

Feature Article

**APPLICATION OF ELECTRON DIFFRACTION IN THE STRUCTURE
CHARACTERIZATION OF POLYMER CRYSTALS***

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Abstract The dependence of properties on the structure and morphology of semicrystalline polymers offers an effective way to tailor the properties of these materials through structure control. To this end, establishing the structure and property relationship is of great importance. For a right characterization of the crystal structure, several techniques can be used. Among these techniques, electron diffraction has its advantage for determining the crystal structure related to specific formation condition since it can combine with bright and dark fields observation of the sample. This feature article describes the application of electron diffraction in determining the crystal structure of semicrystalline polymers with elaborately selected examples. We focus on how the electron diffraction can be used to disclose the crystal structure, mutual orientation of different crystals, as well as the disorders included in the polymer crystals.

Keywords: Electron diffraction; Semicrystalline polymer; Crystal structure; Orientation; Defect.

INTRODUCTION

Polymeric materials have been extensively used in many fields. This is based on the great potential of polymeric materials to meet the requirements for the applications. The reason is that the properties and even functionality of polymeric materials depend strongly on their structures at different scales. While the chemical structure at molecular scale determines the essential property or/and functionality of a polymer, the chain alignment of polymers in the condensed state shows also great influence on their properties and functionality. For example, the alignment of polymer chains in specific direction endows the polymeric material anisotropic properties, leading to an enhancement of some properties along the chain direction. This has been well illustrated by the increase of the electrical conductivity of well-aligned conjugated macromolecules, which can be enhanced by more than a factor of 100 compared with their unoriented counterparts^[1–3]. The influence of chain organization in the crystal on the property and functionality is even pronounced for the semicrystalline polymers. As an example, when the isotactic polypropylene (*i*PP) chains organized in its β -crystal lattice, outstanding macroscopic toughness and ductility can be achieved in comparing with its α -counterpart^[4–6]. Moreover, the poly(vinylidene fluoride) (PVDF) in different crystal forms provides us an ideal example to illustrate the influence of crystal structure on the functionality of the semicrystalline polymers. It was well demonstrated that

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the α -form PVDF crystals composed of helical chains can only be used as common thermoplastics. However, the β -PVDF crystals composed of planar zigzag chains exhibit exceptional piezo- and pyro-electric properties^[7, 8]. Taking these into account, establishing the structure-property relationship of semicrystalline polymers is of great significance for developing high performance polymeric materials through structure manipulation. This leads to the structure characterization of semicrystalline polymers an essential and important issue in the field of polymer physics.

There are many methods to characterize the chain organization and crystal packing of semicrystalline polymers in condensed state, such as, spectroscopy, X-ray diffraction and scattering techniques, microscopy, electron diffraction method, and so on. Among these techniques, electron diffraction combined with bright and dark fields observation of the sample provide an efficient way to determine crystal structure related to specific morphology. Actually, the establishing of folded chain crystallization model of long chain polymers is based on the results of electron diffraction and the bright field observation. The electron diffraction has the advantage of ultrathin film characterization and is especially helpful for disclosing the crystal orientation and mutual relationship between the polymer crystals. Here we presented some examples to show the application of electron diffraction on the structure characterization of semicrystalline polymers. We focus on what kind information we can get from electron diffraction and how should we analyze the electron diffraction.

EXPERIMENTAL

This feature article presents an overview about the use of electron diffraction in structure characterization of semicrystalline polymers. The selected illustrative figures are all related to our research group. Details about experimental procedure can be found in succedent citation of the corresponding literatures. However, a detailed description of the experimental work may be easy for the readers to follow or reproduce the observed structures. Therefore, an experimental section in the light of the related figures is presented here.

Materials and Sample Preparation

The *i*PP used in this study is a commercial grade isotactic polypropylene, with trade number of GB-2401, produced by Yanshan Petroleum and Chemical Corporation, China. The melt flow index of it is 2.5 g/10min. The M_w is about 4.38×10^5 and the peak melting temperature is measured to be 170 °C. The syndiotactic polypropylene (*s*PP) with a stereoregularity of 97% pendant and a melting temperature of *ca.* 160 °C is kindly supplied by Prof. Kaminsky from University of Hamburg, Germany. The polyethylene (PE) is Lupolen 6021DX, produced by BASF AG Ludwigshafen, Germany. The melting point of the used PE is measured by DSC to be 136 °C. The poly(ethylene adipate) (PEA) was purchased as a research-grade material from Aldrich Chem. Co. Its weight-average molecular weight (M_w) determined by gel permeation chromatography (GPC) was about 1.0×10^4 . The poly(1-butene) (*i*PB-1) sample used here was Vestolen BT with viscosity average molecular weight of 5×10^5 , supplied by Chemische Werke Hüls. Syndiotactic propylene-*co*-1-butene copolymers (*s*PPBU) were kindly supplied by Prof. De Rosa of Università di Napoli “Federico II”, Italy.

