Polymer Vol. 37 No. 26, pp. 5959–5963, 1996

0032-3861/96/$15.00+0.00

S0032-3861(96)00565-4

Formation of β-modification of isotactic polypropylene in its late stage of crystallization

József Varga*
Department of Plastics and Rubber, Technical University of Budapest, Müegyetem rkp 3, H-1521 Budapest, Hungary

and Gottfried W. Ehrenstein
Lehrstuhl für Kunststofftechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Am Weichselgarten 9, D-91058 Erlangen, Germany
(Received 27 February 1996; revised 10 May 1996)

In the late stage of the crystallization of isotactic polypropylene (IPP), melt inclusions are encapsulated by the crystallized phase. The contraction caused by the proceeding crystallization within the inclusion leads to a reduced pressure accompanied by the appearance of vacuum bubbles. In the surface layer of the melt surrounding the vacuum bubbles, the polymer chains are subjected to extension during the development of bubbles, which leads to the formation of α-row nuclei. As has been observed during the shear-induced crystallization of IPP, the row-nuclei formed *in situ* can also induce the growth of the β-phase in this case. It was demonstrated that a possible reason for the $\alpha - \beta$ transition on the surface of growing α-spherulites is the local mechanical stress caused by the contraction. Based on experimental results, suggestions are made for the origin of the strongly birefringent phase observed by Duval *et al.* during the crystallization of blends of IPP and IPP grafted with maleic anhydride. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polypropylene; β-modification; extension-induced crystallization)

Introduction

The general regularities of spherulitic crystallization of isotactic polypropylene (IPP) have been essentially discovered[1,2]. However, the late stage of crystallization has some characteristics that were investigated quite recently. During the late stage of crystallization, non-crystallized melt is confined in the space within the crystalline phase as inclusions. From this moment on, the contraction due to crystallization cannot be compensated by material flux, thus crystallization takes place within the inclusions under an ever-decreasing pressure. Some characteristic features of the crystallization under reduced ('negative') pressure were pointed out by Piorkowska and Galeski[3]. They established that the melting point of the portion of crystals, formed from the melt enclosed by the spherulites, was higher than that of the surrounding α-spherulites. Further, they revealed a reduced growth rate of spherulites within the inclusion. The authors attributed these observations to the depression in the equilibrium melting point (T_m^0) due to the 'negative' pressure. At a constant temperature of crystallization (T_c), a reduced equilibrium melting point is equal with decrease in the actual supercooling ($\Delta T = T_m^0 - T_c$). This reduced supercooling explains both for the elevated melting point and the reduced growth rate of the spherulites formed inside the inclusion. Another consequence of the formation of melt inclusions is the appearance of some voids within the completely crystallized inclusions. In samples crystallized at higher temperatures ($T_c > 135°C$), voids as cracks in boundaries between spherulites can be observed[4]. At lower T_c values, however, the 'negative' pressure is released with the formation of vacuum bubbles accompanied by acoustic phenomena which can be detected by sensitive methods[5,6].

The present paper shows the formation of β-modifications of IPP (β-IPP) on the extended surface layer of vacuum bubbles which are generated in the melt inclusions due to contraction during the late stage of crystallization of IPP.

Experimental

Commercial propylene homopolymer, Tipplen H523 (Tisza Chemical Works Ltd, Hungary; with $M_w = 5.2 \times 10^5$ and $M_n = 3.1 \times 10^4$; MFI $= 4$ dg min^{-1} at 230°C and 21.2 N load) was used throughout the experiments. Crystallization and melting processes were studied by polarized light microscopy in a Leitz Dialux 20 equipped with Mettler FP 82 hot stage as described in our previous paper[7]. IPP cut of 20 μm thickness was placed between slide and cover slip and hot pressed on a preparation hot stage. The sample was heated up to 220°C and hold for 5 min prior to the crystallization experiments in order to erase the thermomechanical prehistory. The sample was then cooled to T_c at a rate 5°C min^{-1}. After crystallization, samples were heated starting from T_c (at a heating rate of 2°C min^{-1}) in order to eliminate the tendency to the $\beta\alpha$-recrystallization induced by recooling[1]. The scanning electron microscopy (SEM) studies were carried out on Cam Scan (Electronen Optic Serv.) apparatus. The samples were etched using the permanganic method[8].

