

Highly Active Thermally Stable β -Nucleating Agents for Isotactic Polypropylene

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ABSTRACT: Calcium salts of suberic (Ca-Sub) and pimelic (Ca-Pim) acids were synthesized and implemented as in different grades of isotactic polypropylene (iPP). Propylene homopolymer, as well as random and block copolymers containing these additives, crystallized iPP into pure or nearly pure β modification in the isothermal and nonisothermal crystallization experiments. Recently, Ca-Sub proved to be the most effective β -nucleating agent of iPP. The Ca-Sub nucleating agent widens the upper crystallization temperature range of pure β -iPP formation up to 140°C. In this study the effect of these additives on the crystallization, melting characteristics, and structure of the PP were studied. The degree of crystallinity of β -iPP was markedly higher than that of α -iPP. A widening in the melting peak of the samples crystallized in a high temperature range was first observed and discussed in regard to literature results of the same phenomenon for α -iPP. The morphology of the β -iPP samples was revealed by scanning electron microscopy. Independent of the type of polymer or nucleating agent, hedritic structures were found in the early stages of growth of the β -spherulites. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2357–2368, 1999

Key words: β -polypropylene; β -hedrite; crystallization; lamellar arrangement; melting; β -nucleating agent; recrystallization; scanning electron microscopy; thermal analysis

INTRODUCTION

The addition of β -nucleating agents can lead to the formation of pure or nearly pure β -modification of isotactic polypropylene (iPP).^{1,2} For the manufacturing of β -iPP products under processing conditions, β -nucleating agents with high activity, selectivity, and sufficient physical and chemical stability should be implemented during processing. The most popular highly active β -nucleating agent is γ -quinacridon.^{1–5} The drawback of the use of γ -quinacridone is its intense red color

and its polymorphic nature. Because of the polymorphism, a modification transition can take place during processing and this can consequently lead to the decrease of the β -nucleating activity. We observed in our laboratory that certain salts of aliphatic dicarboxylic acids are also effective β -nucleating agents.^{1,2} The most beneficial selectivity and activity were found for calcium salts of pimelic (Ca-Pim) and suberic (Ca-Sub) acids. In this study the preparation, characterization, and effects of these β -nucleating agents on the crystallization, melting, and structure of iPP was investigated.

EXPERIMENTAL

The β -nucleating agents were combined at a concentration of 0.001–0.1 wt % with commercially

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Table I MFI and Molecular Characteristics of Homopolymers Studied

PP Grade	Code	MFI (dg/min)	M_n (kg/mol)	M_w (kg/mol)	P
Tipplén H384	A-H3	13.4	72.3	219.5	3.03
Tipplén H543	A-H5	5.5	65.4	268.2	4.1
Tipplén H781	A-H7	0.76	128.6	440.9	3.42

available granulates of three PP homopolymers (Tipplén H384F, H543F, and H781) of different melt flow indexes (MFIs), a random ethylene-PP copolymer with an ethylene content of 2.2 mol % (Tipplén R351F), and an ethylene-PP block copolymer (Tipplén K392). The β -nucleated samples will be referred to as B-H3, B-H5, B-H7, B-R3, and B-K3, respectively, while the samples absent of the nucleate will be referred to as A-H3, A-H5, A-H7, A-R3, and A-K3, respectively. The first and second letters describe the nucleate and the polymer type (H for homopolymer, R for random copolymer, and K for block copolymer) and the number refers to the character of the melt flow feature in the trade name. The MFI (2.16 kg/230°C/10 min), molecular weights (M_n , M_w), and polydispersity (P) values for the homopolymers are shown in Table I. The MFI values are 11.0 for the random copolymer and 12.0 for the block copolymer. The β -nucleating agents were mixed with the pellets via powder sprinkling on the surface of the granules followed by homogenization in a Brabender plastograph at 200°C.

The thermal stabilities of the nucleating agents were characterized by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements at a heating rate (V_h) of 20°C/min. For the TGA measurements, a DuPont 9900 (General V2.2A) apparatus was used with N_2 and air atmospheres. A Phillips Micro Müller instrument using Ni-filtered CuK_α radiation was used to perform wide angle X-ray scattering (WAXS).

A Perkin-Elmer DSC-7 instrument recorded the melting and crystallization curves of the samples in N_2 . The samples were heated to 220°C and held for 5 min before crystallization to erase the effects of the thermomechanical history. During nonisothermal measurements, samples were crystallized at a cooling rate (V_c) of 10°C/min. To eliminate the tendency for β recrystallization during partial melting,¹ the final temperature of cooling (T_R) was 100°C. During the isothermal measurements the cooling to the crystallization temperature (T_c) occurred at a rate of 40°C/min. The

samples were melted at a heating rate of 10°C/min beginning from the T_R or T_c .