Highly oriented thin films of *s*PP and PE were prepared according to a melt-draw technique introduced by Petermann and Gohil^[9]. As illustrated in Fig. 1, a small amount of a 0.5 wt% dilute polymer solution in xylene was dispersed uniformly on a preheated glass plate at 130 °C. The xylene solvent was allowed to evaporate at the preparation temperature. After evaporation of the solvent, the thin molten polymer layer of *ca.* 1 μ m was then picked up by a motor-driven cylinder. In this way, we get highly oriented ultrathin *s*PP and PE films with thickness of *ca.* 50 nm. Different *s*PP crystal structures were achieved through changing the drawing speed. Unoriented thin films of the related polymers were prepared by solution casting from their dilute solution of *ca.* 0.2 wt%. Thermal history of samples is described in the corresponding figure captions.

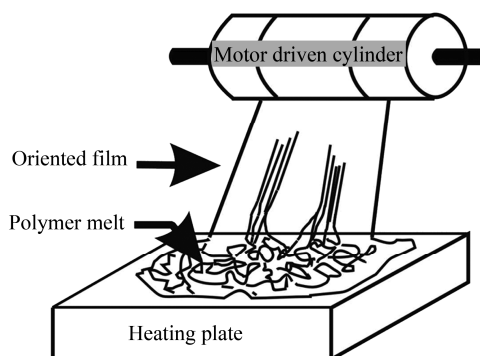


Fig. 1 A sketch for the preparation procedure of highly oriented polymer films

Characterization

Fine structure of PEA crystallized on highly oriented PE substrate on a lamellar scale was obtained using an Agilent 5500 AFM (Agilent Technologies). The AFM was operated in tapping mode using silicon cantilevers with spring constant of 20–30 N/m. The resonance frequencies were set as 140–160 kHz. The scan speed varied from 0.5 line/s to 1.0 line/s. The set-point ratio and amplitude were chosen such that the surface was tracked while maintaining the necessary contrast in the phase images.

For transmission electron microscopy observation and electron diffraction, a JEOL JEM-2100 TEM operated at 200 kV was used in this study. The phase contrast bright-field micrograph of *i*PP solution cast films was obtained by defocus of the objective lens. In order to minimize radiation damage by the electron beam, focusing was carried out on an area, then the specimen film was translated to its adjacent undamaged area and the image was recorded immediately.

RESULTS AND DISCUSSION

Determination of Crystal Structure and Orientation

Polymorphisms are frequently encountered for semicrystalline polymers^[10–17]. Therefore, determining the crystal structure of a polymer sample obtained under specific condition is an essential work. There are many experiments demonstrating the use of electron diffraction technique for disclosing different crystal structures of polymers. We here take the melt-drawn *s*PP thin films as an example to show the successful utilization of electron diffraction for determining its different crystal structures. Figure 2 shows two electron diffraction patterns of the melt-drawn *s*PP thin films under different preparation conditions. The well-defined electron diffraction spots shown in diffraction patterns indicate a high orientation of the obtained thin films. However, one can clearly see that the presented electron diffraction patterns look totally different. This is caused by the formation of different crystal structures depending on stretching speed. Indexing of the diffraction spots demonstrates that all of the electron diffraction spots shown in Fig. 2(a) are accounted for by a crystal form of $(t_2g_2)_2$ helical chains packed in an orthorhombic unit cell with parameters of $a = 1.45$, $b = 1.12$, and $c = 0.74$ nm^[18–22]. On the other hand, all of the diffraction spots shown in Fig. 2(b) can be indexed by a crystal form of all trans (ttt) chains packed in an orthorhombic unit cell with parameters of $a = 0.522$, $b = 1.117$, and $c = 0.506$ nm^[18, 19]. The appearance of (002) and (004) reflection spots of both kind of crystals in the equator direction indicates that the molecular chains of *s*PP in both thin films are horizontal, which is parallel to the drawing direction during sample preparation. These results show that uniaxially oriented thin *s*PP films can be prepared through melt-draw with molecular chains aligned in the drawing direction but packed in different manner.

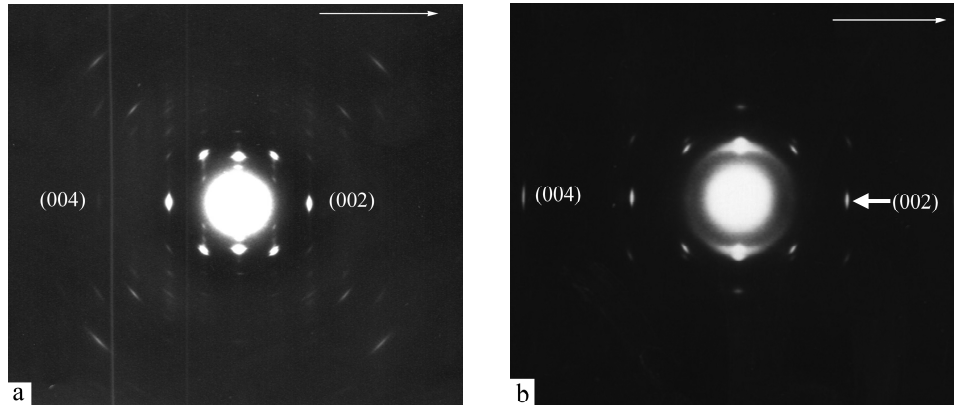


Fig. 2 Electron diffraction patterns of sPP melt-drawn thin films at a pick up speed of (a) 2 cm/s and (b) 20 cm/s
The white arrows represent the drawing direction during film preparation.

