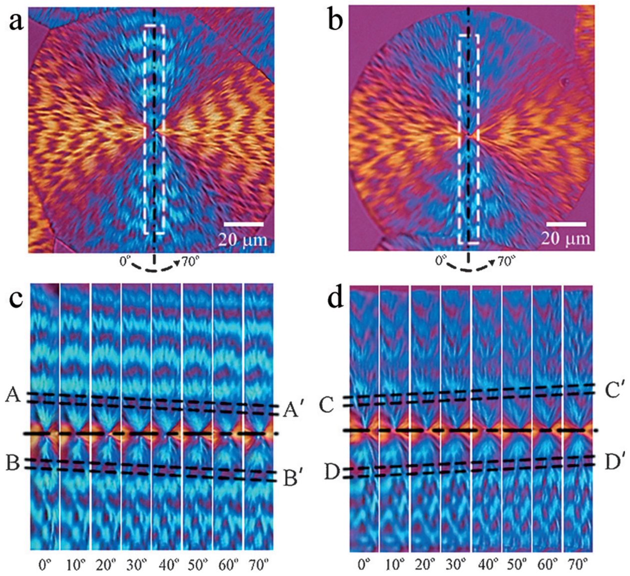

Figure 4. a, b) PLM images of iP2VP crystallized isothermally at 120 °C with (*R*)-HMA (a) and (*S*)-HMA (b). c, d) Vertical sections of PLM images (a) and (b), respectively. The series of images of spherulites was captured during rotation. The values at the bottom show the rotation angle in the right-handed positive sense.

by the preferential handedness of the helical-chain conformation, as induced by the introduced chiral dopant. Thus, homochiral evolution from the chain conformation to the hierarchical structure was observed.

Since the iP2VP crystal shows overall chirality, all the chains in the lamellae should possess the same helical conformation. Thus, the helical conformation of chains within one lamella should be determined by the initial nucleation. The helical conformation of iP2VP chains was determined by the chiral dopant added to the solution, and subsequently maintained in the solid state (Figure 2 b). Therefore, it is reasonable to infer that the conformation of the chains resulting from the primary nucleation is mainly dominated by the original chain conformation, which will be related to the introduced chiral dopant. Consequently, the helical sense of iP2VP chains should presumably match that of the nucleus for the growth of the crystal. Accordingly, the helical chains in the crystalline state should possess the same handedness as in the amorphous state, thus leading to the twisting of the lamellae in a specific direction. However, it was also possible to find the opposite handedness to that resulting from the preferential lamellar twisting. We speculate that heterogeneous nucleation is inevitable, since the isothermal crystallization can only be conducted at a low crystallization temperature, as a higher temperature may cause the sublimation of the introduced chiral dopant owing to its low melting point, as well as the dissociation of HMA owing to the weakness of its association with the iP2VP. As a result, a small population of opposite handedness (less than 20 %) was occasionally found among the twisted lamellae with the preferred handedness.

To further examine the suggested mechanisms with respect to crystallization through self-assembly directed by the introduced chiral dopants, we carried out electron diffraction (ED) experiments on the crystallized thin films and obtained interesting single-crystal diffraction patterns. Figure 5 a shows a [00*l*] zonal diffraction pattern of intrinsic iP2VP. The diffractions are indexed on the basis of a frustrated trigonal crystal structure with a unit cell with the parameters $a = b = 15.49$ Å and $c = 6.56$ Å.[10,11] Consistently, the dimensions of a and b were both determined as 15.5 Å on the basis of the (300) and (030) reflections. For the crystallization of the iP2VP complex, it is intuitive to suggest that the introduced chiral dopants should be expelled from the crystalline iP2VP owing to the large size of the HMA, so that the crystallization of the mixture of iP2VP and HMA should adopt an excluded mode. As a result, crystallization of the iP2VP complex will give a crystallite with a crystalline structure similar to that of neat iP2VP. This hypothesis is supported by the observation of similar ED patterns (Figure 5 b) and FTIR spectra (see Figure S4) for neat iP2VP and iP2VP crystallized with (*R*)- and (H)-HMA. Consistently, similar wide-angle X-ray diffraction results (see Figure S5) were found for crystallites of both neat iP2VP and its complexes with HMA, thus providing further evidence that there is no significant variation in the unit-cell size in three dimensions for the crystallized iP2VP and the complexes. Accordingly, it is reasonable to infer that the introduced chiral dopants serve as guiding materials for the formation of twisted lamellae with a preferred handedness.