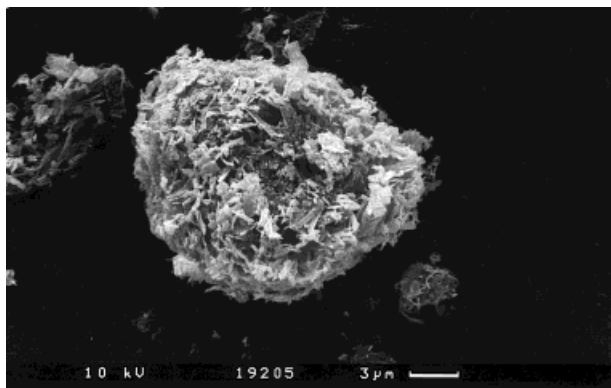
Scanning electron micrographs (SEMs) were taken by a Cam Scan (Elektron Optic Serv.) instrument. For the SEM investigations the samples were partially crystallized between two glass plates at 141°C and then transferred to a metal plate for rapid chilling. By this method the primary crystallized large sized morphological formations were fixed and embedded in a microcrystalline environment. The crystallized films were then etched by the permanganate method of Olley and Basset.⁶

RESULTS AND DISCUSSION

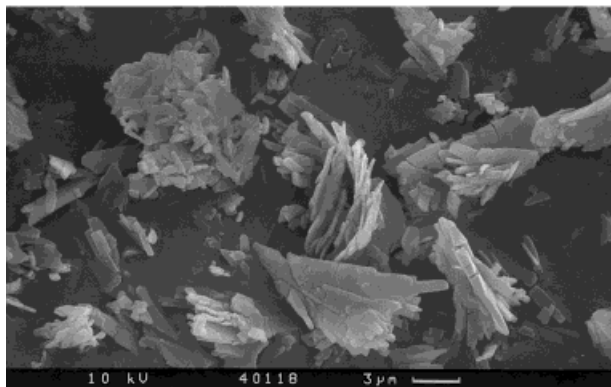
Preparation and Characterization of New β -Nucleating Agents

Equimolar amounts of an aqueous solution of $CaCl_2$ were added to the aqueous solution of a sodium salt of the selected dicarboxylic acid while stirring. Ca salts, which were precipitated as a fine white powder, were filtered, washed with ethanol, and dried in a vacuum at room temperature.⁷ The SEM records showed similar agglomerates of crystalline lamellae for both nucleating agents (Fig. 1). The Ca salts contained 1 mol of crystal water, which had to be removed before use by thermal treatment at 220°C. Finally, the crystals were milled to a fine powder.

According to the DSC and TGA measurements in the nitrogen atmosphere, these Ca salts have excellent thermal stability. It can be established by the loss of mass evident by the TGA traces that Ca-Pim loses 1 mol of crystal water in the range between 110 and 170°C before annealing. The TGA traces of the thermally treated Ca-Pim and Ca-Sub revealed a loss of mass between 390 and 530°C where the organic substances decomposed and $CaCO_3$ was formed, which then transformed to CaO above 550°C (Fig. 2). The experimental measurements of the loss of mass were practically identical to the theoretically calculated ones



(a)



(b)

Figure 1 SEM micrographs of thermally treated (a) Ca-Pim and (b) Ca-Sub.

(shown in parentheses in Fig. 2). No endothermic peak indicating the melting of Ca-Pim and Ca-Sub was observed in the corresponding DSC trace

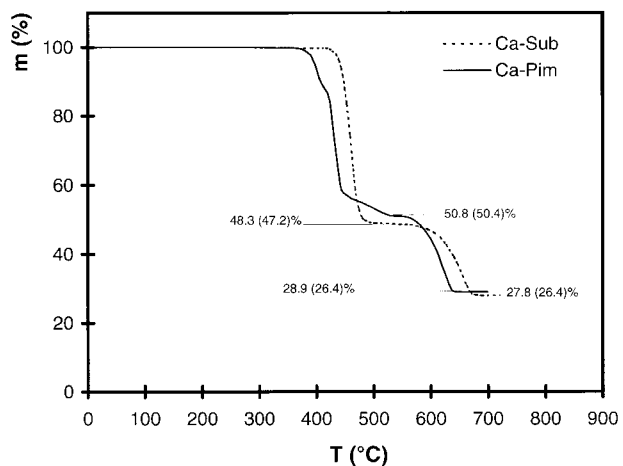


Figure 2 TGA traces of thermally treated nucleating agents; $V_h = 20^\circ\text{C}/\text{min}$.

