Colloid Polym Sci (2007) 285:1149–1155
DOI 10.1007/s00396-007-1669-x

ORIGINAL CONTRIBUTION

Crystallization behavior of a propylene-1-butene random copolymer in its α and γ modifications

Qingqiang Gou · Huihui Li · Zhenqiang Yu · Erqiang Chen · Yudong Zhang · Shouke Yan

Received: 7 December 2006 / Accepted: 5 March 2007 / Published online: 17 April 2007

Abstract A random propylene-based copolymer containing 1.0 mol% 1-butene as co-unit, synthesized with Ziegler-Natta catalyst and then fractionated to make the sample having a uniform in molecular microstructure, was investigated by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXD), and atomic force microscopy (AFM). In the DSC curves, one can see clearly the endothermic peaks corresponding to the melting of α-iPP crystals and a group of broad endothermic peaks associated to the melting of the γ-iPP crystals. Wide-angle X-ray diffraction results indicate that both the α and γ modifications can be formed in the copolymer in a wide temperature range. The γ fraction increases first with increasing the crystallization temperature at the expense of its α component, which has been explained according to crystalline structures of iPP in its α and γ forms, and then decreases with increasing crystallization temperature as the crystallization of iPP in its γ phase has been suppressed at high temperatures. The γ-iPP content in the copolymer reaches maximum at the temperature of 130 °C. The in situ X-ray diffraction characterization on the isothermal crystallization process at 130 °C indicates that, as long as the γ-iPP can be detected, it takes always ca. 25% of the overall crystallinity. This leads to the conclusion that α- and γ-iPP crystals grow simultaneously during the crystallization process. The fact that the α and γ phases cannot be distinguished by morphological observation leads to the conclusion that they may intermix within one spherulite.

Keywords α-iPP · γ-iPP · Crystallization · DSC · WAXD · AFM

Introduction

Isotactic polypropylene (iPP) is one of the semicrystalline polymers that exhibit pronounced polymorphisms and morphologies depending on its tacticity, molecular weight, thermal treatments, and mechanical handling. At least three different crystalline structures of iPP, designated as α, β, and γ forms, have been reported [1–7]. Among them, the structural and morphological studies on the monoclinic α-form of iPP, conventionally produced by melt crystallization, were followed extensively since its first synthesis and characterization by Natta et al. in the 1960s [8]. The morphological studies on the γ phase of iPP have, however, received much less attention, and the early work had not been well continued for a long time [9, 10]. Even though the γ phase is a substantive phase of iPP, it usually co-crystallizes with its α counterpart under special conditions, such as, low M_w specimen, crystallization of conventional iPP under high pressure and incorporation of a few percent of comonomer at atmospheric pressure [3, 11, 12] Therefore, the γ phase of iPP had remained rather elusive for many years.

Q. Gou · H. Li · S. Yan (✉)
Beijing National Laboratory for Molecular Sciences,
State Key Laboratory of Polymer Physics and Chemistry,
Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100080, People's Republic of China
email: skyan@iccas.ac.cn

Z. Yu · E. Chen
Department of Polymer Science, School of Chemistry,
Peking University,
Beijing, People's Republic of China

Y. Zhang (✉)
Beijing Research Institute of Chemical Industry, SINOPEC,
Beijing 100013, People's Republic of China
e-mail: doctorydzhang@yahoo.com.cn

Q. Gou
Graduate School, Chinese Academy of Sciences,
Beijing 100039, China

The real breakthrough in our understanding of the γ phase structure dates from 1989 when Meille and Bruckner proposed the non-parallel chain packing in a orthorhombic unit cell with parameters a=0.854 nm, b=0.993 nm, and c=4.241 nm [2]. The chemical and physical requirements of its formation are, however, the subject of ongoing research. This has been revived by the recent development of the new metallocene catalyst systems, which allow incorporation of large contents of comonomers, for producing well-defined iPP copolymers with high stereoregularity. As a result, interest in the structural and morphological characterizations of γ iPP has increased in the past few years. During the recent years, a number of studies have been focused on the structure formation and characterization of the α and γ phase of iPP [13–21].

