

A unique morphology of freeze-dried poly(ethylene oxide) and its transformation

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Abstract

Freeze-dried poly(ethylene oxide) (PEO) samples were prepared from a 1×10^{-2} wt.% solution in benzene. After isothermal crystallization at 318.2 ± 0.1 K, a unique spherulite-like morphology with special inner structure was observed by transmission electron microscope. The crystal structure was identified to be the triclinic form. The molecular chains in it adopt the planar zigzag conformation, which was only found in the sample under tension. However, it was revealed in this paper that the triclinic crystals formed in the freeze-drying process can exist at room temperature for a long period. After being heated at a temperature far above the equilibrium melting point of PEO and cooled down to 318.2 ± 0.1 K, they transformed to the common monoclinic form. The resulting crystals show a great variety of regular polygonal shapes with multiple twin patterns. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene oxide); Freeze-dried; Transformation

1. Introduction

Poly(ethylene oxide) (PEO) has been extensively investigated in the past decades [1–9]. Kovacs studied the isothermal growth, thickening, melting and morphology of PEO [1–3]. A general morphological map illustrated the dependence upon molar mass and supercooling [4]. Molecular segregation and nucleation of PEO were examined by Wunderlich [5,6]. Cheng reported thickening and thinning of transient crystal and morphology of low molar mass PEO fractions [7,8].

The unit cell of PEO is monoclinic with $a = 0.805$, $b = 1.304$, c (fiber axis) = 1.948 nm and $\beta = 125.4^\circ$ and there are four chains of 7_2 helix per cell [9]. PEO can also assume various crystal modifications in the complex forms when incorporated with small molecules such as urea, thiourea [10] and HgCl_2 [11], in which, however, polymer chains still have a helical conformation. Later, a triclinic modification with $a = 0.471$, $b = 0.444$, $c = 0.712$ nm, $\alpha = 62.8$, $\beta = 93.2$ and $\gamma = 111.4^\circ$ was found in a PEO sample stretched about two-fold after necking at room temperature through in situ wide angle X-ray diffraction technique [12]. As indicated by authors, the planar zigzag chains pass

through the unit cell. After the tension is removed away, the chain conformation turns back to 7_2 helix quickly.

Recently, we reported the formation of a unique triclinic form in the freeze-dried PEO [13]. The molecular chains adopt the planar zigzag conformation. However, in contrast to what reported in the literature [12], we found the planar zigzag chain conformation is rather stable at room temperature. In this paper, we shall report the study on the transformation from the triclinic form to the monoclinic one. The later is more thermodynamically stable and shows bountiful regular morphologies of single crystals and multiple twins.

2. Experimental

A sample of PEO was purchased from polymer laboratories Inc.; it had a number-average molar mass of 1.39×10^6 with a polydispersity of 1.15. The PEO was dissolved in benzene to make a concentration of 1×10^{-2} wt.%. Before use, the solution was heated to 353.2 K for 30 min to dissolve any crystals that might form when the solution was kept for a long time. Reagent benzene was used with normal safety precaution after distillation.

The freeze-drying method was used for the preparation of specimens. A 1×10^{-2} wt.% solution of PEO in benzene was dropped directly onto copper grids with an ultra-fine syringe, and the copper grids had been covered with a

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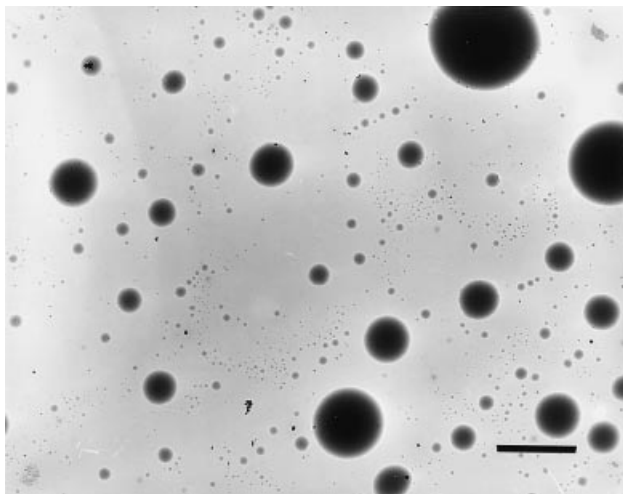