---

* To whom correspondence should be addressed

Figure 1 Formation of crack-like material-deficient boundaries between spherulites during high-temperature crystallization (T_c = 135°C)

Results and discussion

'Cracked' spherulite boundaries evolved at higher crystallization temperatures ($T_c \geq 135$°C) are shown in *Figure 1*. At lower T_c values, the appearance of bubbles in the melt region encapsulated by the spherulites, the growth of the crystal front having strong negative birefringence and partial melting of the structure developed on the surface of the bubbles are illustrated in *Figure 2*. Bubbles emerged practically in an instant at the same time (*ca* 4 min at T_c = 125°C) after the encapsulation of the melt. During heating, the strongly birefringent phase melts in the temperature range characteristic for the melting of β-IPP, i.e. between 153 and 155°C (*Figure 2c*). The formation of β-IPP is confirmed by the strong negative birefringence of the related structures and its melting behaviour. Moreover, not only the melting but also the recrystallization characteristics of the strongly birefringent phase reflect the presence of the β-modification[1,2]. Thermo-optical studies revealed that after heating to temperatures between the melting points of α- and of β-modification, the strongly birefringent β-phase recrystallized into α-modification during subsequent cooling. If the sample had been cooled to room temperature before melting, the β-phase recrystallized into α-modification during the partial melting. This resulted in a higher melting point of the recrystallized product than that of the α -spherulites originally formed in the sample[1,2].

The above phenomenon is easily reproducible. After the melt had been encapsulated, within a shorter or longer time (depending on T_c), an instantenous bubble formation and growth of β-phase on it always took place (*Figures 3a, 3b* and *3c*). However, due to occasional concomitant phenomena, more complex structures, including the α-phase, may also be formed. Firstly, the acoustic waves arising during the bubble formation could generate α-nuclei in high density in the vicinity of some bubbles. These induce a micro-spherulitic α-phase growth in the encapsulated melt (see the arrow in *Figure 3b*). This is clearly perceptible after the separate melting of the β-phase (*Figure 3e*). Secondly, besides the appearance of fixed-sized bubbles, ever-growing slowly propagating bubbles may be produced as well (see the arrows in *Figures 3c* and *3d*). On the surface of these bubbles no β-phase develops. During isothermal crystallization, first only one bubble appeared. It is believed that the other bubbles in the vicinity of the growing spherulitic front (*Figure 3b*) are induced by mechanical (acoustic) wave associated with the formation of the first one. The existence of acoustic waves during the bubble formation and their intensity distribution as a function of the time was shown experimentally by Galeski and co-workers[5,6].

Figure 2 Growing of the crystal front of the β-modification (T_c = 125°C) on vacuum bubbles formed in the encapsulated melt (a and b) and the residual structure after separate melting of the β-phase at 158°C (c)

The formation of β-IPP on the vacuum bubbles can be attributed to the mechanical loading of the crystallizing melt. In the surface layer of the melt surrounding the suddenly expanding vacuum bubbles, the polymer chains are subjected to extension, which can lead to the formation of α-row-nuclei. As has been observed during the shear-induced crystallization of IPP, the α-