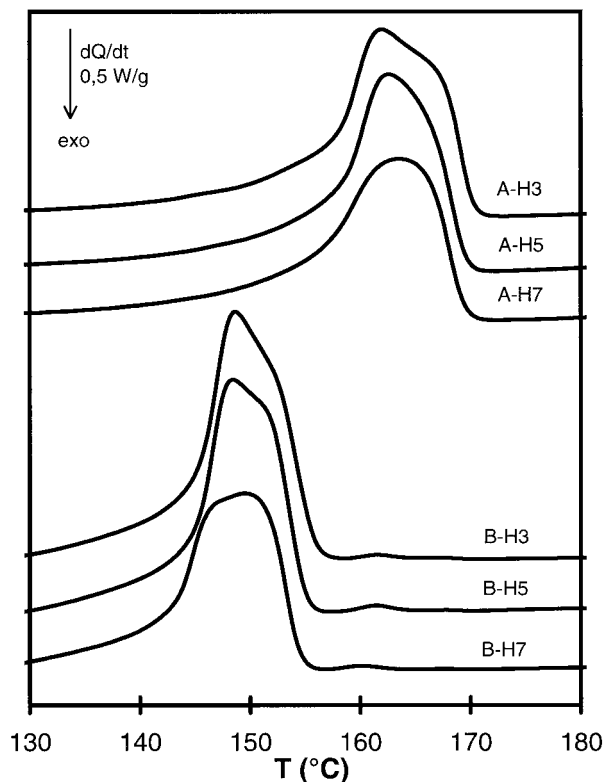


Figure 3 Melting curves of β -nucleated and nonnucleated homopolymers; $V_c = V_h = 10^\circ\text{C}/\text{min}$; 0.1 wt % Ca-Pim.

before 390°C . Presumably, the melting point of Ca salts are above the temperature range of their decomposition. Comparing the different additives, Ca-Sub was slightly more stable up to approximately 450°C . The decomposition character of the nucleating agents in air was similar, although the decomposition steps started at $20\text{--}30^\circ\text{C}$ lower.

Crystallization and Melting Characteristics of β -Nucleated Samples

The DSC measurements revealed the melting and crystallization characteristics of the nucleated samples under isothermal and nonisothermal conditions. β -Nucleated homopolymers and copolymers containing 0.1 wt % Ca-Pim crystallized essentially in β modification as indicated by the high β -melting peaks in Figures 3 and 4. Only a small peak referring to the presence of the α modification appeared in the melting curves. In the homopolymers and block copolymer the peak and final temperatures of α and β melting (T_{mp} and T_m) were practically identical. However, the crystallinity of the block copolymer was some-

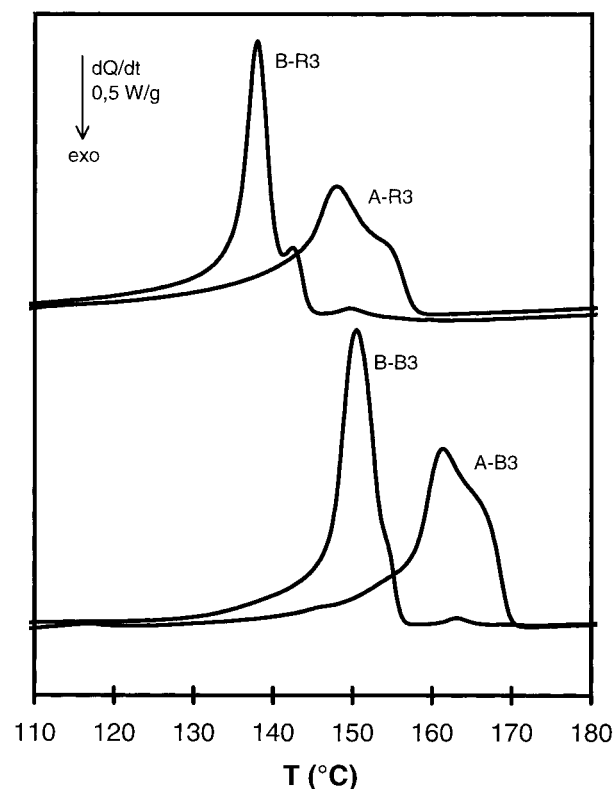


Figure 4 Melting curves of β -nucleated and nonnucleated random and block copolymers; $V_c = V_h = 10^\circ\text{C}/\text{min}$; 0.1 wt % Ca-Pim.

