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Stabilization of metastable phase II of isotactic polybutene-1 by coated carbon

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Summary

Stabilization effect on metastable phase II of isotactic polybutene-1 (iPB-1) by coated carbon has been investigated by transmission electron microscopy (TEM) and electron diffraction (ED) techniques. The results indicate that after evaporating carbon, the phase II-I crystal transformation time is greatly prolonged from 9 days for carbon-uncoated samples to 120 days for carbon-coated ones under atmospheric pressure, while under high pressure (50 bar), the phase transformation time increases from 5 min for the former to 20 min for the latter. The stabilization effect on metastable phase II of carbon coated iPB-1 is attributed to a surface fixing effect of the evaporated carbon.

Introduction

Isotactic polybutene-1 (iPB-1) exhibits abundant polymorphs. Generally, melt crystallization under atmospheric pressure produces form II with 11/3 helical chains packed in a tetragonal unit cell [1] (a=b=1.542, and c=2.105 nm). The form II is a metastable state. Standing at room temperature, it spontaneously transforms into stable Form I, a denser crystal structure with 3/1 helical chains packed in a hexagonal or trigonal until cell [2] (a=b=1.77 nm, c=0.65 nm). It should be pointed out that the spontaneous solid-solid crystal transformation from form II to form I certainly results in some changes of physical properties of iPB-1, e.g., the shrinkage of molded objects caused by the densification, which, from a practical standpoint, limits considerably the applications of the material. The properties of form II, such as density, hardness and tensile strength [3] are different greatly with that of form I. Therefore, the research on retarding or stopping as well as speeding up the crystalline transformation will be helpful for deeper understanding and extensive application of the material.

It is known that vacuum evaporated carbon has strong surface fixing effect on polymer crystals [4-8]. By evaporating a thin layer of carbon the crystalline structure of highly oriented thin films [4-6] or single crystals [6,7] of polyethylene can be retained after complete melting and subsequent recrystallization. In addition, the dissolution resistance of the carbon-coated polyethylene crystals increases greatly [5,8].

In this communication, some experimental results are presented regarding the stabilization of metastable phase II by evaporated carbon in melt-crystallized lamellae of iPB-1, and the surface fixing effect of the evaporated carbon on the lamellae is discussed.

Experimental

IPB-1 used in this work (M_n= 450,000) was purchased from Polymer Laboratories with a melting temperature of 122°C.

The iPB-1 films, about 30-40 nm thick, were prepared by casting 0.1 wt% xylene solution of the polymer on the surface of glycerol at 100°C. After evaporation of the solvent, the thin films were transferred onto copper grids and then heated to 160°C for 15 min and subsequently crystallized isothermally at 95°C for 2 h. To compare the phase transition behavior, the films were coated ca. 3.0 nm thick carbon on single or two surfaces immediately after the heat treatment, and both carbon-coated and carbon-uncoated films were aged under atmospheric pressure or 50 bar pressure at room temperature for different time.

An ion beam coater model 681 made by Gatan Inc. was used to evaporate carbon, with the chamber base pressure 1×10^{-7}Torr and the carbon deposition rate 0.025 nm s^{-1}.

A JEM 2010 transmission electron microscope (TEM) operated at 200 kV was used in this study. Bright-field (BF) electron micrograph was obtained by defocusing the objective lens [9].

Results and Discussion

Figure 1 shows BF electron micrograph and the corresponding ED pattern of iPB-1 thin films as crystallized isothermally from the melt at 95°C for 2 h. The dark regions in the BF electron micrograph represent lathlike lamellae of iPB-1. The sharp diffraction spots in the corresponding ED pattern can be indexed as (200) and (220) reflections according to the tetragonal unit cell (a=b=1.542 nm, c=2.105 nm), which clearly indicates that iPB-1 melt crystallization at this temperature results in metastable form II, and the crystals exhibit a single crystal-like orientation, i.e., with their *c*-axis (the chain direction) perpendicular to the film plane, and *a*- and *b*-axes in the film plane. These results are similar to those reported in the literature.

In order to clearly compare the phase transformation behavior between the carbon-coated and carbon-uncoated thin films of iPB-1, first of all, it is needed to examine the phase transformation of carbon-uncoated sample. Figure 2 shows two series of ED patterns which indicate the occurrence of the transformation of the carbon-uncoated thin films. Just after the preparation, the crystals in the films show the ED pattern typical of form II (Figure 2a). After one day of aging, reflections corresponding to form I appeared in the ED patterns (Figure 2b), while after 9 days, the reflections of form II disappeared completely, and only those of form I were observed (Figure 2c). It should be pointed out that most of the transformed crystals exhibited “twinned” hexagonal patterns. However, untwinned hexagonal patterns were occasionally observed (Figure 2b’ and c’). This result is essentially the same as those reported by Holland et al. [10] and Tosaka et al. [11].