It should be pointed out that different electron diffraction patterns may not unambiguously associate to the formation of different crystal structures. Different crystal orientations can also produce different electron diffraction patterns. An example is shown in Fig. 3, which shows two electron diffraction patterns of highly oriented PE thin films. These two diffraction patterns look quite different. The diffraction pattern shown in Fig. 3(a) displays much less reflection spots than the one shown in Fig. 3(b). A detailed analysis of the diffraction patterns indicates that all of the reflection spots shown in both patterns can be successfully accounted for by the same orthorhombic unit cell with axes $a = 0.74$, $b = 0.494$, and $c = 0.2534$ nm^[23], indicating the same crystal structure. The differences between these electron diffraction patterns are actually caused by the different crystal orientation, even though the same chain alignment along the drawing direction during film preparation as judged from the same location of the (002) diffraction spots. This can be identified through the exposing surface of the thin film. To disclose the exposing surface of a thin film, we can choose two diffraction spots which are not aligned in the same direction and build an array with the h , k , l in the first line and those of the chosen two reflection spots, indicated as (h_1, k_1, l_1) and (h_2, k_2, l_2) , in the second and third lines, respectively. In this way, we get

$$\begin{pmatrix} h & k & l \\ h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \end{pmatrix} \quad (1)$$

From array (1), when removing the corresponding line and column of h , we get

$$\begin{pmatrix} k_1 & l_1 \\ k_2 & l_2 \end{pmatrix} \quad (2)$$

The absolute value of array (2) provides us the h index. In the same way, we will get the k and l indexes accordingly. Through simplification of the obtained h , k and l values, we will get the lattice plane of the exposing surface for the checked sample, and therefore determine its exact crystal orientation. As an example, we choose the (002) and (020) reflection spots from Fig. 3(a) and get

$$\begin{pmatrix} h & k & l \\ 0 & 0 & 2 \\ 0 & 2 & 0 \end{pmatrix}$$

According to the described way, we get 4, 0, 0 for the h , k , l indexes, respectively. Through simplification, we know that the (100) lattice plane is the exposing surface of the film shown in Fig. 3(a). Same results will be obtained no matter which reflection spots in Fig. 3(a) are selected. This indicates that the PE thin films with electron diffraction pattern shown in Fig. 3(a) have a fixed (100) exposing surface, *i.e.*, a double orientation with the b - and c -axes of the unit cell in film plane while the a -axis perpendicular to the film plane^[24]. For the diffraction pattern shown in Fig. 3(b), different results are obtained. Choosing the (002) and (020) reflection spots, we will get the (100) as exposing surface. However, the (002) and (110) reflection spots lead to the (110) as exposing surface, while the (002) and (200) reflection spots lead to the (010) as exposing surface. This seems hard to be understood. It reflects actually the true orientation status of the crystals in the film, *i.e.*, a fiber orientation with the chain axis in the film plane and along the drawing direction during sample preparation, while the crystallographic a - and b -axes rotated randomly about the chain direction^[25]. As a result, there are really crystals with different exposing lattice planes, which bring much more lattice planes in Bragg diffraction condition.

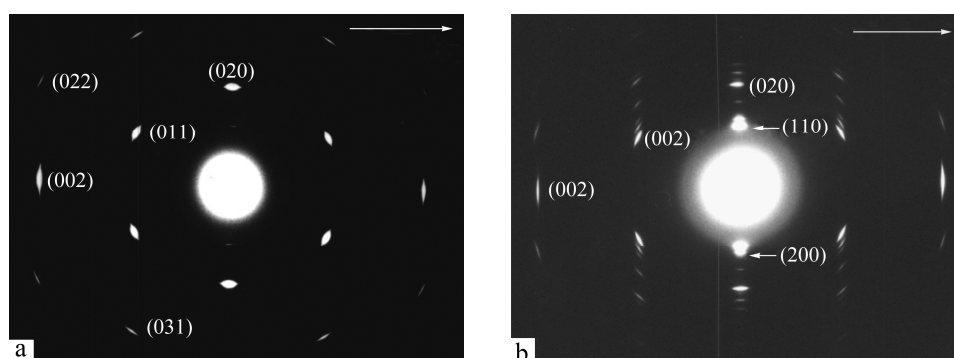


Fig. 3 Electron diffraction patterns of highly oriented PE thin films with different crystal orientation. The white arrows represent the drawing direction during film preparation.