what lower than that of the homopolymers. Due to the irregular chain structure, α and β modifications of the random copolymer both had 10°C

lower melting temperatures, lower crystallinity, and higher ability to be supercooled than corresponding modifications to the homopolymer or block copolymers (Table II). Comparing the effectiveness of the different β -nucleating agents, the salt of suberic acid proved more active than Ca-Pim. In the presence of Ca-Sub, the crystallization temperature range was higher and the portion of α -iPP was lower. The difference was enhanced with decreasing additive concentration. With decreasing nucleator concentration, the α content increased up to 5–8% at the lowest additive concentration (Figs. 5, 6, Tables II, III). Due to the lower β -nuclei density and the lower crystallization temperature at low nucleator concentrations, the spontaneous α nuclei originally present in the sample were able to grow to a larger size, thus leading to an increase in the α -iPP content. The shoulder or the duplication appearing on the high temperature side of the β -melting peak was the result of the $\beta\beta'$ recrystallization.¹ This exothermic structure perfection process overlapped the endothermic melting of the original crystals. The recrystallization became more prevalent at low nucleating agent concentrations (Figs. 5, 6) at which the crystallization temperature range was lower and less perfect crystals were formed.

Melting enthalpies for the nucleating agent free and β -nucleated samples were in the range between 80 and 90 J/g (Tables II, III), while the respective values for the β -nucleated samples

Table II Crystallization and Melting Characteristics of iPP Samples Nucleated by Ca Salt of Pimelic Acid

Samples	β Nucleant (%)	T_{co} ($^\circ\text{C}$)	T_{cp} ($^\circ\text{C}$)	$T_{mp}(\alpha)$ ($^\circ\text{C}$)	$T_{mp}(\beta)$ ($^\circ\text{C}$)	$\Delta H_f(\alpha)$ (J/g)	$\Delta H_f(\beta)$ (J/g)	$x(\alpha)$ (%)	$x(\beta)$ (%)
A-H3	—	115	103	162	—	89.3	—	61.1	—
A-H5	—	113	105	162.8	—	86.2	—	59.0	—
A-H7	—	110	100.5	163.5	—	80.7	—	55.3	—
B-H3	0.1	119.8	116.2	—	—	1.0	92.0	—	81.4
B-H5	0.1	119	115.7	—	148.2	1.1	89.3	—	79.0
B-H5	0.01	120.1	116.7	162	150.1	3.9	83.6	—	74.0
B-H5	0.001	117.8	113.3	162	150.1	6.3	80.0	—	70.8
B-H7	0.1	116.6	112.3	—	149.4	1.1	81.0	—	71.7
A-K3	—	118	108	161.5	—	78.4	—	53.7	—
B-K3	0.1	121.7	118.4	—	150.5	0.8	80.0	—	70.8
A-R3	—	104	98	148	—	64.7	—	44.3	—
B-R3	0.1	111.2	108.9	—	138.0	2.2	62.9	—	55.7

The results are based on DSC curves recorded at the cooling and heating rate $V_c = V_h = 10^\circ\text{C}/\text{min}$. T_{co} and T_{cp} are the initial and peak temperatures of crystallization, respectively; $T_{mp}(\alpha)$ and $T_{mp}(\beta)$ are the peak temperatures of melting of the α and β modifications, respectively; $\Delta H_f(\alpha)$ and $\Delta H_f(\beta)$ are the melting enthalpies of α and β modifications, respectively; and $x(\alpha)$ and $x(\beta)$ are the degrees of crystallinity of α and β modifications, respectively).

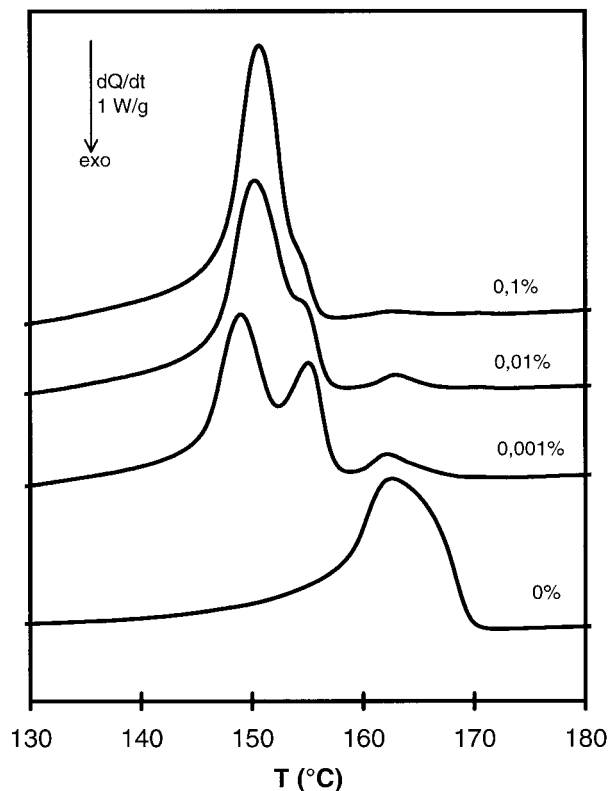


Figure 5 Effect of the concentration of Ca-Pim on the melting curves of H5 homopolymer; $V_c = V_h = 10^\circ\text{C}/\text{min}$.