Fig. 1. Electron micrograph of circular micro-crystals of triclinic PEO. The scale bar indicates 1 μm .

colloid film, reinforced with evaporated carbon before use. The copper grids were put onto the top surface of a copper block, most of which was immersed in liquid nitrogen. Hence, the solution froze in a fraction of a second. The frozen solvent was sublimated at 258.2–263.2 K in an ice-bath under vacuum. In order to get rid of trace benzene possibly remained between segments, the silicon–oil diffusion pump was used to reach a fine vacuum and lasted at least for 5 h. After the total sublimation of the solvent, the freeze-dried sample was obtained. The sample was treated in two different ways. In one case, the freeze-dried sample was directly put into a thermostat to allow isothermal crystallization at 318.2 ± 0.1 K for 2 h. In the other case, the sample was first heated at 363.2 K for 15 min, and then

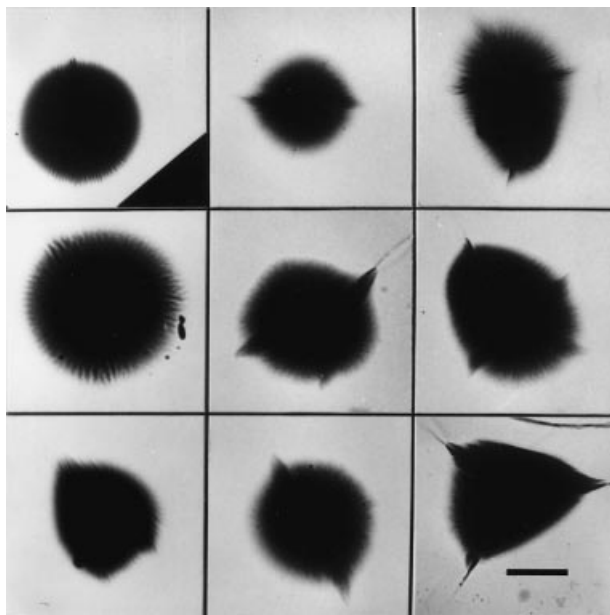


Fig. 2. A collection of electron micrographs of unique spherulite-like morphologies found in the freeze-dried PEO. The scale bar indicates 1 μm .

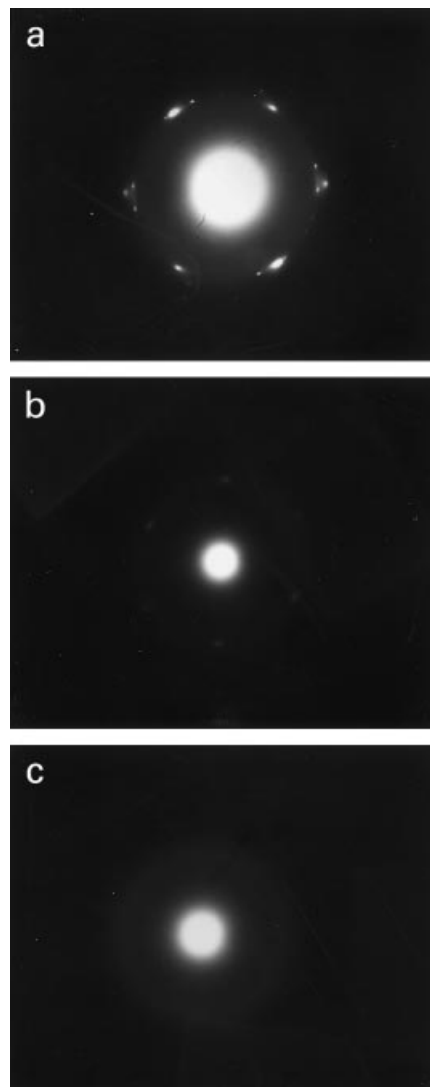


Fig. 3. Irradiation change of electron diffraction patterns of triclinic PEO under exposure of electron radiation with the beam intensity of 9×10^{-14} A cm^{-2} for various times: (a) 0; (b) 2; (c) 3.5 min.

cooled down and crystallized isothermally at 318.2 ± 0.1 K for 2 h.