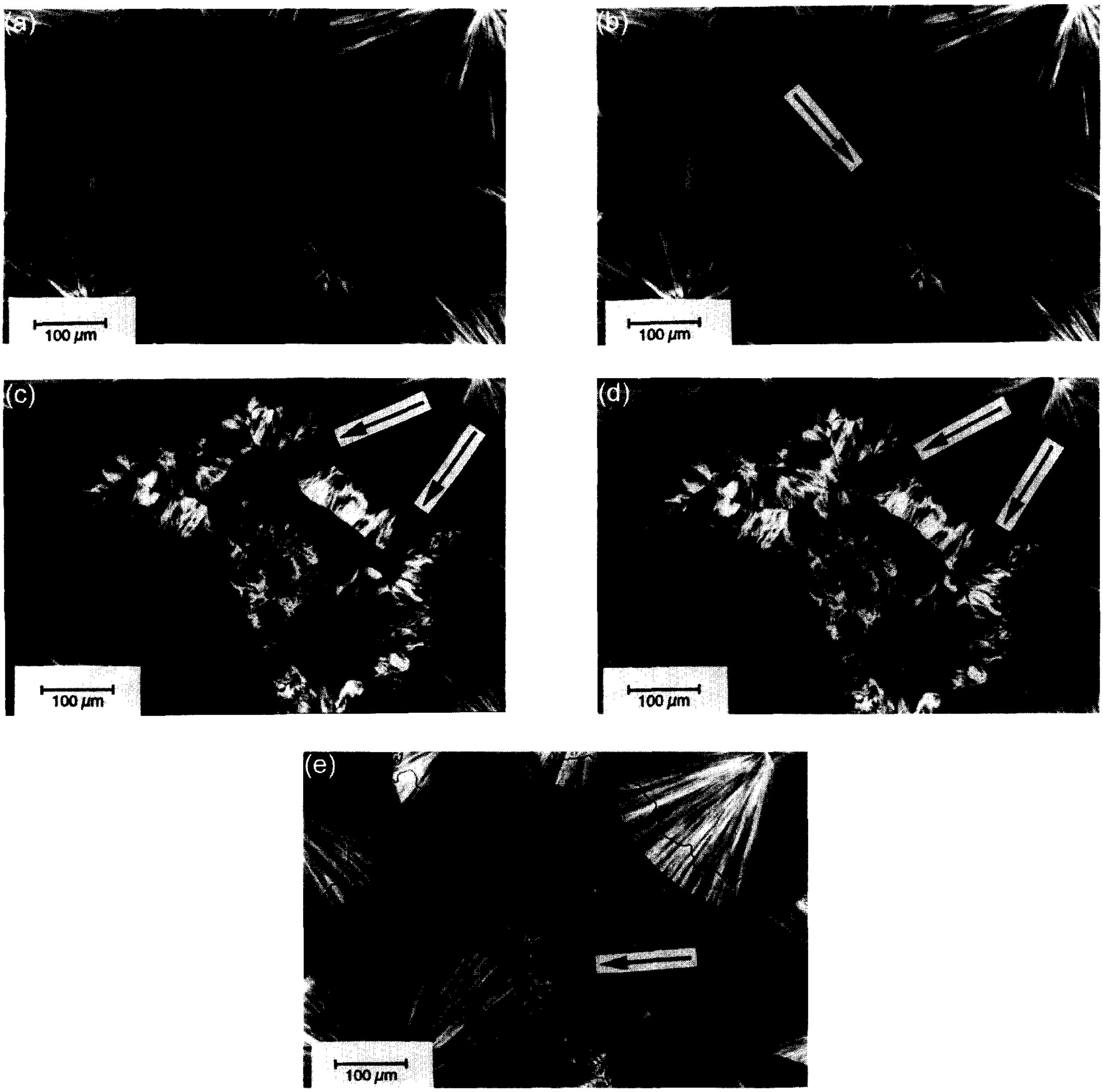

Figure 3 β-Phase growth on vacuum bubbles ($T_c = 125$°C) and its melting: (a) encapsulated melt; (b) appearance of bubbles; (c) growth of crystals in encapsulated melt; (d) structure after crystallization; (e) residual structure after separate melting of the β-phase at 158°C

row-nuclei formed *in situ* induce the growth of the β-phase. A detailed discussion about the growth of β-phase on α-row nuclei generated by shear stresses in the melt is given in ref. 7. The rules of supermolecular structure formation during the shear-induced crystallization of IPP were reported in several papers[1,2,7,9–11]. It was established among others that melt shearing generated first α-row nuclei, on the surface of which a secondary αβ-nucleation took place[7]. As a consequence of this, a cylindritic band of β-modification develops if the growth rate of the β-modification is higher than that of the α-modification. This condition is met between $T(\beta\alpha) = 140$°C and $T(\alpha\beta) = 100$°C[1,7]. It was also shown that for the formation of β-phase (and thus for the row-nuclei) a critical deformation rate is necessary[11]. This is why no β-phase grows on the surface of slowly propagating bubbles. It has been proved by the present results that α-row nuclei can be formed, and will induce the crystallization of β-phase, due to tensile loading of the melt *(extension-induced crystallization)* following the above mechanism[7]. The jagged α-cylindritic band as grown from the surface of the α-row nuclei produced by melt extension can be observed as a ring around the vacuum bubble after the separate melting of the β-phase (see the arrows in *Figures 2c* and *3e*).