In summary, a method for controlling the handedness of twisted lamellae in banded spherulites of a stereoregular vinyl polymer with a chiral dopant has been developed. Upon the complexation of an enantiomer of HMA, the chains of iP2VP exhibit a preferred helical conformation by ICD not only in solution but also in solid films. The helical chain conformation

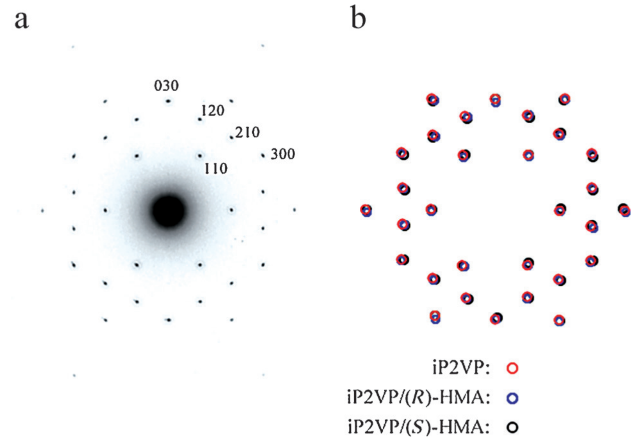

Figure 5. a) TEM ED pattern of iP2VP crystallized isothermally at 120 °C with (*R*)-HMA. b) Comparison of the ED patterns of neat iP2VP and the iP2VP/HMA complexes.

of iP2VP can be identified by CD spectroscopy. The mirror imaging of the CD spectra suggests the formation of right- and left-handed helical chains of iP2VP through complexation of (*R*)- and (*S*)-HMA, respectively. The twisted lamellae in the ring-banded spherulites of iP2VP that are formed in the presence of HMA exhibit a preferred handedness which depends on the chirality of dopant. The helical sense is determined in the primary nucleation. According to the unique crystallization behavior of iP2VP, all the polymer chains present the same helical conformation within the crystalline lamellae. As a result, the lamellae in the iP2VP spherulites exhibit a preferred twisting sense in accordance with the helical sense of the polymeric-chain conformation through homochiral evolution upon crystallization.

Experimental Section

The synthesis of isotactic poly(2-vinylpyridine) (iP2VP) was described previously in detail.[4] In brief, iP2VP was synthesized by the isospecific polymerization of 2-vinylpyridine with 4-*tert*-butylphenylmagnesium bromide as the initiator. The resulting polymer was purified by removing the atactic P2VP through boiling cosolvent extraction (THF/methyl ethyl ketone, 1:2) in a Soxhlet extractor. The resulting insoluble polymer was dried under vacuum to provide iP2VP as a pale-yellow powder. The isotacticity of iP2VP used in the present study was 95 % (*mm* %), as measured by ^{13}C NMR spectroscopy. The molecular weight (M_n) of the sample was 37 000 g mol^{-1}, and the polydispersity ($Đ$) was 1.37, as determined by Waters gel permeation chromatography (GPC) with the solvent THF on an instrument equipped with a refractive-index detector. The molecular weight and polydispersity of the polymer were calculated with respect to polystyrene standards.

Solutions of iP2VP and the iP2VP/HMA complexes were prepared by using 1,2-dichloroethane as the solvent. Film samples of the P2VP/HMA complexes were prepared by solvent evaporation on microscope glass slides for PLM and on quartz plates for CD spectroscopy. The film thickness was controlled by the solution concentration. The average thickness of the film for the observation of spherulites was about 2 μm, which could be obtained with a concentration of 8 mg mL^{-1}. The film thickness of samples for CD measurement was approximately 0.5 nm, which was obtained with a concentration of 2 mg mL^{-1}. The concentration of solutions for CD measurement was 0.2 mg mL^{-1} for iP2VP in 1,2-dichloroethane.