were somewhat higher. The degree of crystallinity (x) can be determined from the calorimetric data with the knowledge of the melting enthalpy of the completely crystalline α - and β -iPP (ΔH_f°). Although the literature values of the melting enthalpy vary,¹ a comparison between $\Delta H_f^\circ(\alpha)$ and $\Delta H_f^\circ(\beta)$ determined via identical methods always reveals a higher value for α -iPP than for β -iPP. The values for the degree of crystallinity in Tables II and III were calculated using $\Delta H_f^\circ(\alpha) = 146 \text{ J/g}$ and $\Delta H_f^\circ(\beta) = 113 \text{ J/g}$.^{8,9} These melting enthalpies were determined by the linear extrapolation of the melting enthalpies plotted against the temperature of crystallization (T_c) up to the equilibrium melting temperature (T_m°). It is clear from the data shown in Tables II and III that the crystallinity of β -nucleated samples crystallized at a constant cooling rate is higher than of α -iPP. This fact may be explained by the thermodynamic and crystallographic dependencies. The most important thermal parameter for crystallization is the supercooling (ΔT defined as $T_m^\circ - T_c$), which shows how far the polymer crystallizes from its melt-crystal equilibrium state. The lower the supercooling, the more perfect the crystals formed

and, consequently, the higher the crystallinity. Due to the presence of the β -nucleating agent, β -iPP crystallizes at a temperature range of 10 – 15°C higher than its nonnucleated counterpart. On the other hand, $T_m^\circ(\alpha)$ was found to always be higher than $T_m^\circ(\beta)$.¹ Therefore, the β -nucleated samples crystallize with much lower supercooling, which might explain their higher crystallinity. The higher crystallinity cannot be interpreted by the frustrated unit cell of β -iPP,¹⁰ assuming that the chain regularity requirement is not so strict as in the case of α -iPP, and such less stereoregular chains enable the ordering to form into the β -crystal lattice. Comparing the relative growth rate of the α and β modifications of a random propylene copolymer,^{1,11} it was unambiguously stated that a disturbance in the regularity of iPP chains results in a reduced tendency toward β crystallization.

Isothermal crystallization experiments were conducted between 110 and 145°C for H5 with $0.1 \text{ wt } \%$ additive concentration. The crystallization exotherm was characterized by the time of the highest crystallization rate (t_{max}). Similar to the nonisothermal experiments, Ca-Sub was pro-

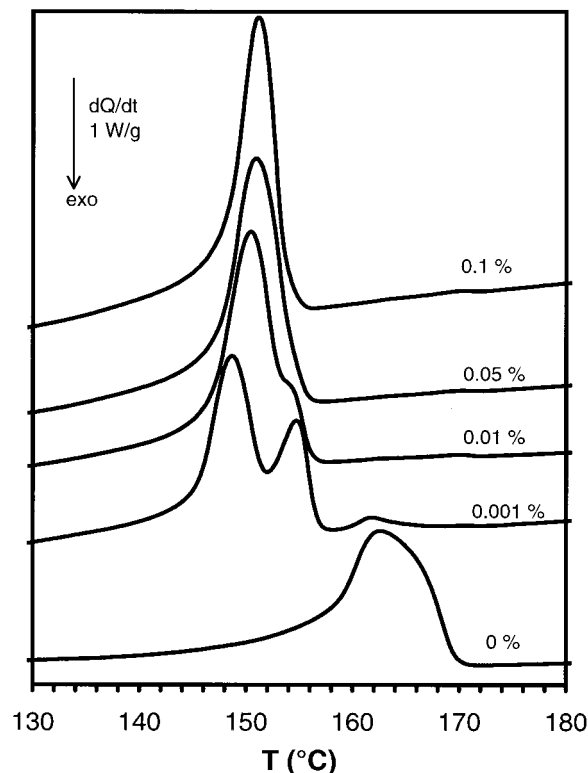


Figure 6 Effect of the concentration of Ca-Sub on the melting curves of H5 homopolymer; $V_c = V_h = 10^\circ\text{C}/\text{min}$.