Determination of Mutual Orientation Relationship between the Crystals

The above descriptions have illustrated the application of electron diffraction in determining the crystal structure and orientation. In this section, the use of electron diffraction in characterizing the mutual orientation relationship between polymer crystals, which is very important for polymer composites having special crystallographic interactions^[26–40], will be described. For this aspect, we first present the oriented structure of PEA crystallized on the PE substrate with a fiber orientation as presented in Fig. 3(b)^[27]. Figure 4 shows an AFM image (left) and a diffraction pattern (right) of a PEA/PE double-layered sample, which has been heat-treated at 85 °C (higher than the melting point of PEA but below the melting point of PE) for 5 min and then cooled to 27 °C for isothermal crystallization. From the AFM image, left part of Fig. 4, we see a cross-hatched lamellar structure of PEA crystallized on the oriented PE substrate. One may simply associate this structure with an orientation of the PEA chains inclined with an angle to the chain direction of PE. This is, however, not the case. The exact orientation relationship between the PEA and PE crystals can be obtained through a detailed analysis of the superimposed diffraction pattern. The corresponding electron diffraction pattern is shown in the right part of Fig. 4. The well defined reflection spots indicate some kind of orientation of both PE and PEA crystals. For clarity, a sketch of the observed diffraction pattern with the main reflections being indexed is shown in Fig. 5, in which the reflections coming from the PEA crystals are presented in short lines and those coming from PE substrate crystals are presented as solid ellipses. Clearly, the diffraction pattern of PE oriented substrate has a close resemblance with the one presented in Fig. 3(b). All of the reflection spots of PEA appeared in the diffraction pattern have been successfully accounted for by a monoclinic unit cell with parameters $a = 0.547$, $b = 0.724$, $c = 1.155$ nm, and $\beta = 113.5^\circ$ ^[41–43]. The appearance of only (200) reflection spots of PEA in the meridian direction together with several (00 l) reflections, including the (002), (003), (004) and (005) reflection spots,

indicates that the (010) lattice plane of the PEA is in contact with the PE substrate crystals. Moreover, it is found that the angle between the $[00l]$ directions of PE and PEA crystals are $\pm 23.5^\circ$. It seems that the crystallization of PEA on PE substrate with molecular chains $\pm 23.5^\circ$ apart from each other. However, taking the monoclinic unit cell structure of PEA into account, a parallel chain alignment of both polymers leads to the location of $(00l)$ diffractions exactly in the direction 23.5° inclined to the $[002]$ direction of PE as schematically illustrated in Fig. 6. In this case, the cross-hatched lamellar structure tells us a fact that the PEA chains in their lamellar crystals are folded in the $\{001\}$ lattice planes. The determination of this mutual orientation helps us to understand the origin of the induced epitaxial crystallization. It rests on a geometric matching between the interchain distances of PEA in its monoclinic form along the $[100]$ direction and PE along its b -axis direction. The discrepancy is only 1.2%, which is well with the upper limit for the occurrence of polymer epitaxy^[26].

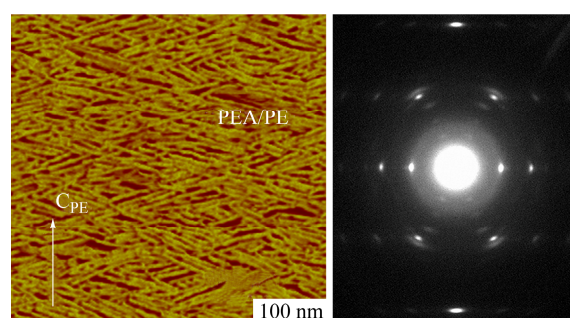


Fig. 4 An AFM height image (left) and its corresponding diffraction pattern (right) of a PEA/PE double-layered sample, which has been heat-treated at 85°C for 5 min and then cooled to 27°C for isothermal crystallization
The molecular chain direction of PE substrate crystals is indicated by a white arrow.

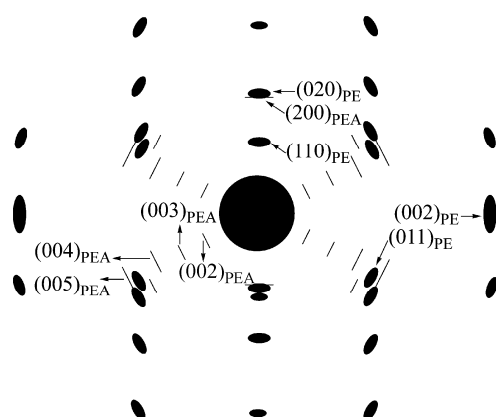


Fig. 5 A sketch of the electron diffraction pattern shown in Fig. 4
The solid ellipses represent the reflection spots of PE, while the short lines represent the electron diffractions of PEA.