After crystallization, the sample was immediately quenched to 273.2 K and observed with a Philips CM-12 transmission electron microscope (TEM). The operating voltage is 120 kV. Images and selected-area electron diffraction pattern were recorded at room temperature.

3. Results and discussion

3.1. Planar zigzag form of PEO

Fig. 1 shows the morphologies of the freeze-dried PEO prepared from 1×10^{-2} wt.% solution after isothermal crystallization. Apparently, they are circular particles with very different radius in size, ranging from tens of nanometers to

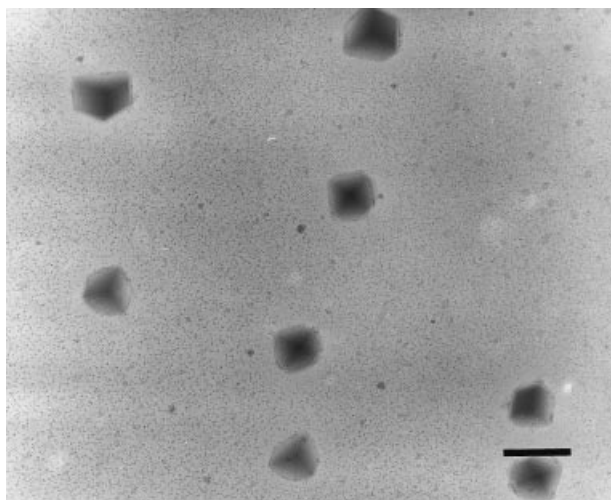


Fig. 4. Electron micrograph of regular-shaped crystals of monoclinic PEO. The scale bar indicates 1 μm .

several microns. It is pertinent to note here that the solution concentration is just near to the critical overlapping concentration C^* , which is estimated to be around 3×10^{-2} wt.% according to the dilute solution criteria put forward by de Gennes [14]. Below C^* , it is generally regarded that single-chain coils exist in the solution. However, because of dynamic collision between coils due to thermal motion, Cheng et al. found a dynamic contact concentration C_s , which is usually one to two orders of magnitude lower than C^* [15]. They argued that only below C_s can molecular chains become well separated in solution. Otherwise, aggregates of coils with different sizes would form when the concentration is above C_s . Even in the freeze-drying process, there is also a high possibility for the aggregation to occur. As a result, it was

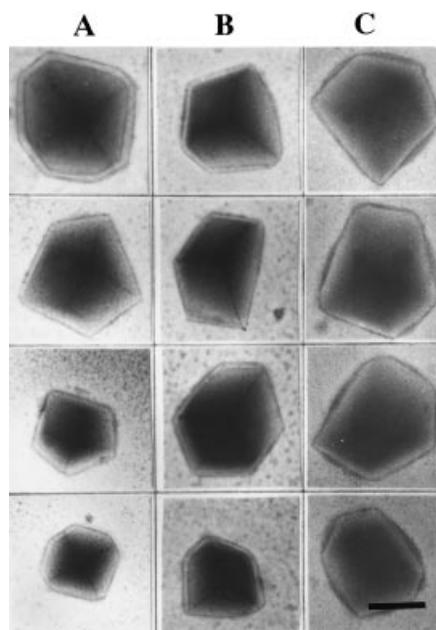


Fig. 5. A collection of electron micrographs of regular-shaped morphologies of PEO with multi-twin patterns. The scale bar indicates 1 μm .

not a surprise to see that the particles have a wide distribution of sizes.