Table III Crystallization and Melting Characteristics of Homopolymer H5 Nucleated by Ca-Sub

Samples	β Nucleant (%)	T_{co} (°C)	T_{cp} (°C)	$T_{mp}(\alpha)$ (°C)	$T_{mp}(\beta)$ (°C)	$\Delta H_f(\alpha)$ (J/g)	$\Delta H_f(\beta)$ (J/g)	$x(\alpha)$ (%)	$x(\beta)$ (%)
A-H5	0	115	103	162	—	89.3	—	60.9	—
B-H5	0.1	123.6	120.5	—	151.2	—	87.8	—	77.7
B-H5	0.05	123.0	119.5	—	151.3	—	89.9	—	79.6
B-H5	0.01	121.7	117.8	—	150.8 ^a	0.6	89.2	—	78.9
B-H5	0.001	119.1	114.7	162	148.6 ^a	3.7	84.1	—	74.4

The results are based on DSC curves recorded at the cooling and heating rate $V_c = V_h = 10^\circ\text{C}/\text{min}$. Refer to Table I for variables.

^a Double melting peaks.

nouncedly more effective than Ca-Pim as indicated by the lower t_{\max} values at each temperature investigated (Fig. 7). The DSC melting traces revealed the β -iPP content of the crystallized samples in Figures 8 and 9. The lowest temperature during the experimentation was limited by the crystallization rate of the samples, which increased with decreasing T_c . Under a T_c of 120°C , the samples started to crystallize before the T_c was reached. Therefore, the crystallization was not purely isothermal. Including the lowest T_c , the samples crystallized in β form up to a certain temperature, above which appreciable α -iPP content appeared and increased monotonously with temperature. The degree of crystallinity of the β -nucleated samples crystallized isothermally was found to be higher than that of α -iPP, although the difference decreased [$x(\alpha)_{125^\circ\text{C}} = 62.5\%$, $x(\beta)_{125^\circ\text{C}} = 79.0\%$] compared to noniso-

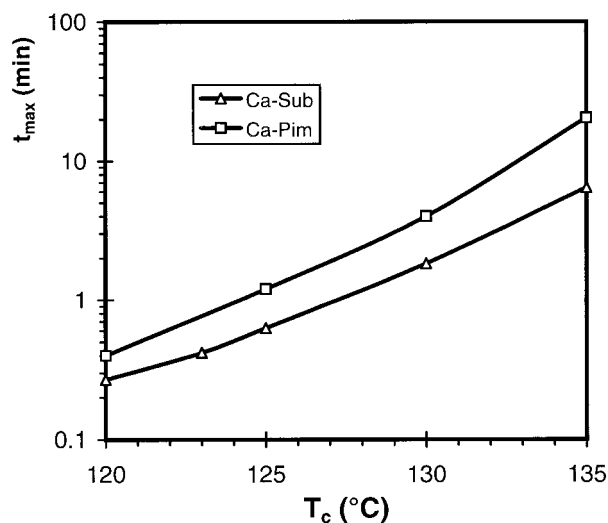


Figure 7 Crystallization peak time (t_{\max}) of H5 samples nucleated with 0.1 wt % Ca-Sub and Ca-Pim and crystallized isothermally at different T_c s.

thermal crystallization. The samples with Ca-Pim crystallized into nearly pure β -iPP up to 135°C , above which a significant α -iPP content was obtained. In the presence of Ca-Sub pure β modification was formed up to 140°C , which was referred to as the theoretical upper temperature