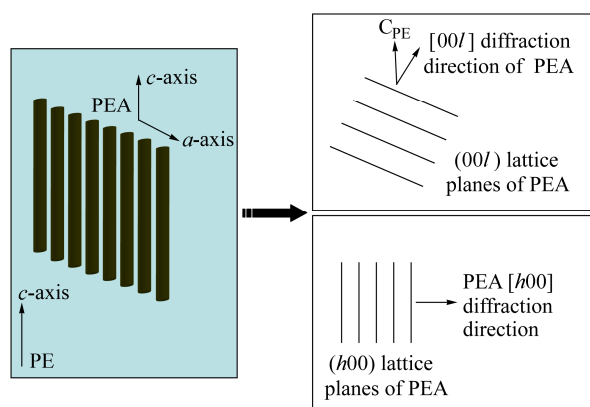


Fig. 6 A sketch displaying the chain orientation of PEA with respect to the PE substrate crystals and the location of $[00l]$ and $[h00]$ directions of the PEA lamellar crystals

Analysis of mutual orientation is important for disclosing orientation relationship not only of polymer composites but also for homopolymers. The most frequently encountered cases are the analyses of twinned crystals, such as that happened for sPP^[44]. Another illustrative example is the unique wide angle lamellar branching of α -iPP, which can be obtained from solution crystallization of the cast film^[45], the so-called quadrites^[46, 47], spherulitic crystallization in the bulk^[48, 49], and fiber spinning^[50–52]. As presented in Fig. 7(a), cross-hatched lamellar structure consisted of lamellae *ca.* 100° inclined to each other reveals the characteristic

lamellar branching feature. To understand this special structure of *i*PP, electron diffraction analysis is necessary. The result, see Figs. 7(b) and 7(c), shows that the crystallographic *b*-axes of both mother and daughter lamellae are in common, *i.e.*, the two sets crystalline lamellae with the (010) planes in contact. The *a*- and *c*-axes of the daughter lamellae aligned parallel to the *c*- and *a*-axes of the mother lamellae, respectively. This provides us hint for interpreting this phenomenon in terms of geometric matching with a rather small mismatching between the *a*- and *c*-axes (2.3%) of the monoclinic unit cell with parameters of $a = 0.666$, $b = 2.078$, $c = 0.650$ nm and $\beta = 99.62^\circ$ [53]. On a molecular scale, it reflects actually the favorable interaction of the methyl groups, which can only be achieved by rotating the helix axes for *ca.* 100° when the helices of same handedness (in reality opposite handedness is required) are encountered^[54].

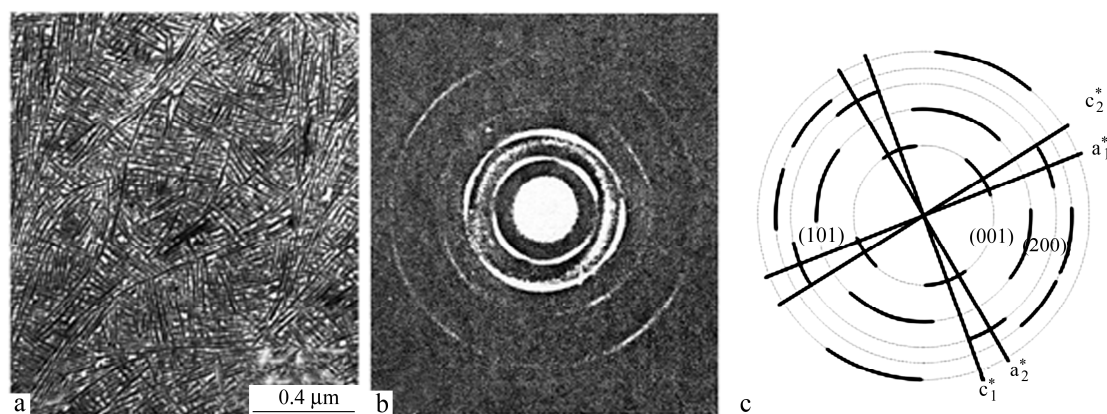


Fig. 7 Phase contrast bright field transmission electron micrograph (a) and its corresponding diffraction pattern (b) of a solution cast *i*PP thin film and (c) a sketch of the diffraction pattern shown in part (b)