Fig. 2 shows a collection of typical morphologies on observing particles at a slightly higher magnification. These particles seem to be of two-dimensional (2D) species; each of them is likely made up of bundles of delicate lamellar ribbons, which radiate from the center of the particle. Of special interest is the observation of the vague ridges in the interior of those circular particles. It was speculated that they might be related to micro-facets and micro-sectors as found in regular-shaped polygonal PEO single crystals.

Through selected-area electron diffraction technique, these circular particles were identified to be the triclinic modification of PEO crystal [13]. Such a unique crystal form was found only in the sample stretched about two-fold at room temperature before [12]. Close observation reveals that the lamellar may grow from the same nucleus and seem to keep some crystallographic coherence and thus give an ED pattern of single crystal, as indicated by Fig. 3(a). However, they still present a 'spherulite-like' structure apparently. The incident electron beam is assumed to be parallel to the c -axis (fiber axis) of the examined crystal and gives a $(001)^*$ ED pattern. This means that the chain axis should be normal to the substrate. Therefore, these lamellar ribbons prefer to grow from homogeneous nucleation rather than from heterogeneous nucleation via the carbon surface.

Under exposure of electron radiation with the beam intensity of 9×10^{-14} A cm^{-2} for 2 min, it was found that the electron diffraction intensity gradually diminished (Fig. 3b). After 3.5 min, the ED pattern disappeared completely (Fig. 3c). The total-end point dose (TEPD) [16,17] was estimated to 0.002 C cm^{-2} . It seems that the planar zigzag form has a better electron irradiation resistance than its helical counterpart.

3.2. Phase transition

In order to destroy all the original structures formed in the freeze-drying process, the freeze-dried sample was first heated at 363.2 K for 15 min, then cooled to 318.2 K to allow an isothermal crystallization for 2 h. Note the equilibrium melting temperature of PEO is 342.0 K. It was found that the triclinic form had transformed to the monoclinic one, which is more thermodynamically stable and commonly seen in most cases. Fig. 4 shows single crystals of the monoclinic PEO with regular morphologies. It is seen that twin boundaries are rather distinct emerging along smooth prisms of the crystal. It should be emphasized here that twin boundaries can be easily distinguished from the usual sector boundaries, which often appears as slight ridges originating from an apex instead [18].

Examining a large number of such PEO single crystals, a multitude of unique twins were found, as displayed in Fig. 5. These morphologies can be explained from a rational combination of two basic $(hk0)$ twin modes, namely the (100) and (120) twins, on the basis of the former work by Kovacs et al. [18].

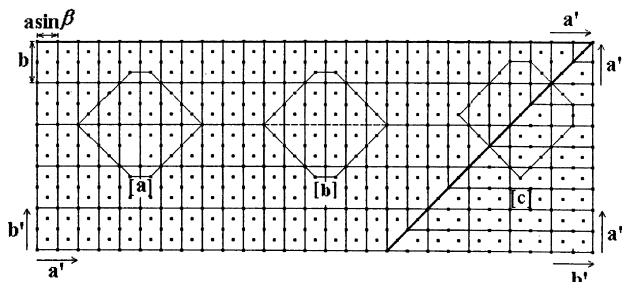


Fig. 6. Projection of the PEO lattice along the c -axis (chain direction) including a (100) twin boundary (thick dashed line) and a (120) twin boundary (thick solid line).

The monoclinic PEO has a chain conformation of 7_2 type (2 turns per 7 monomer units). Attention should be given to the fact that $2a \sin \beta$ is close to b . Hence, the projection along the c -axis appears tetragonal when two unit cells are combined together [18–21]. Fig. 6 represents an illustrative drawing of the projection of the monoclinic form along the c -axis direction. In general, the basic crystal habits of PEO are (120) and (010) prism faces. The simplest ($hk0$) habit is a square with four (120) faces. Part (a) of Fig. 6 represents a hexagonal appearance, in which (010) faces develop and truncate the b^* apices of the square. As a result, the crystal shape turns to be hexagonal and dependent on the (010) face development. In fact, the hexagonal-shaped single crystals are most frequently observed. Parts (b) and (c) show its two basic twin modes, i.e. (100) and (120) twinning, respectively. The identification of the twin modes is based on the morphological features of the overall shape of crystal and twin boundaries.