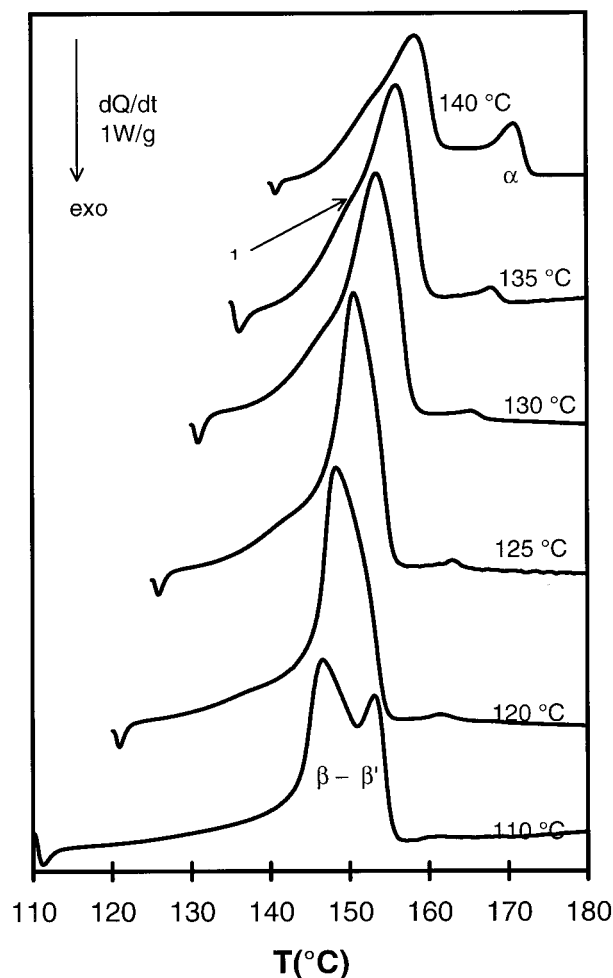


Figure 8 Melting curves of B-H5 samples crystallized isothermally; $V_h = 10^\circ\text{C}/\text{min}$; 0.1 wt % Ca-Pim.

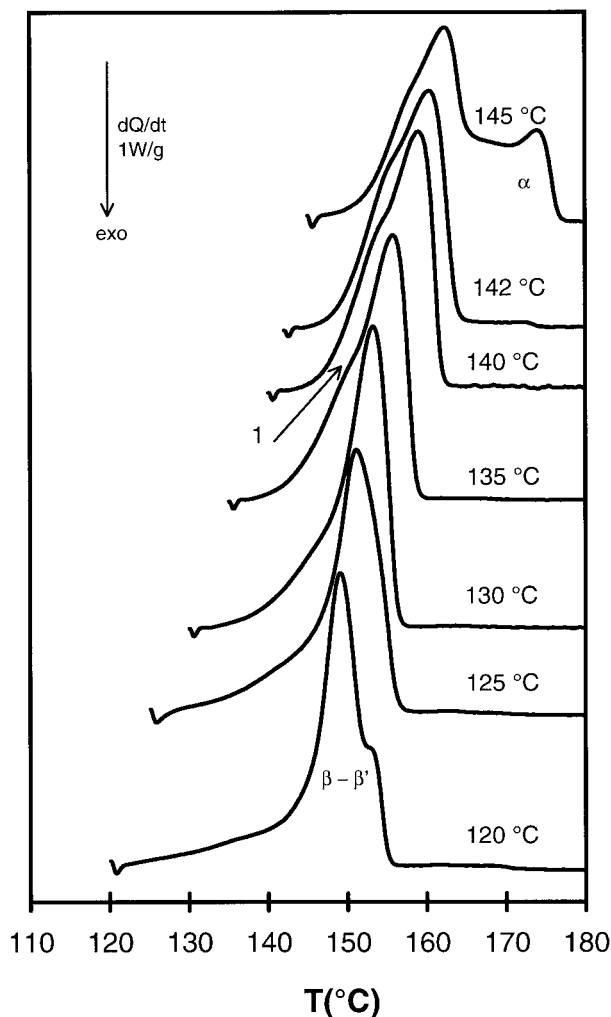


Figure 9 Melting curves of B-H5 samples crystallized isothermally; $V_h = 10^\circ\text{C}/\text{min}$; 0.1 wt % Ca-Sub.

limit for β -iPP formation [$T(\beta\alpha) = 140^\circ\text{C}$].^{1,12} Above this temperature the α nuclei were formed by secondary $\beta\alpha$ nucleation on the surface of the growing β -spherulites. These α nuclei can grow into α -spherulite segments, which can reach smaller or larger size, depending on the growing time. If the crystallization time is long, these α segments can encompass the original β -spherulite, which results in a mixed polymorphic composition.¹² The experimental results of the β -iPP were essentially in accord with our earlier observations.^{1,12} However, the earlier statement of the definition of $T(\beta\alpha)$ should be revised. Based on the high temperature isothermal crystallization experiments, $T(\beta\alpha)$ refers to the upper temperature limit of the formation of pure β -iPP. It can be established from these results that with the help of Ca-Sub, pure β -iPP can be prepared at much higher temperatures than previously predicted in