Through systematic studies on the dependence of γ phase upon chain defects and comonomer units, it is reported that the chain defect, which brings on structural irregularities in the long chains of propylene polymer, is a very important factor governing in the information of γ phase [14]. For example, 100% of the γ structure has been developed with a chain defect concentration greater than 4.4%. The effect of the incorporated co-units, independent of the chemical nature of the co-unit, in enhancing the fractional content of the γ modification is found to be the same as the role of chain defects in the iPP homopolymer. However, differences in the partitioning of the co-units, such as ethylene, l-butene, l-hexene and l-octene, between the crystalline and noncrystalline regions lead to contents of the γ phase that differ among the copolymers. As the gamma phase is favored in low M_w specimen, higher gamma contents have been found in propylene–hexene and propylene–octene copolymers, in which the co-units are rejected from the crystal lattice.

The kinetics study demonstrated that endotherms corresponding to both α and γ-iPP increase with time at different temperature. Analysis on the heat of fusion of two endothermic peaks integrated from differential scanning calorimetry (DSC) experiments, it was found that the α-iPP quickly reaches a constant value, which decreases with increasing crystallization temperature, while its γ-iPP counterpart increases continuously with time at any crystallization temperature. Moreover, a temperature dependence of γ-iPP content was also reported. Normally, the γ-iPP content increases with increasing crystallization temperature in low temperature range, then reaches a maximum value, and finally decreases with further increase of the crystallization temperature. The reason for this phenomenon is, however, not quite clear so far.

In the present work, X-ray diffraction was employed to characterize the α and γ iPP structures in a propylene-1-butene random copolymer with low 1-butene content, ca. 1.0 wt%, which was not covered in literatures. In particularly, we focus our attention on the in situ crystallization process to elucidate kinetic influence on the γ crystallization of the copolymer. The purpose of this manuscript is to present the experimental details and some new results regarding the formation mechanism of the γ-iPP.

Experimental

Materials

The propylene-1-butene random copolymer used in the present study was synthesized through a gas-phase polymerization process with an isospecific Ziegler-Natta catalyst. To make the sample uniform in molecular weight, temperature rising elution fractionation (TREF) technique was used for fractionating the sample. C^{13}NMR technique was employed to characterize the propylene sequence length in the copolymer and the 1-butene content. The characteristic data of the used copolymer are summarized in Table 1. The results show that the sample exhibits essentially high isotacticity without head-to-head or tail-to-tail monomeric units.

WAXD

For crystalline structure characterization, a Philips diffractometer (Philips X'pert Pro with X'Celerator detector) with CuKα radiation (λ=1.542 Å) was used in this study. The sample stage was set horizontally, and the diffraction peak positions were calibrated with silicon powder (2θ>15°) and silver behenate (2θ<10°), respectively. A temperature control unit (Paar Physica TCU 100), calibrated by Philips Company, in conjunction with the diffractometer, was utilized to study the structure evolution of the propylene-1-butene random copolymer during isothermal crystallization process at different temperatures. Peak assignment for the γ and α phases follows the previous designations by Bruckner and Meille and Turner-Jones [2, 3]. The overall crystallinity and the percentage of γ phase in total crystal

Table 1 Characteristics of propylene-1-butene random copolymer sample

Molecular mass M_n, g/mol	M_w/M_n	Melting point (°C)	Butene content (mol%)	PP sequence length n_P
1.82×10^5	2.35	155.80	1.0	96.20

were calculated according to the method reported by Turner-Jones [3]. We take the peak heights of the characteristics $(117)_\gamma$ reflection at $2\theta=19.8°$ and the typical $(130)_\alpha$ reflection at $2\theta=18.3°$ to calculate the γ content according to the following equation: $H\gamma/(H\alpha+H\gamma)$, where the H_γ and H_α represent the peak heights of $(117)_\gamma$ and $(130)_\alpha$, respectively.

To characterize the temperature influence on the crystallization behavior of the copolymer, the samples were first heated up to 180 °C for 10 min in flowing nitrogen atmosphere, and then cooled down to the predefined temperatures for isothermal crystallization. The period of crystallization at each temperature was set fivefold the crystallization time as determined by DSC measurement. For in situ tracking, the isothermal crystallization process of the sample at 130 °C, the sample was first heated to 180 °C for 10 min in flowing nitrogen atmosphere, and subsequently cooled to 130 °C at a cooling rate of approximately 10 °C/min for isothermal crystallization. During the isothermal crystallization process, series 1D WAXD intensity profiles were recorded from the beginning of crystallization over 240 min.

DSC

Calorimetric measurements were performed in a differential scanning calorimeter (Perkin Elmer DSC-7) under nitrogen flow. Temperature calibration was carried out with indium as a standard. At first the samples were heated up to 200 °C, held at the temperature at least 10 min, and subsequently cooled down to the desired temperature at a rate of 100 °C/min for isothermal crystallization.

