

Directed crystallization of isotactic poly(2-vinylpyridine) for preferred lamellar twisting by chiral dopants



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ABSTRACT

As reported in our previous work, banded spherulites of isotactic poly(2-vinylpyridine) (iP2VP) with preferred handedness of twisted lamellae can be formed by the inducement of chiral dopants, *i.e.*, (*R*)- or (*S*)-hexahydromandelic acids (HMAs). In the present work, we systematically studied the behaviors of chirality transfer in the crystallization of iP2VP associated with the chiral dopant. As evidenced by the signatures of the split-type Cotton effect of circular dichroism (CD) spectra, the chains of iP2VP exhibit exclusive *conformational chirality*, *i.e.*, induced circular dichroism (ICD), due to the complexation of chiral dopants (*configurational chirality*) with the lone-pair electron of the iP2VP. With the same growth axis along the radial direction of the banded spherulites, as indicated by selected area electron diffraction (SAED), the helical sense of the twisted lamellae of the iP2VP with ICD can be driven by the chiral dopants. The handedness of the helical chains remains after crystallization with intrinsic crystalline structure of iP2VP, which was revealed by the corresponding results of CD spectroscopy. As a result, a homochiral evolution from the *configurational chirality* of chiral dopant to the *hierarchical chirality* of crystallized iP2VP can be developed through directed crystallization of the iP2VP by chiral HMAs.

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1. Introduction

Chirality transfer is an intriguing phenomenon which occurs widely in nature. By mediating through covalent or non-covalent bonds, an achiral host can acquire the chiroptical properties of a chiral system [1]. When the achiral molecules or polymer chains binding with chiral guests, induced chirality can be detected by circular dichroism (CD), *i.e.*, induced CD (ICD), in the absorption region of the achiral host [2]. In general, the ICD behaviors employ polymers with conjugated or peptide-based backbones [3–5]. For instance, Yashima and coworkers reported helical polyacetylenes in which both the main chain helicity and axial chirality of the pendants are induced by non-racemic alcohols, and the memorized macromolecular helicity and axial chirality can be used for the separation of enantiomers [6]. The examples of polyolefins and vinyl polymers with induced chirality are rare because most of the

vinyl polymers with stereoregularity that possess a mirror plane are not optically active [7–9]. Recently, the induced chirality of a vinyl polymer, isotactic poly(2-vinylpyridine) (iP2VP), has been achieved by using chiral acids through complexation, and the ICD was found to be strongly dependent upon the tacticity of the iP2VP, and the acidity of chiral acid and its bulkiness [10].

Banded spherulite consisting of cooperatively twisting lamellar crystals is a common morphological feature in semi-crystalline polymers [11,12]. It is generally accepted that the banding in spherulites reflects the radial growth of twisted lamellae due to the imbalanced stresses at opposite fold surfaces [13–15]. The difference of surface stresses can be related to different factors including chain tilting (*e.g.* polyethylene) [11,16], chemical structure of chain folds (*e.g.* polyamide) [17] and main chain/side chain chirality (*e.g.* biopolymers) [18,19]. The origin of lamellar twisting for crystallized polymers has been widely studied in the past decades [13–16,20–23], but the relation between the helical sense of twisted lamellae and the chiral sense of polymers is still an open question. On the basis of lamellar twisting and scrolling in a variety of polymers, lamellar twisting in polymers is a consequence of

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unbalanced stresses resulting from different chain conformations on the opposite surfaces of the lamellae [15,20,24–26]. The formation of lamellar crystals with preferred twist sense is referred to the chirality transfer from intrinsic chiral centers of polymer chains to hierarchical structures [27]. Nevertheless, how to achieve the chirality transfer of self-assembled polymers at different scales, in particular with homochiral evolution, remains challenging. In general, the formation of chiral structures with high order requires a parallel close packing scheme and effective interaction upon helical packing [27,28]. Hence, the hierarchical helical texture is rarely observed in chiral liquid crystals due to the ineffective interaction of helical packing [29,30]. Interestingly, the chirality transfer from helical chain to hierarchical helical structure might be achieved by crystallization of polymers at which van der Waals interactions give the propagation of chirality from conformational level to hierarchical structure, such as banded spherulites in enantiomeric poly(epichlorohydrin)s [31] and poly(propylene oxide)s [32] and chiral polylactides [18,19,33]. The correlation between the helical conformation of polymer chains and the preferred sense of the lamellar twisting is usually achieved in the self-assembled textures of optically active enantiomeric polymers with intrinsic chiral center in the main chains. For stereoregular polymers such as the iP2VP, it will be intrinsic to examine the development of homochiral evolution in the crystallization of the iP2VP with ICD.