The determination of mutual orientation is sometimes much helpful for understanding the phase transition of polymer crystals. As well known, the isotactic poly(1-butene) (*i*PB-1) is one of the semicrystalline polymers exhibiting pronounced polymorphisms depending on thermal treatment and mechanical handling. Four different polymorphs, designated as I, II, III, and I', have been reported in the literatures^[55–62]. It was confirmed that the *i*PB-1 chains possess the same 3/1 helical conformation in both forms I and I'^[55–59]. The difference between these two forms is that the form I crystals exhibit a twinned hexagonal structure, while form I' crystals occur in an untwinned hexagonal form. Form II is packed in a tetragonal unit cell with 11/3 helical chains^[60–62]. Crystallization of *i*PB-1 at atmospheric pressure leads to the formation of *i*PB-1 form II, which is thermally less stable and readily undergoes a crystal-crystal transformation into the densely packed form I when aged at room temperature^[63–65]. Electron diffraction analysis has provided us a fully understanding of the phase transition. As the transformation takes days or even weeks, we have sufficient time to get the diffraction patterns of each individual crystals and their superimposition. As shown in Fig. 8, while the form II shows a tetragonal diffraction pattern (Fig. 8a), the diffraction pattern of the form I (Fig. 8b) exhibits a twinned hexagonal feature. From the superimposed electron diffraction pattern of an incompletely transformed sample (Fig. 8c), we can find that the (110) lattice planes of the tetragonal and hexagonal *i*PB-1 crystals are parallel to each other. This helps us to explain the phase transformation on a molecular scale. As shown in Fig. 9, during the transformation, the isochiral (110) plane of the tetragonal crystal becomes the isochiral (110) plane of the transformed hexagonal crystal^[66, 67]. In this way, the helix displacement is minimized and the energetically unrealistic change of helix chirality is avoided at the same time. Moreover, the twinned hexagonal feature of transformed form I *i*PB-1 crystals can also be easily understood under the consideration that the identical $(110)_{II}$ and $(\bar{1}\bar{1}0)_{II}$ planes due to the high lattice symmetry can both initiate the transformation from form II to form I.

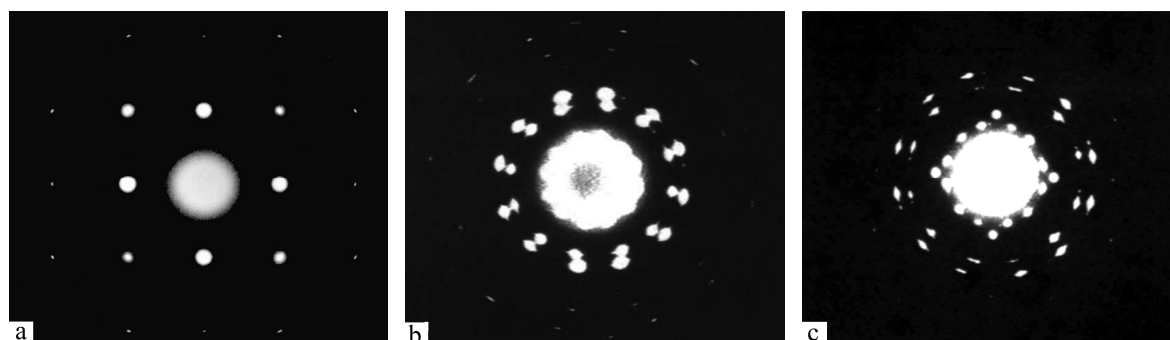


Fig. 8 Electron diffraction patterns of (a) the tetragonal, (b) the twinned hexagonal *iPB*-1 crystal and (c) a superimposed electron diffraction pattern of a *iPB*-1 thin film with both tetragonal and twinned hexagonal *iPB*-1 crystals owing to incompleteness of the phase transition (Reproduced from Ref. [68] with permission. Copyright © 2002 Wiley Periodicals, Inc.)

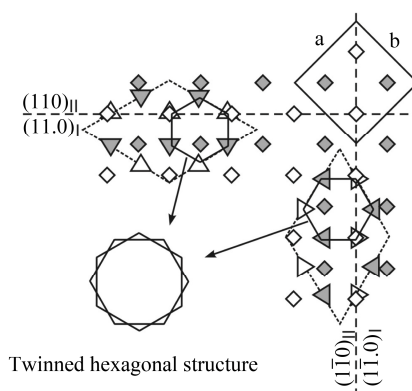


Fig. 9 A sketch illustrating the transformation of *iPB*-1 crystal from its tetragonal form to twinned hexagonal form

A tetragonal unit cell of form II and two hexagonal unit cells of form I are indicated. The helical chains of form II and form I crystals are represented as squares and triangles, respectively. The different helical hands are shown as light and shaded symbols. The twinned hexagonal structure is presented in the lower left corner of the picture. (Reproduced from Ref. [68] with permission. Copyright © 2002 Wiley Periodicals, Inc.)

Determination of the Crystal Defects

Another important role of electron diffraction in the structure characterization is the determination of defects in polymer crystals. For this issue, we take the syndiotactic poly(propene-*co*-1-butene) (*sPPBU*) random copolymers as an example. The *sPPBU* samples maintain crystallinity over the whole range of the comonomeric content, even though the crystallization habit of the copolymers is influenced by the comonomeric units^[44, 68–72]. A nearly linear expansion of the *a*- and *b*- axes of the unit cell from the values of *sPP* to those of *sPB*-1 with increasing of 1-butene content indicates that the comonomeric units are both included in the unit cells of the homopolymers, *i.e.*, the cocrystallization 1-butene and propene parts. This originates from the very similar crystal structures of *sPP* and *sPB*-1 in their stable two-fold helical chain forms. The incorporation of comonomeric unit leads to the copolymers crystallizing in modification having structure intermediate between those of *sPP* and syndiotactic poly(1-butene) (*sPB*-1) homopolymers, in which disorder in the alternation of right and left-handed helical chains along the axes of the unit cell and disorder in the stacking of *bc* layers of chains piled along the *a*-axis are always presented^[69, 71]. To characterize the existing form of these disorders, electron diffraction of the single crystals can provide precise indexing of the reflections and therefore more information about the kinds and the amount of structural disorder with respect to the comonomeric composition. Figure 10