AFM

The crystalline morphologies were monitored by NanoScope III, Tapingmode SPM from Digital instruments. The sample was prepared by spin-coating its xylene solution on freshly cleaved mica surface. After evaporation of the solvent, the copolymer thin film was heated to 180 °C for 10 min and then quenched to predetermined crystallization temperature for 48 h. Then, the phase images were captured in tapping mode at ambient conditions.

Results and discussion

In this report we selected a propylene-1-butene random copolymer with relatively uniform molecular microstructure treated by use of a TREF technique because no detailed investigation of this kind of copolymer was given in the literatures. Figure 1 shows a set of DSC endothermic curves of the propylene-1-butene random copolymers isothermally crystallized at a series of crystallization temperatures for a sufficiently long time to ensure the completion of the crystallization. From Fig. 1, it can be seen that there exists an obvious peak on each DSC curve, which is normally associated to the melting of α-iPP. As expected, the main melting peaks shift to higher temperature, and become sharper with increasing isothermal crystallization temperature. In the lower temperature range, ca. 10 °C lower than the main melting peaks, a group of broadened endothermic peaks with a melting range of about 20 °C can be recognized with careful inspection.

These broadened peaks display a trend of becoming narrower and clearer as the crystallization temperature increases from 90 to 135 °C. These parts correspond to the melting of its γ-iPP counterpart. It should be pointed out that these peaks are not as clear as that observed by Alamo et al. [14]. This originates from the fact that the propylene-1-butene copolymers have a lower γ phase content compared with other propylene-based copolymers, even though the amount of γ-iPP increases with the increasing 1-butene content. On the other hand, it was reported that the chain defects (regio and stereo) encourage the formation of γ-iPP. For example, 100% of the γ structure could be developed with a chain defect concentration greater than 4.4%. In the present study, the sample used has a relatively lower content of 1-butene, ca. 1.0 mol %, and no artificial induced chain defects, e.g., region and stereo defects. Moreover, the different catalysts may also play a specific role on the regularity of the copolymers. As a result, the obtained DSC curves are not at all similar to that reported by Alamo et al. [14].

It should be pointed out that an exact integration of the heat of fusion for the peaks associated to the α and γ

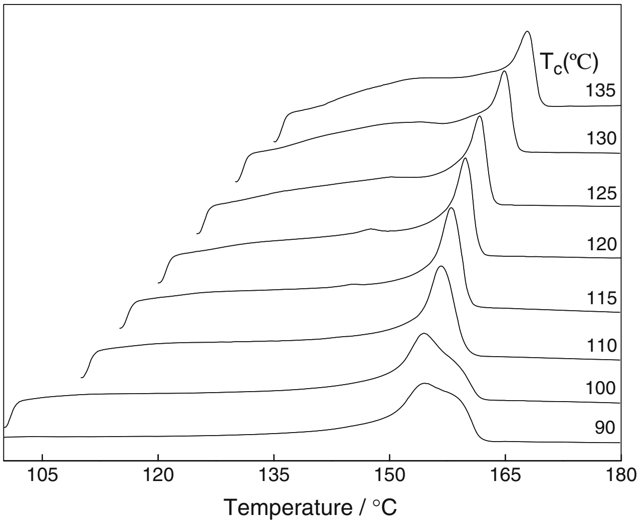

Fig. 1 DSC endothermic curves of the propylene-1-butene random copolymers crystallized isothermally at different crystallization temperatures for sufficient long time. The crystallization temperatures are indicated in the diagram

polymorphs can be hardly performed as the severe overlap of the main peaks and the broadened peaks. Therefore, calculation of the contents of the α and γ polymorphs from the heat of fusion as conducted by Alamo et al. is very difficult here. To get extract content of the α and γ polymorphs and elucidate the growth processes of the α- and γ-iPP crystals in the propylene-1-butene copolymer, in situ WAXD experiments have been conducted to track the crystallization process of the propylene-1-butene copolymer. Figure 2 presents a set of 1D WAXD intensity profiles of the propylene-1-butene copolymer as a function of isothermal crystallization temperature. The peak assignments for the α and γ polymorphs follow the previous designations of Bruckner et al. and Turner-Jones, namely, the peaks at $2\theta=19.8°$ and $2\theta=18.3°$ are attributed to the characteristic reflections of γ (117) lattice plane and α (130) lattice plane, respectively [2, 3, 20].