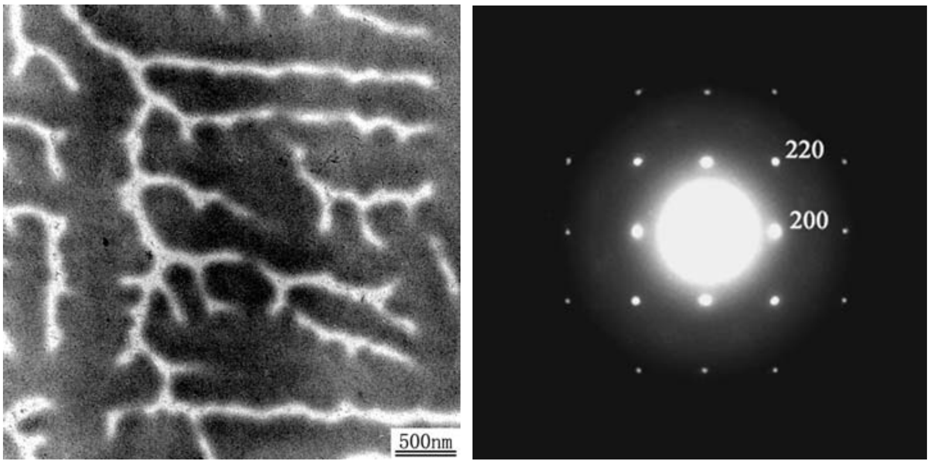

Figure 1. BF electron micrograph and the corresponding ED pattern of iPB-1 thin films crystallized isothermally at 95°C for 2 h

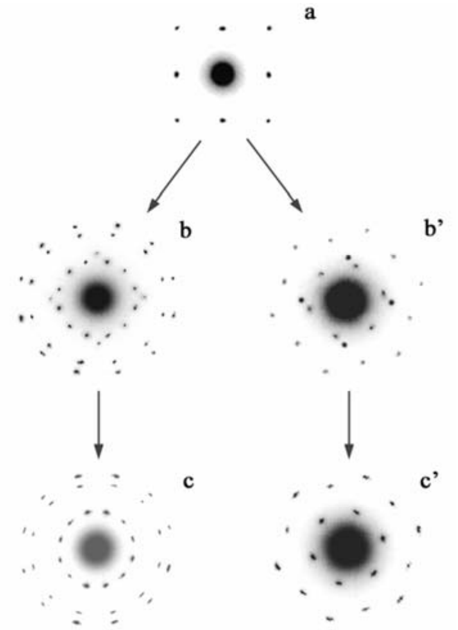

Figure 2. ED patterns of carbon-uncoated iPB-1 films: as-prepared (a), after 1 day (b, b') and after 9 days (c, c')

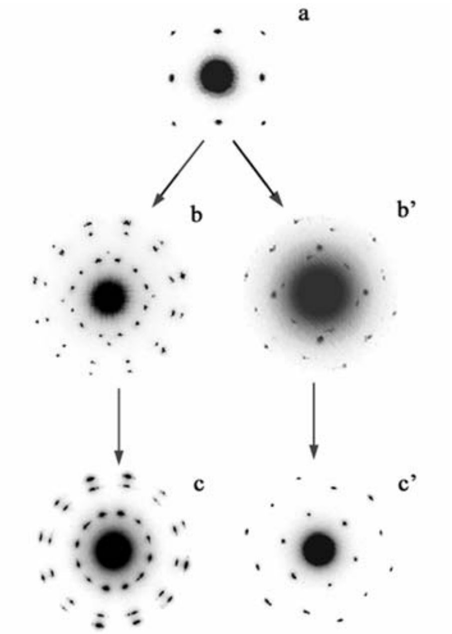

Figure 3. ED patterns of single surface carbon-coated iPB-1films: as-prepared (a), after 23 days (b, b') and after 120 days (c, c')

The phase transition behavior of carbon-coated films is different from that of carbon-uncoated ones. Figure 3 shows the ED patterns of the phase transition of single surface carbon-coated films. Until the 23rd day the phase II-I crystal transition could be observed (Figure 3b) and the transition has completed in 120 days after preparation of the single surface carbon-coated films (Figure 3c). In addition, just like the carbon-uncoated films, majority of form II crystals transformed into “twinned” form I, while only small amount of transformed “untwinned” form I could be detected (Figure 3b’ and c’). As for the two surfaces carbon-coated films, after aging as long as twelve months, some untransformed form II crystals in local regions of the films still could be observed by ED diffraction.