PLM experiments were carried out in an Olympus BX-51 equipped with a CCD camera. UV/Vis absorption and CD spectra were acquired with a JASCO J-815 spectrometer. Solution samples were placed in a cylindrical quartz cell with a light path of 1.0 mm.

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[1] a) J. H. K. K. Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma, E. W. Meijer, *Nature* **2000**, *407*, 167–170; b) J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, N. A. J. M. Sommerdijk, *Chem. Rev.* **2001**, *101*, 4039–4070; c) J. J. L. M. Cornelissen, M. Fischer, N. A. J. M. Sommerdijk, R. J. M. Nolte, *Science* **1998**, *280*, 1427–1430; d) C. Y. Li, S. Z. D. Cheng, J. J. Ge, F. Bai, J. Z. Zhang, I. K. Mann, L. C. Chien, F. W. Harris, B. Lotz, *J. Am. Chem. Soc.* **2000**, *122*, 72–79.

[2] a) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, B. L. Feringa, *Science* **2004**, *304*, 278–281; b) R.-M. Ho, M. C. Li, S.-C. Lin, H.-F. Wang, Y.-D. Lee, H. Hasegawa, E. L. Thomas, *J. Am. Chem. Soc.* **2012**, *134*, 10974–10986; c) M.-C. Li, H.-F. Wang, C.-H. Chiang, Y.-D. Lee, R.-M. Ho, *Angew. Chem. Int. Ed.* **2014**, *53*, 4450–4455; *Angew. Chem.* **2014**, *126*, 4539–4544; d) R.-M. Ho, Y.-W. Chiang, S.-C. Lin, C.-K. Chen, *Prog. Polym. Sci.* **2011**, *36*, 376–453.

[3] a) E. Yashima, K. Maeda, Y. Okamoto, *Nature* **1999**, *399*, 449–451; b) E. Yashima, K. Maeda, H. Iida, Y. Furusho, K. Nagai, *Chem. Rev.* **2009**, *109*, 6102–6211; c) E. Yashima, K. Maeda, Y. Furusho, *Acc. Chem. Res.* **2008**, *41*, 1166–1180.

[4] L.-C. Chen, Y.-C. Mao, S.-C. Lin, M.-C. Li, R.-M. Ho, J.-C. Tsai, *Chem. Commun.* **2012**, *48*, 3668–3670.

[5] V. P. Panov, L. A. Kazarin, V. I. Dubrovin, V. V. Gusev, Y. É. Kirsh, *J. Appl. Spectrosc.* **1974**, *21*, 1504–1510.

[6] N. Berova, L. D. Bari, G. Pescitelli, *Chem. Soc. Rev.* **2007**, *36*, 914–931.

[7] a) A. Keller, *J. Polym. Sci.* **1959**, *39*, 151–173; b) H. D. Keith, F. J. Padden, *J. Polym. Sci.* **1959**, *39*, 123–138; c) A. Keller, *J. Polym. Sci.* **1955**, *17*, 351–364.

[8] a) R.-M. Ho, K.-Z. Ke, M. Chen, *Macromolecules* **2000**, *33*, 7529–7537; b) C. Y. Li, S. Z. D. Cheng, X. Weng, J. J. Ge, F. Bai, J. Z. Zhang, B. H. Calhoun, F. W. Harris, L.-C. Chien, B. Lotz, *J. Am. Chem. Soc.* **2001**, *123*, 2462–2463; c) B. Lotz, S. Z. D. Cheng, *Polymer* **2005**, *46*, 577–610; d) C. Y. Li, D. Yan, S. Z. D. Cheng, F. Bai, T. He, L.-C. Chien, F. W. Harris, B. Lotz, *Macromolecules* **1999**, *32*, 524–527.

[9] D. Maillard, R. E. Prud'homme, *Macromolecules* **2008**, *41*, 1705–1712.

[10] T. Okihara, L. Cartier, G. O. R. Alberda van Ekenstein, B. Lotz, *Polymer* **1999**, *40*, 1–11.

[11] M. Puterman, F. J. Kolpak, J. Blackwell, J. B. Lando, *J. Polym. Sci. Part B* **1977**, *15*, 805–819.

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