From Fig. 2, it can be found that crystallization temperature is an important and sensitive factor governing the formation of the γ-iPP. At temperatures below 90 °C, the characteristic peak of γ phase is hardly identified on the X-ray density profiles. With increase of crystallization temperature, the γ_{117} peak appears gradually and gets highest at temperature of 130 °C. With further increase of the crystallization temperature, e.g., at 140 °C, the γ_{117} peak decreases again, indicating that the formation of γ-iPP at this temperature has been depressed. For clarity, the dependence of the γ phase content, defined as $H_{\gamma 117} / \left(H_{\alpha 130} + H_{\gamma 117}\right)$, on the isothermal crystallization temperature is shown in Fig. 3.

One can note that the content of γ-iPP increases at first quickly up to ca. 25%, and then decreases sharply down with further increase of crystallization temperature. A maximum of γ-iPP content is obtained at isothermal crystallization temperature of about 130 °C, suggesting that 130 °C is the optimum crystallization condition for generating γ-iPP in the used propylene-1-butene copolymer. This is in good agreement with the results of Alamo et al. on the study of propylene–ethylene and propyelene-1-hexene copolymers [13]. According to the above X-ray diffraction result, a question may be raised about the fact that neither high nor low crystallization temperature is favorable of formation of γ-iPP in the propylene-1-butene copolymer. This can be explained on the basis of the molecular aspects of iPP in its α and γ crystal modifications.

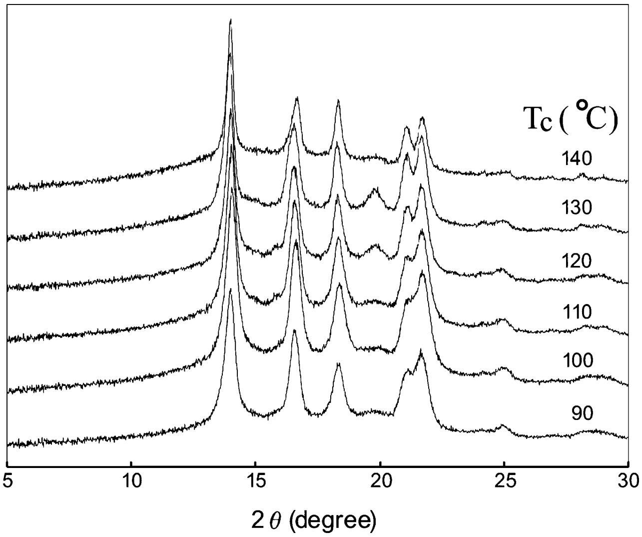

Fig. 2 WAXD experimental results of the copolymers crystallized isothermally at different temperatures as indicated in the diagram for sufficient long time

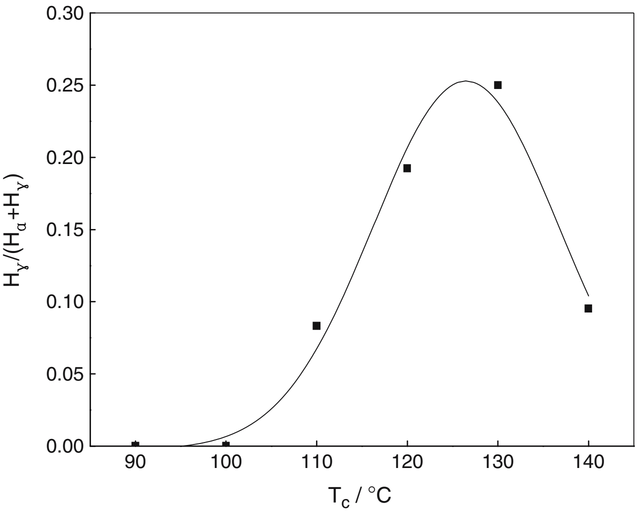

Fig. 3 Fractional content of the γ polymorph in the propylene-1-butene copolymer as a function of crystallization temperature

It is well documented that α-iPP exhibits a unique wide-angle lamellar branching, which is an intrinsic property of it and manifests itself under many crystallization conditions, e.g., growth from thin molten layer (see Fig. 4a) and in solution crystallization (see Fig. 4c). The phenomenon was observed in the early 1960s, but an understanding of it on a molecular level was achieved only nearly 20 years later [9, 22–24]. Taking the molecular subgroups, i.e., the side methyl groups, and the hand of helices into account, Lotz et al. [9, 24] has successfully explained that the branching takes place whenever two successive *ac* layers are made of chains of the same hand, whereas the crystallographic unit cell requires that they are of opposite hand. On the other hand, the crystalline structure of γ-iPP has long been a puzzle problem. Until 1989, Meille and Bruckner have proposed a structure, which departs from common principles of polymer crystallography, in that the chain axes in the structure are not parallel [2].