It is seen from Fig. 5 that crystals in column A and column B show very clear twin boundaries inside. In fact, they are multiple twins based on the combination of (120) and (100) twin modes. Two typical morphologies are schematically outlined in Fig. 7. Fig. 7(a) shows octagonal-shaped twins, corresponding to the crystals in column A of Fig. 5. It is seen that the crystals are originated from a square with (120) faces truncated by the (010) faces at the four apices. However, the (120) face is shortened and rounded by the emergence of the four (120) twin

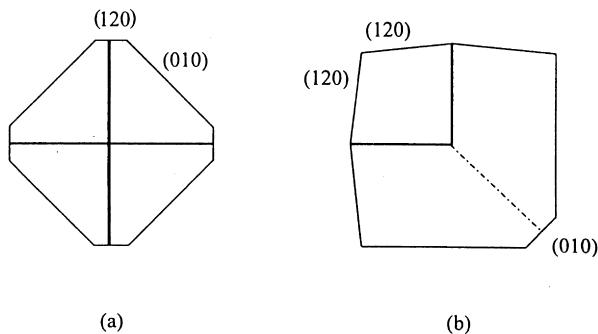


Fig. 7. Schematic illustration of multi-twin patterns: (a) four-fold (120) twinning; (b) (120) and (100) complex twinning. The solid line indicates (120) twin boundary and the dotted line indicates (100) twinning.

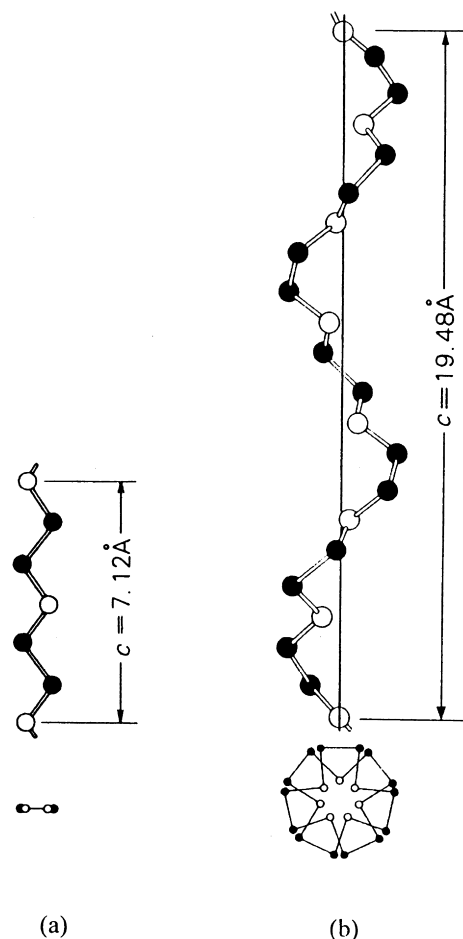


Fig. 8. Schematic illustration of two chain conformations of PEO: (a) planar zigzag; (b) 7_2 helix.

boundaries. Fig. 7(b) displays the crystal with three internal twin boundaries (two (120)s plus one (100)), as featured by the morphologies in column B, Fig. 5. Obviously, a slight, more or less rounded (010) apex can develop between the two (120) prism faces. This can cause the whole face to depart from (120) and become slightly roof-shaped, symmetrically about the emergence point of the twin boundary.

Compared to morphologies in columns A and B, there are no visible boundaries from the basal plane of the crystals in column C. These crystals must have been melted, resulting in a slight increase of volume. Moreover, the lateral prisms of the crystal also become somewhat rounded. A hawk-eye observation reveals that traces of twin boundaries are still present in the center of crystals.