shows an electron diffraction pattern of the *s*PB-1. All of the reflection spots are accounted for by the orthorhombic unit cell with axes $a = 1.681$, $b = 0.606$, and $c = 0.773$ nm as proposed by De Rosa *et al.*^[73, 74]. Moreover, it is noteworthy that only the reflections with $h + k = 2n$ appear in the diffraction pattern. The systematic absence of $h + k = 2n + 1$ indicates a C-centered packing of isochiral helical chains according to the space group C2221. In particular the presence of the strong (110) reflection and the absence of the (010) reflection are the clear evidence of the centering of the ab face of the unit cell. A sketch of this packing model projected along the chain axis is given in right part of Fig. 10. A diffraction pattern of the *s*PP single crystals is shown in Fig. 11. The sharp electron diffraction spots correspond to the ($hk0$) reflections, with sharp and well-defined (200) and (020) reflections. This electron diffraction pattern indicates the same packing of the $(t_2g_2)_2$ helical chain conformation in an orthorhombic unit cell as that of the melt-drawn films presented in Fig. 2. The right part of Fig. 11 is a sketch of this packing model projected along the chain axis. From Fig. 10 and Fig. 11, one can easily recognize the different packing manners of *s*PB-1 and *s*PP single crystals. The electron diffraction patterns of their random copolymers with the content of one comonomeric unit lower than 10 mol% are essentially the same as that of the homopolymer single crystal of the rich component. When the ratio of both comonomeric units is around 50 mol%, as presented in Fig. 12, streaks reflecting the existence of structure defects can be clearly observed. With close inspection, one can find the differences between the diffraction patterns of the copolymers with 34.7 mol% and 52.1 mol% propene, respectively. For the copolymer with 34.7 mol% propene, see Fig. 12(a), the broadened (200) and (400) reflection spots located at the same positions as those in Fig. 10. Streaks connecting the (110) reflections of the *s*PB-1 single crystals are clearly observed. The observed streaks indicate the presence of disorder in the stacking of bc layers. In the electron diffraction pattern of a copolymer with 52.1 mol% propene, see Fig. 12(b), streaks are also observed. It is, however, somewhat different from those shown in Fig. 12(a). There are clear intensity maxima at the locations of (220) and (020) reflection spots of the *s*PP single crystals as shown in Fig. 11. This indicates that the B-centered packing of *s*PP shown in Fig. 11 is the predominant packing scheme in the single crystals of the copolymer with propene content of 52.1 mol%. The different streaks appeared in Figs. 12(a) and 12(b) demonstrate the different mutual influence of the 1-butene and propylene components on the crystallization of the rich phase homopolymer. It is well explained that the appearance of the streaks reflects the existence of defects caused by shift of consecutive bc layers along the b -axis. As presented in Fig. 13, the propene-rich *s*PPBU samples exhibit a prevailing mode of B-centered packing as that of the *s*PP single crystal (right part of Fig. 11) with the presence of a $b/4$ shift along b -axis direction. The shift produces a local arrangement of the chains same as in the C-centered packing of the *s*PB-1 single crystals (Fig. 13B). On the other hand, the 1-butene-rich copolymers, a mode of packing of the C-centered form of *s*PB-1 (Fig. 10) becomes prevalent over that presented in Fig. 11. In this case, local arrangement of the chains same as in the B-centered form of *s*PP (Fig. 13A) becomes a defect due to the presence of a $b/2$ shift disorder of the *s*PB-1 crystals^[71].

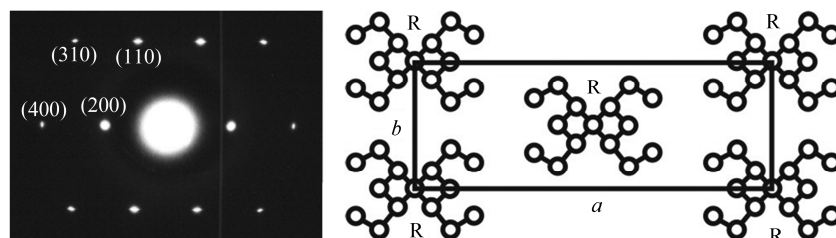


Fig. 10 An electron diffraction pattern of the *s*PB-1 single crystal (left) and a sketch of its packing model projected along the chain axis (right) (Reproduced from Ref. [71] with permission. Copyright © 2010 American Chemical Society.)