The non-parallelism of the γ-iPP chains proposed by Meille and Brückner can be actually summarized in simple terms with respect to the α-phase lamellar branching, in a way that chain axis rotation leading to lamellar branching of α-iPP has become a crystallographic element of symmetry in the γ-phase unit-cell. Taking all those into

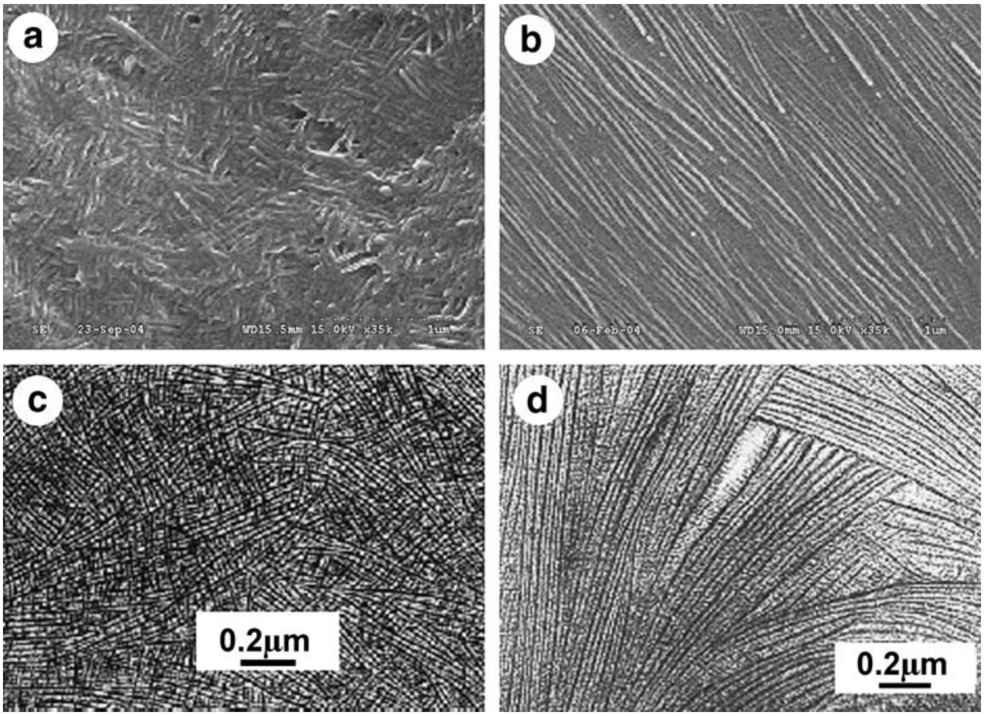

Fig. 4 Scanning electron micrographs (**a** and **b**) and transmission electron micrographs (**c** and **d**) of α-form iPP crystallized isothermally at (**a**) 110 °C, (**b**) 138 °C, (**c**) 100 °C, and (**d**) 130 °C. The samples of (**a**) and (**b**) were melt-crystallized, while the samples of (**c**) and (**d**) were solution-cast films

account, one may suggest that the formation of γ phase plays a similar role in avoiding steric conflicts of the helical chains as the wide-angle branching. In this case, the increment of γ phase with increasing crystallization temperature can be explained as follow. As shown in Fig. 4, the wide-angle lamellar branching of α-iPP decreases with increasing crystallization temperature; compare Fig. 4b with a. This can be more clearly seen from the transmission electron micrographs of the solution cast ultrathin films; compare parts c and d of Fig. 4.

The decrease of lamellae branching leads to the change of optical property of the spherulites from positive to negative. Considering that the content of γ-iPP in the copolymer first increases with crystallization temperature while its overall crystallinity remains almost unchanged, it is concluded that the fractional content of the γ polymorph increases at the expense of the alpha phase. We can therefore imagine that the decline of branching ability in the α form of iPP with increasing temperature is compensated by the formation of γ-iPP crystals for avoiding steric conflicts of the helical chains encountered during crystallization. At even higher temperature, e.g., 140 °C, the crystallization of iPP in its γ phase may be suppressed due to the lower melting point compared with its α counterpart. This leads to not only the depression of γ-iPP but also a reduction in overall crystallinity; see Fig. 3.