3.3. Packing energy consideration

There is no mechanical stress applying to the molecular chains. Why can the freeze-dried PEO develop into the planar zigzag form, which is only stable under the strain at room temperature? When the solution was frozen abruptly, the solvent benzene crystallized first (the melting point of benzene is around 278.2 K). Chain coils of PEO are

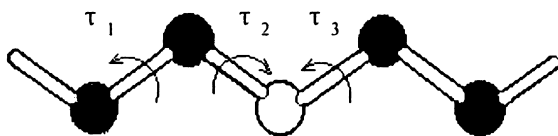


Fig. 9. Schematic illustration of torsion angles in a PEO chain-repeating unit.

most likely to suffer from the tension associated with the force of crystallization of solvent benzene. The effect just equals to be a situation when the sample is stretched using a mechanic elongation device. Hence, the planar zigzag conformation develops instead of the formation of the 7_2 helix.

It was reported when the tension is removed away, the planar zigzag chains will rapidly transform to the 7_2 helical conformation again [12]. However, we found this form can exist at room temperature for a long time. Only after being heated at a temperature (363.2 K) far above its equilibrium temperature (342.0 K) for a period of time to destroy all the original structure can it transform to the common monoclinic form. The two atomic models corresponding to two different modifications of PEO are illustrated in Fig. 8(a) and (b), respectively. Torsion angles defined for a PEO repeating unit are shown in Fig. 9. The energy map for the chain conformation under dihedral symmetry ($\tau_2 = \tau_3$) is known from the literature [22]. There are two lower energy minimums: one is at $\tau_1 = 60^\circ$, $\tau_2 = \tau_3 = 180^\circ$, $E = -1.9$ kcal/mol, and the other is at $\tau_1 = \tau_2 = \tau_3 = 180^\circ$, $E = -2.0$ kcal/mol. The former closely corresponds to the right and left-handed (7_2) helices (actually $\tau_1 = \pm 64.97^\circ$ and $\tau_2 = \tau_3 = \pm 171.75^\circ$). The later is related to the planar zigzag conformation.

On the basis of the known crystal structure of the two modifications, energy calculations were carried out. The results revealed that intramolecular potential energy of the planar zigzag form and the helix form is -1.6 and -1.9 kcal/mol, and intermolecular contribution is -6.3 and -6.0 kcal/mol, respectively [22]. Summing up the two parts, it is seen that the total packing energy of the two forms is equivalent to -7.9 kcal/mol. Naturally, one may ask why the helix form is so frequently observed while the planar zigzag one is rarely found except under tension. The answer to this question may be attributed to the two following reasons. First, the monoclinic PEO with 7_2 helix form prefers to form twins and multi-twins. Generally speaking, pure PEO single crystals are always less perfect, i.e. two or more crystal fragments often form at the different sites and are connected by loose materials, especially in the case of high molecular weight. If they coalesced into twin orientation, the resulting crystal would correspond to a lower packing energy. Second, the motion of molecular chains in the monoclinic phase seems to be more active, thus the crystal could rearrange easily, resulting in a more stable crystal by thickening even at room temperature.

Recently, Nakaoki et al. reported a spontaneous formation of the planar zigzag modification when syndiotactic

polypropylene (s-PP) was quenched to ice water from its melt [23]. Even brought back to room temperature, this planar zigzag form is still stable for a long period. Their observation is a good analogy to ours. It was known that molecular chain of s-PP is also accessible to planar zigzag conformation. In this sense, we proposed here that our experimental observation may be a universal phenomenon, i.e. when polymer chains are quenched from the hot solution or the melt, stress is applied to the molecular chains. Although the helix form is often thermodynamically stable to most semi-crystalline polymers, the planar zigzag conformation forms instead at this time. The situation is just like the case in which the molecular chains are elongated by a mechanic device. However, the accessibility to stable tt conformation for molecular chains is the sine qua non of the occurrence of the aforementioned phenomenon.

Acknowledgements

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