The morphology of the β-phase developed on the vacuum bubble is shown in *Figure 4*. The structure in the vicinity of this vacuum bubble consists of flat-on lamellae with a large number of screw dislocations on their surfaces. Since the β-lamellae are prone to twist along the growth direction, one can observe some lamellae in edge-on or in an intermediate stage, as well

Figure 4 SEM picture on the β-phase developed on a vacuum bubble at $T_c = 130°C$

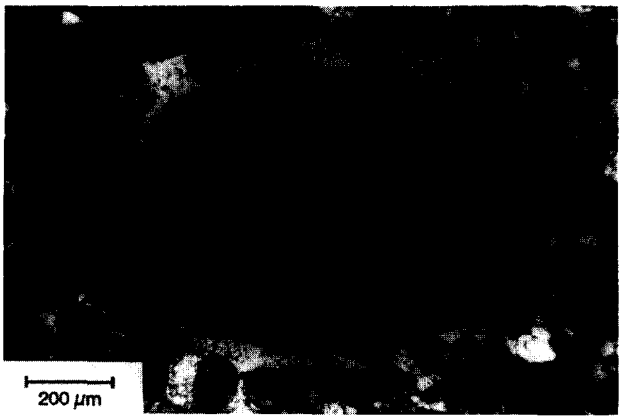

Figure 5 Vacuum bubble and the β-phase grown on its surface in an extrusion weld (melt temperature: 240°C, welding rate: 4 mm s^{-1})

Figure 6 Strongly birefringent β-spherulite segments growing off from α-row nuclei. These were formed in the extended surface layer of the weld. (Extrusion-welded sample; melt temperature: 240°C, welding rate: 4 mm s^{-1})

(*Figure 4*, lower left side). This SEM picture resembles that of Olley[8], taken by transmission electron microscopy (TEM) on β-IPP. Based on this SEM picture, it can also be claimed that the plane direction of lamellae agrees with the direction of the α-row nuclei (i.e. the tensile loading direction).

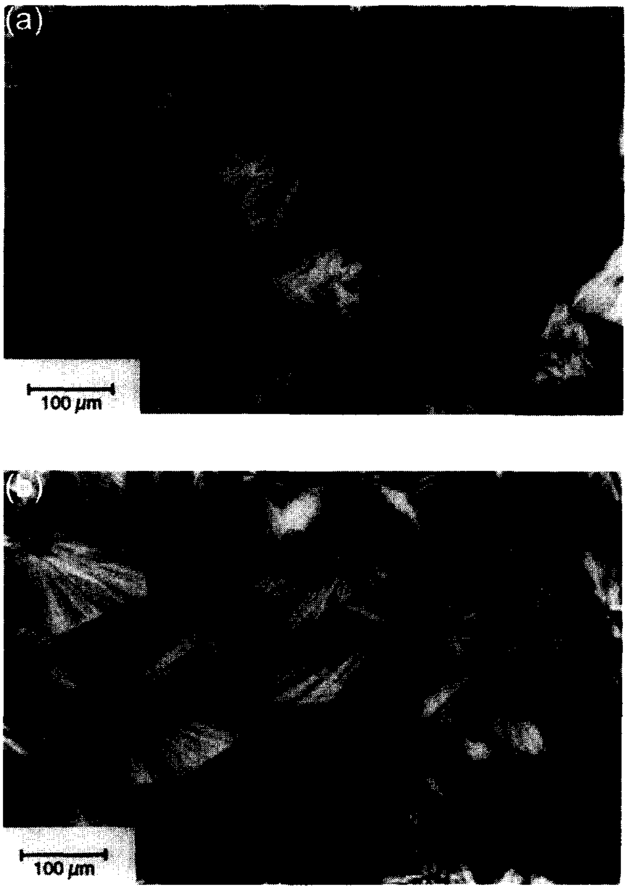

Figure 7 Twin spherulites formed during the $\alpha - \beta$ transition on the surface of α-spherulites growing in the encapsulated melt at $T_c = 120°C$ (a), and the residual structure after the separate melting of the β-phase at 158°C (b)

It is of importance to demonstrate some practical consequences of the above phenomenon. During the processing of plastics, the contraction due to crystallization is compensated by an appropriate holding pressure in order to avoid the formation of vacuum voids or holes. In some techniques, however, such as in extrusion welding[12], no holding pressure can be applied. Consequently, inside the recrystallized weld voids with β-modification on their surface should appear. In fact this is demonstrated in *Figure 5* where a stripe of highly birefringent β-modification around the bubble is clearly perceptible. It should also be pointed out that the presence of β-IPP can be detected in plastics products in the vicinity of zones subjected to tensile stresses in the molten state during processing. α-Row nuclei, which induce the crystallization of β-phase, are produced on the extended surface of melt by the fountain flow on the course of injection moulding[2]. This results in the formation of β-rich crystalline bands along the knit-lines of the melt fronts (see e.g. Figure 32 in ref. 2). A similar instance is given in *Figure 6*, where a strongly birefringent β-cylindritic band has grown off from the extended surface layer of the extrusion weld. It is clearly perceptible that the β-phase has developed from point-like β-nuclei located along the α-row nuclei, that were formed on the extended melt surface.