To confirm this, an experiment was performed with the sample first crystallized at 140 °C to a time point at which the intensity of the X-ray diffraction profile did not change anymore, and then cooled down to room temperature. The X-ray intensity profile of thus prepared sample is given in Fig. 5. It is clear that the characteristic γ_{117} diffraction at 2θ= 19.8° appears after cooling the sample to room temperature. Meanwhile, the overall crystallinity increases with respect to that shown in Fig. 3. Nevertheless, the γ-iPP takes still ca. 25% of the overall crystallinity. This confirms that the crystallization of γ-iPP is suppressed at 140 °C.

As the maximum γ-iPP is obtained at about 130 °C during the in situ isothermal crystallization process, the isothermal crystallization kinetics of the propylene-1-butene copolymer was in situ studied at this temperature by X-ray diffraction. Figure 6 shows the time-resolved WAXD intensity profiles of the propylene-1-butene copolymer

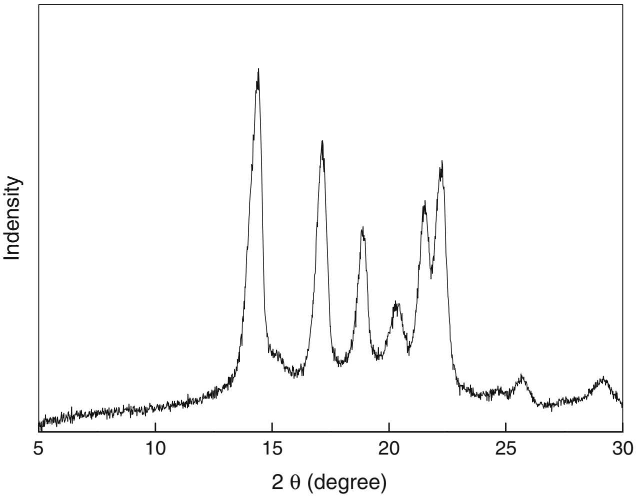

Fig. 5 The X-ray intensity profile of a propylene-1-butene copolymer, which was first crystallized at 140 °C for 48 h, at the time point the intensity of the X-ray diffraction profile did not change anymore, and then cooled down to room temperature

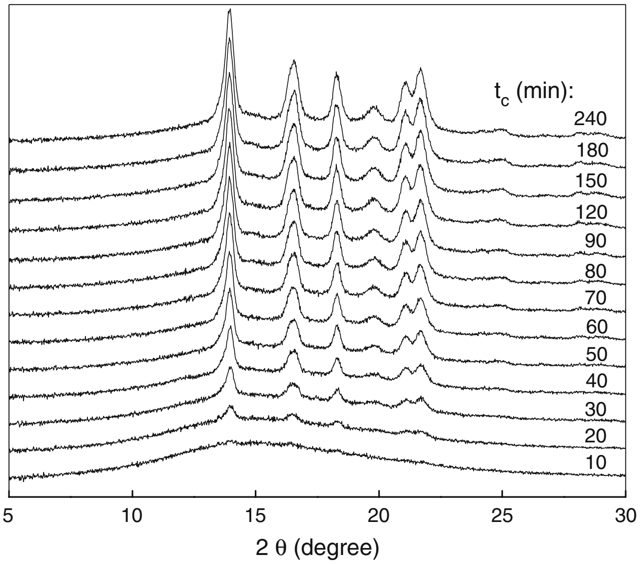

Fig. 6 WAXD intensity profiles of the propylene-1-butene copolymer recorded at different times during the isothermal crystallization process at 130 °C

crystallized isothermally at 130 °C. In the first 10 min, except for the amorphous background contributed by the isotropic melt, no characteristic diffraction peaks either for the α- or γ form can be found. This indicates that the crystallization of propylene-1-butene copolymer has not been started yet. The diffraction spectra of α-form iPP can be clearly seen after 20 min crystallization, while the characteristic peak of γ-form iPP at $2\theta = 19.8°$ is only visible after 30 min crystallization at 130 °C. Hereafter, the diffraction intensities of both α- and γ-iPP crystals get higher and higher with the lapse of time.