Recently, we found that the induced chirality of the iP2VP chains can be further transferred to hierarchical superstructure by crystallization of the iP2VP in the presence of chiral dopants, giving banded spherulite composed of twisted lamellae with preferred handedness [34]. Herein, we aim to systematically investigate the ICD behaviors of the iP2VP by association with introduced chiral dopants, (*R*)- or (*S*)-hexahydromandelic acids (HMAs) and the corresponding mechanisms of directed crystallization of the iP2VP with ICD by the chiral dopants. By taking advantage of the strong non-covalent interaction between pyridine rings and organic acids, the configurational chirality of HMAs can transfer to the conformational chirality of iP2VP chains as determined by CD spectroscopy. With the control of same growth axis for crystallization along the radial direction of the spherulites, lamellar twisting with preferred handedness can be obtained by the use of chiral dopant to give banded spherulitic texture. Finally, a hypothetical mechanism for the chirality transfer in the directed crystallization of iP2VP driven by chiral dopants is proposed.

2. Experimental section

2.1. Synthesis of isotactic poly(2-vinylpyridine)

The synthesis of isotactic poly(2-vinylpyridine) (iP2VP) was described in detail in our previous report [10]. The number average molecular weight (M_n) of the sample is 37000 g/mol, and the polydispersity (\mathcal{D}_M) is 1.37, determined by a Waters gel permeation chromatograph (GPC) equipped with a refractive index (RI) detector using THF solvent. Molecular weight and \mathcal{D}_M were calculated relative to linear PS standards.

2.2. Sample preparation

The solution of neat iP2VP and iP2VP/HMA complexes for CD measurement was prepared by using 1,2-dichloroethane as solvent with a polymer concentration of 0.3 mg/mL. Thin film samples were prepared by drop casting the solution on microscope glass slides for PLM observation, and quartz glass or silicon wafer was used as substrate for CD or for FTIR measurement. The film thickness was controlled by the solution concentration. The average thickness of

the film for PLM observation was about 2 μm , which could be obtained with concentration of 8 mg/mL. The film thickness for CD and for FTIR measurement is about 0.5 μm , which was obtained with concentration of 2 mg/mL. Thin film samples prepared for TEM experiment were prepared by drop casting the solution (0.2 mg/mL) on freshly cleaved mica covered with carbon film. The thickness of the film is less than 250 nm. Then the film was transferred onto copper grid after crystallization. The crystallization experiment was performed with a hot stage (INTEC HCS302) controlled by a processor (INTEC mK1000) under N_2 atmosphere.

2.3. Characterization

UV–Vis absorption and the corresponding CD spectra were acquired using a JASCO J-815 spectrometer. Solution samples for CD measurement were placed in a cylindrical quartz cell with a light path of 1.0 mm at ambient temperature. FTIR absorption were acquired using a JASCO FVS-6000 spectrometer.

PLM experiments were carried out in an Olympus BX-51 equipped with a CCD camera. The sense of lamellar twist in the banded spherulites was measured by using a goniometric stage [19].

Transmission Electron Microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained with a JEOL JEM-2100 microscope at 200 kV. TEM samples were shadowed by Pt/C with the angle of 30° tilted to the surface for enhancing the contrast.

3. Results and discussion

3.1. Induced circular dichroism of iP2VP

Fig. 1 shows the CD and corresponding UV–Vis spectra of iP2VP in the presence of (*R*)- or (*S*)-HMAs in 1,2-dichloroethane solution at different molar ratios (*i.e.*, the moles of HMA to the molar monomer units of 2VP in the P2VP) in comparison with neat iP2VP. In the presence of chiral HMAs, Cotton effect with mirror image can be observed whereas the spectrum of neat iP2VP shows CD silent. The CD signal is attributed to the π - π^* transition of the pyridine rings in iP2VP which contributes the absorption peak at approximately 260 nm [10]. The mirror-imaged CD spectra in the UV–visible region of iP2VP are attributed to the ICD behaviors of iP2VP through acid–base interaction (*i.e.*, complexation) [4,5,35,36].

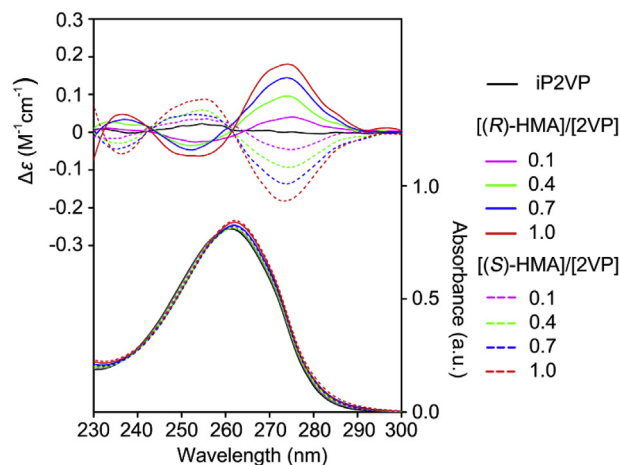


Fig. 1. CD and corresponding UV–Vis absorption spectra of iP2VP with (*R*)- or (*S*)-HMAs in 1,2-dichloroethane at different molar ratios. The solution concentration of iP2VP is 0.3 mg/mL.

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