Our observations corroborate the fact that tensile loads to IPP melt promote the formation of β-phase. Therefore it is surprising that Galeski and co-workers[5,6] did not mention the appearance of β-modification, though they had conducted systematic investigations on the late stage of crystallization of IPP, including even an acoustic emission study on the bubble formation. On the other hand, it is worth noting that Duvall *et al.*[13] reported similar structures to those in *Figures 2* and *3* when a blend of IPP with maleic anhydride grafted IPP was crystallized. In their Figures 3–5 in ref. 13, the appearance of a strongly birefringent β-phase on the vacuum bubble formed in the encapsulated melt is clearly discernible. However, the authors delivered a doubtful explanation to this phenomenon, and to the formation of the structure observed. They supposed that the strongly birefringent phase had resulted from a separate crystallization of the chemically modified (grafted with maleic anhydride) IPP. Since the strongly birefringent phase in the cited blends *appeared always within the encapsulated melt and only on the bubbles*, it is reasonable to accept our interpretation related to the formation of β-IPP. In fact, the latter was supported by the melting experiments of the authors themselves[13] where the strongly birefringent phase melted in melting temperature range of β-IPP (at 154–155°C).

In the later stage of the crystallization of IPP, another, less reproducible, manifestation of formation of β-modification was observed as shown in *Figure 7*. In this case, the β-phase has developed from pointlike nuclei (i.e. punctiform on the level of the optical resolution) located on the surface of α-spherulites growing inside the encapsulated melt. From these nuclei, segments of strongly birefringent β-spherulites have developed, resulting in characteristic $\alpha\beta$-twin-spherulites (*Figure 7a*). These strongly birefringent spherulite segments melt around 153–155°C, which is the melting range of β-IPP (*Figure 7b*). Consequently, this structure is not identical to the negatively birefringent α-phase observed by Piorkowska and Galeski[3] because the latter is α-modification with higher melting temperature. It can be established on the basis of the residual structure after the β-phase has melted (*Figure 7b*), that the shape of the $\alpha\beta$-spherulite boundary line becomes similar to a logarithmic spiral evolved in consequence of the α–β transition on the growing front of the spherulites[2]. Since the β-phase was produced without bubble appearance in this case, it is supposed that the formation of β-nuclei in the encapsulated melt is induced by a local stress due to contraction.

To summarize the above results, it can be concluded that, in the late stage of crystallization of IPP, the local tensile stress created within the encapsulated melt induces the growth of the β-modification.

Acknowledgement

One of the authors (J. V.) gratefully acknowledges the financial support given by Deutsche Forschungsgemeinschaft (DFG) for an appointment by invitation at the Friedrich-Alexander Universität.

References

1 Varga, J. in 'Polypropylene: Structure, Blends and Composites', (Ed. J. Karger-Kocsis), Vol. 1, Chapman and Hall, London, 1995 chapter 3
2 Varga, J. *J. Mater. Sci.* 1992, **27**, 2557
3 Piorkowska, E. and Galeski, A. *J. Polym. Sci., Polym. Phys. Edn* 1993, **31**, 1285
4 Monasse, B. and Haudin, J. M. *Colloid Polym. Sci.* 1985, **263**, 822
5 Galeski, A., Koenczoel, L., Piorkowska, E. and Baer, E. *Nature* 1987, **325**, 40
6 Galeski, A. Piorkowska, E. Koenczoel, L. and Baer, E. *J. Polym. Sci., Part B. Polym. Phys.* 1990, **28**, 1171
7 Varga, J. and Karger Kocsis, J. *J. Polym. Sci., Polym. Phys. Edn* 1996, **34**, 657
8 Olley, R. H. *Sci. Prog. Oxf.* 1986, **70**, 17
9 Varga, J. and Karger-Kocsis, J. *Composites Sci. Techn.* 1993, **48**, 191
10 Varga, J. and Karger-Kocsis, J. *Polymer* 1995, **36**, 4877
11 Dragaun, H., Hubeny, H. and Muschik, H. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 1779
12 Gehde, M. and Ehrenstein, G. W. *Polym. Eng. Sci.* 1991, **31**, 495
13 Duvall, J., Selliti, C., Myers, C., Hiltner, A. and Baer E. *J. Appl. Polym. Sci.* 1994, **52**, 207