It is known that pressure is one of important factors which affect the phase II-I transformation of iPB-1 [12]. The ED patterns of the phase transition of iPB-1 films under 50 bar pressure are shown in Figure 4. Under high pressure, the phase II-I transformation of the carbon-uncoated films has completed in 5 min (Figure 4a), while for the carbon-coated films completing the phase transformation needs about 20 min (Figure 4b). Clearly , although the high pressure can tremendously accelerate the phase transformation, the retardation effect of the evaporated carbon on the phase II-I transformation of iPB-1 is obvious. The phase transformation time determined by electron diffraction is shown in Table 1. It should be pointed out that only the “twinned” hexagonal patterns were observed after the transformation under high pressure. A reasonable explanation is that, compared with the phase transformation to “untwinned” form I, the phase transformation to “twinned” crystals is relatively fast [12], while high pressure just enhance this difference between the two transformation processes.

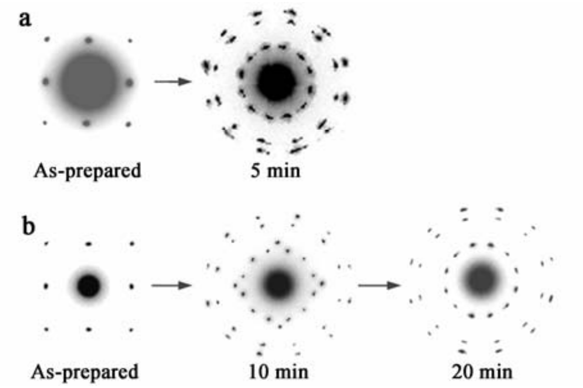

Figure 4. ED patterns of carbon-uncoated (a) and carbon-coated (b) iPB-1films aged under 50 bar pressure for different time

Table 1. The phase II-I transformation of carbon-coated and carbon-uncoated iPB-1 films

Time after preparation	Carbon-uncoated samples		Single surface carbon-coated samples	
	Start transition	Finish transition	Start transition	Finish transition
Under atmospheric pressure (day)	1	9	23	120
Under 50 bar pressure (min)		5	10	20

The retarded phase II-I crystal transformation of melt-crystallized lamellae of iPB-1 results unambiguously in the conclusion that the vacuum evaporated carbon film exhibits a strong surface fixing effect on the metastable form II crystals. The fixing effect should be mainly attributed to the formation of carbon-polymer interface layer. During the vacuum evaporation process, the sputtered carbon atoms could diffuse into the polymer, especially in the initial deposition stage. Although the diffusivity of the small penetrant into the polymer crystals has been proven to be very small, compared with that in the amorphous phase [13], a relatively sharp carbon-polymer interface layer could be formed. It should be pointed out that the presence of defects in the lamellar surface could enhance the diffusivity of the carbon atoms, and thus increase the local interface layer thickness. Unambiguously, the mobility of the fold chain ends and local chain segments which are embedded in the carbon-polymer interface layer are strongly confined by the neighboring carbon atoms. The local confinement in chain mobility is considered as a kind of carbon atom induced physical cross-linking [14] or the interaction of a carbon atom with a single chain [15]. On the other hand, the chemical interaction of deposited carbon with the polymer could not be completely ruled out. Although the evaporated amorphous carbon is unreactive, if free radicals are produced during the sputtering process, as suggested by Yan [5], it could be linked to the polymer by chemical interaction.

It is known that the solid-solid crystal transformation from metastable form II to stable form I accompanies lattice dimensional shrinkage (approximately-4% in the (110) II-(110) I) plane and about –20% in the direction normal to these planes) and lateral shifts of the molecular chains [16,17], as shown in Figure 5. Clearly, it is the local confinement in chain mobility caused by the evaporated carbon that retards greatly the phase II-I crystal transformation of iPB-1.

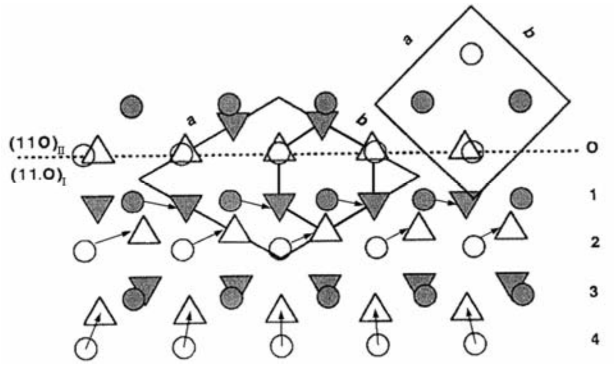

Figure 5. A scheme indicating form II–I transformation of iPB-1 according to Fujiwara [16]. A tetragonal cell of form II and a hexagonal (trigonal) cell of form I are indicated. 11/3 and 3/1 helices of form II and form I are represented as circles and triangles, respectively.

Conclusion

Under both the atmospheric and high pressures, the solid-solid crystal transformation of iPB-1 from metastable form II to stable form I can be greatly retarded by vacuum evaporated carbon. This phenomenon is attributed to a surface fixing effect of evaporated carbon. By physical or chemical interaction between the carbon and the polymer in the carbon-polymer interface layer, the mobility of local chains in the crystals is strongly confined, and, therefore, the metastable phase II is greatly stabilized.

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