According to this result, one may argue that the α-iPP crystals form about 10 min earlier than its $\gamma\gamma$ counterpart and initiate the crystal growth of the γ component. However, considering the relatively lower intensity of the characteristic reflection of γ-iPP with respect to the α-iPP and the very weak reflections of the α-iPP crystals displayed in Fig. 6 after 20 min crystallization, there is the possibility that the formation of γ-iPP has been overlooked. Therefore, more detailed analysis is of great importance. For this purpose, the overall crystallinity of the propylene-1-butene copolymer together with the content of the γ-iPP as a function of crystallization time is presented in Fig. 7. From Fig. 7, it is found that the overall crystallinity increases rapidly at the beginning, then slows down gradually after 10 min of crystallization, and finally reaches an equilibrium state after ca. 150 min.

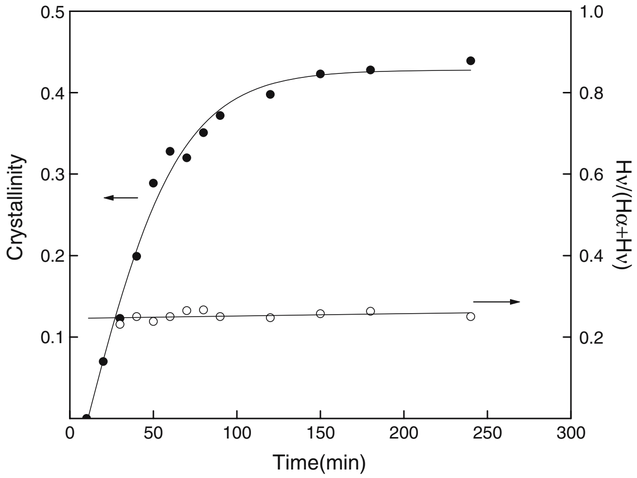

Fig. 7 Crystallinity and content of the γ-modification of the propylene-1-butene copolymer as a function of isothermal crystallization time at 130 °C

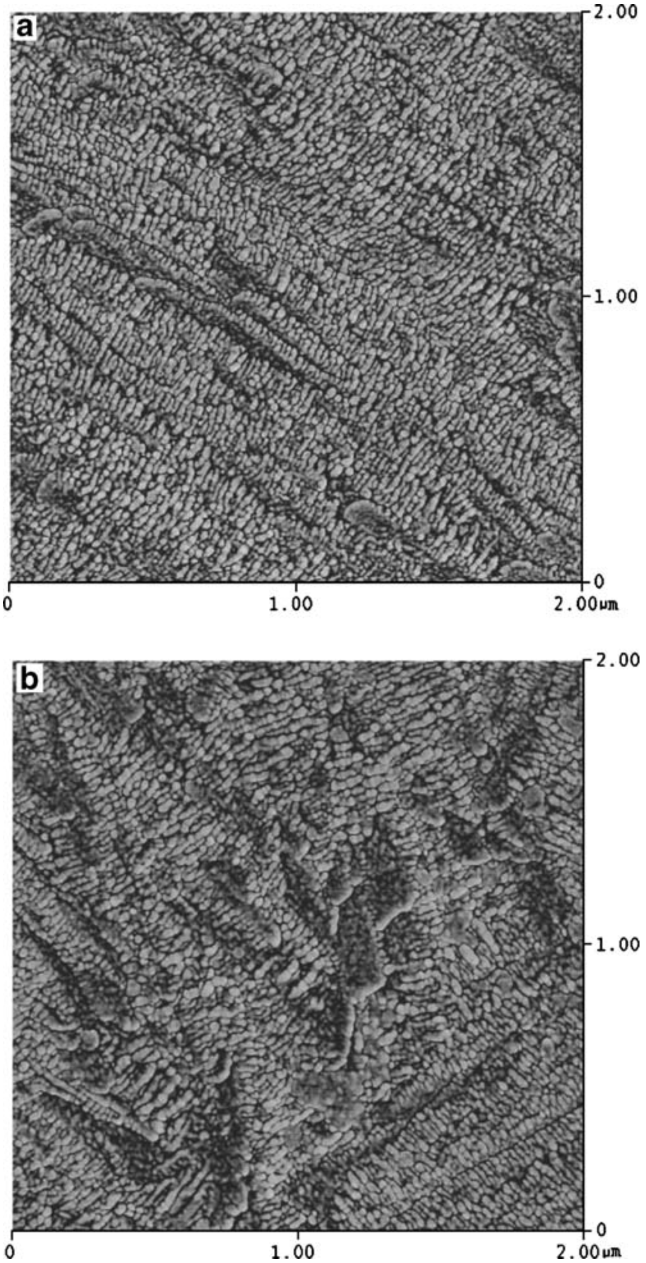

Fig. 8 Atomic force micrographs of the propylene-1-butene copolymers crystallized isothermally at (**a**) 130 °C and (**b**) 90 °C, respectively