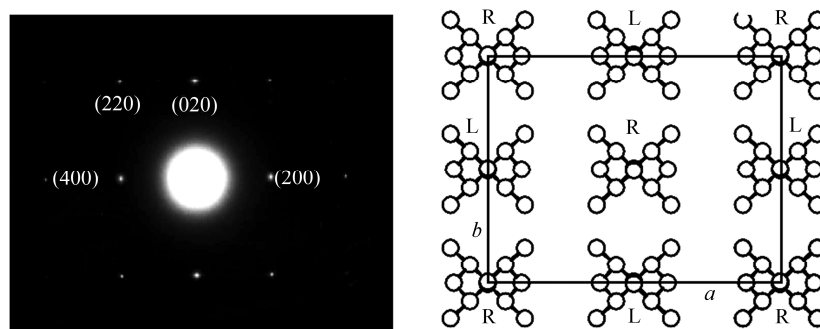


Fig. 11 An electron diffraction pattern of the sPP single crystal (left) and a sketch of its packing model projected along the chain axis (right) (Reproduced from Ref. [71] with permission. Copyright © 2010 American Chemical Society.)

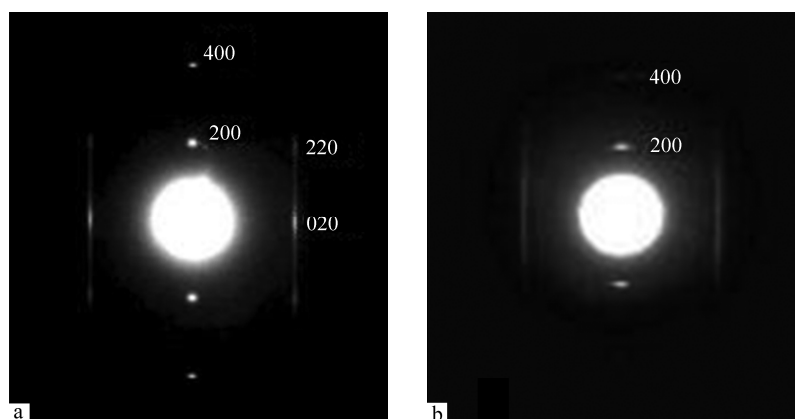


Fig. 12 Electron diffraction patterns of the sPPBU single crystals with propene content of (a) 34.7 mol% and (b) 52.1 mol% (Reproduced from Ref. [71] with permission. Copyright © 2010 American Chemical Society.)

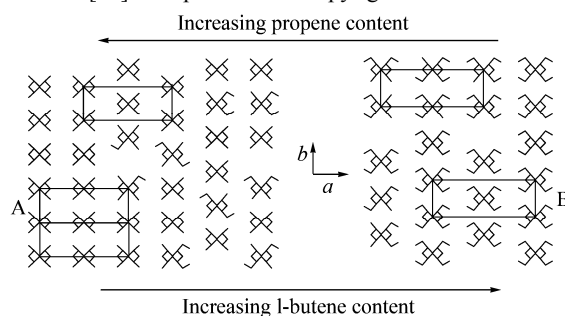


Fig. 13 Models of packing of $s(2/1)_2$ helical chains of sPPBU copolymers as a function of butene concentration: the unit cells of the B-centered sPP (A) and the C-centered isochiral form of sPB-1 (B) For propene-rich copolymers $b/4$ shift defects produce local arrangements of chains as in the C-centered form of sPB-1 (B) in a prevailing mode of packing of the B-centered form of sPP (A). At high butene content, $b/2$ shift defects produce local arrangements of chains as in the B-centered form of sPP (A) in a prevailing mode of packing of the C-centered form of sPB-1 (B). (Reproduced from Ref. [71] with permission Copyright © 2010 American Chemical Society.)

CONCLUSIONS

Electron diffraction is a very useful method for structure characterization of semicrystalline polymers. First of all, it is quite efficient in determining the crystal structure and its orientation. With help of electron diffraction, the polymorph behavior of polymers can be precisely identified. Second, structure relationship between polymer

crystals can be precisely illustrated through the analysis of electron diffraction. This is important for disclosing the origin of induced crystallization behavior of polymers with specific crystallographic interaction, such as the surface-induced epitaxial crystallization of polymers. It provides the mutual chain orientation as well as the contact planes of the polymer pair. For homopolymers, electron diffraction analysis can help to understand some special crystallization habit of polymers, such as the unique wide angle lamellar branching of α -iPP. Moreover, during the phase transition of a polymer crystal, the superimposed electron diffraction pattern will tell us whether there exists a fixed mutual orientation relationship between the original and transformed crystals. The recognition of some fixed structure relationships will lead to a sophisticated understanding of the transformation mechanism on a molecular scale. Third, the electron diffraction is able to reveal the disorders included in the polymer crystals by the appearance of streaks. A detailed analysis of the diffraction pattern of syndiotactic poly(propene-co-1-butene) random copolymers suggests that the propene and 1-butene components in the syndiotactic poly(propene-co-1-butene) random copolymers can cocrystallize in the same unit cell with evident defects. The defects existing in the propene-rich copolymers are caused by a $b/4$ shift of the bc layers in sPP unit cell. On the other hand, the defects existing in the 1-butene-rich copolymers are caused by a $b/2$ shift of the bc layers in sPB-1 unit cell.

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