This implies that the crystallization of the used propylene-1-butene copolymer has basically finished in about 150 min at 130 °C. The crystallinity of the sample at present condition is somewhat less than 40%. Another issue concerns the ratio of γ-iPP in the crystallized copolymer during the crystallization process. As can be seen from Fig. 7, once it is detectable, the γ-iPP takes up ca. 25% of the overall crystallinity. This keeps unchanged all the time during the whole crystallization process. From this result, we can conclude that the growth of α and γ-iPP crystals proceeds simultaneously. Moreover, it is found that the iPP α and γ phases are difficult to be distinguished via AFM observation (see Fig. 8), even after selective melting of the lower melting point γ-iPP crystals (data not given in the text). These results suggest that in bulk crystallized iPP, the α and γ phases should be intermixed.

Conclusions

The crystallization behavior of a TREF-fractionated random copolymer of propylene with a small amount of 1-butene comonomer, synthesized with a Ziegler-Natta catalyst, was investigated. The results indicate that both the α and γ modifications can be formed in the copolymer in a wide temperature range. It is found that the γ fraction increases first with the crystallization temperature at the expense of its α component, which can be explained according to crystalline structures of iPP in its α and γ forms, and then decreases with increasing crystallization temperature as the crystallization of iPP in its γ phase has been suppressed at high temperatures. The in situ X-ray diffraction characterization on the isothermal crystallization process at 130 °C, which has been attested to be the optimal condition for γ crystallization, indicates that as long as the γ-iPP can be detected, it takes always ca. 25% of the overall crystallinity. This leads to the conclusion that α- and γ-iPP crystals grow simultaneously during the crystallization process. These phases can, however, not be distinguished by morphological observation as they may intermix.

Acknowledgments The financial support of the Outstanding Youth Fund (No. 20425414), the National Natural Science Foundations of China (No. 50521302, 20423003, 20574079, and 20604031), and the 973 programs from MOST of China are gratefully acknowledged.

References

1. Turner Jones A, Aizlewood JM, Beckeet DR (1964) Makromol Chem 75:134
2. Bruckner S, Meille SV (1989) Nature 340:455
3. Turner-Jones A (1966) Polymer 7:23
4. Turner-Jones A (1971) Polymer 12:487
5. Guidetti GP, Busi P, Giulianelli I, Zannetti R (1983) Eur Polym J 19:757
6. Bruckner S, Meille SV, Petraccone V, Pirozzi B (1991) Prog Polym Sci 16:361
7. Campbell RA, Phillips PJ, Lin JS (1993) Polymer 34:4809
8. Natta G, Corradini P (1962) J Polym Sci 58:1191
9. Lotz B, Graff S, Wittman JC (1986) J Polym Sci Polym Phys Ed 24:2017
10. Alama RG, Ghosal A, Chatterjee J, Thompson KL (2005) Polymer 46:8774
11. Mezghani K, Phillips PJ (1997) Polymer 38:5725
12. Mezghani K, Phillips PJ (1998) Polymer 39:3735
13. Alamo RG, Kim M-H, Galante MJ, Isasi JR, Mandelken L (1999) Macromolecules 32:4050
14. Hosier IL, Alamo RG, Esteso P, Isas JR, Mandelkern L (2003) Macromolecules 36:5623
15. Nogales A, Hsiao BS, Somani RH, Srinivas S, Tsou AH, Balta-Calleja FJ, Ezquerra TA (2001) Polymer 42:5247
16. Foresta T, Piccarolo S, Goldbeck-Wood G (2001) Polymer 42:1167
17. Auriemma F, Rosa CD, Boscato T, Corradini P (2001) Macromolecules 34:4815
18. Rosa CD, Auriemma F, Circelli T, Waymouth RM (2002) Macromolecules 35:3622
19. Auriemma F, Rosa CD (2002) Macromolecules 35:9057
20. Hosier IL, Alamo RG, Lin JS (2004) Polymer 45:3441
21. Auriemma F, Rosa CD (2006) Macromolecules 39:7635
22. Khoury FJ (1966) J Res Natl Bur Stand 70A:29
23. Padden FJ, Keith HD (1966) J Appl Phys 37:4013
24. Lotz B, Wittman JC (1986) J Polym Sci Polym Phys Ed 24:1541