earlier studies with different β -nucleating agents.¹

The temperature of the melting peak depends on the crystallization temperature and is independent of the type of β nucleator. The melting curves of the samples crystallized at $T_c < 125^\circ\text{C}$ show doubled β peaks (β - β' in Fig. 8) due to the tendency of recrystallization caused by higher structural instability. During heating, the originally thin lamella is partially melted and undergo a lamellar thickening process. In this temperature range the T_m is independent of T_c and the high temperature peak refers to only the recrystallized part of the sample. The melting curves recorded after crystallization at medium T_c (125–135 $^\circ\text{C}$) comprises a single, sharp peak. T_m increases monotonously with T_c and no appreciable recrystallization occurs. Above a T_c of 135 $^\circ\text{C}$, widening and duplication of the melting peak reappears (mark 1 in Figs. 8, 9); however, the T_{mp} and T_m both increase monotonously with T_c . This phenomenon was not previously observed in the literature for β -iPP. Nevertheless, a similar melting behavior was found and intensively studied for α -iPP.^{1,13–19} Due to the high β -nucleating activity of Ca-Sub, this high melting temperature peak widening can be studied up to a T_c of $\sim 145^\circ\text{C}$. The intensity of the shoulder of the melting peak seems to increase up to 142 $^\circ\text{C}$. In the case of the highest T_c (145 $^\circ\text{C}$), it is difficult to determine if the duplication is less intense; at the least it does not increase further. Unfortunately, samples crystallized at higher T_c could not be included in the investigation because only a small fraction of the sample crystallized in β form.

Studying the melting features of α -iPP might help reveal information about the widening of the melting peak for β -iPP crystallized at a high temperature range. Based on the results of several research groups, four separate ranges of T_c can be distinguished for α -iPP, resulting in different melting profiles.^{1,13–19} The samples crystallized isothermally at low temperature ($T_c < 112^\circ\text{C}$) showed strong peak duplication. When increasing the T_c between 112 and 132 $^\circ\text{C}$, a single melting peak was observed at even lower heating rates. Above a T_c of 132 $^\circ\text{C}$ a high temperature peak duplication was found; however, this phenomenon was not evident at a T_c of 152 $^\circ\text{C}$. The samples crystallized above 152 $^\circ\text{C}$ with the help of self-nucleation led to a high temperature single melting peak once again. The latter T_c region was absent for β -iPP because during self-seeding of the β -nucleated samples α modifications form.²⁰

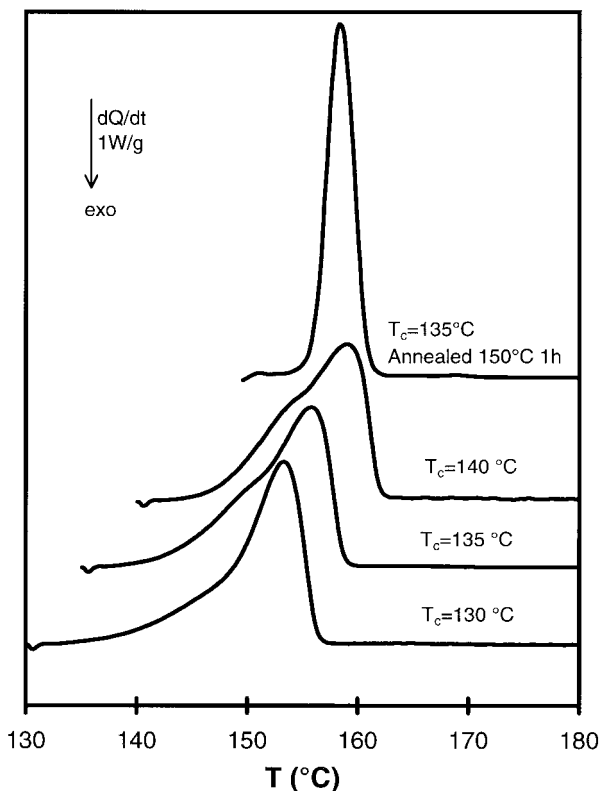


Figure 10 The effect of the annealing on the melting profile of B-H5 samples. One of the samples was crystallized isothermally at 135°C and then at 150°C for 1 h. The others were crystallized at 130, 135, and 140°C. $V_h = 10^\circ\text{C}/\text{min}$; 0.1 wt % Ca-Sub.

The high temperature peak duplication of α -iPP has been explained in several, sometimes controversial, ways.¹ Samuels¹³ could not give a satisfactory interpretation for the phenomenon, although he suggested numerous assumptions. Kamide and Yamaguchi¹⁴ attributed this peak duplication to the annealing effect during the high temperature crystallization. They believe that lamellar thickening occurs for older crystallites. Therefore, they possess a more ordered structure and consequently a higher melting temperature. Based on our results, this explanation can be excluded because the crystallization time did not lead to any changes in the shape of the melting curve of β -nucleated iPP crystallized above 135°C. Yadav and Jain,¹⁵ on the other hand, derived the peak duplication from the fractional crystallization of molecules with different stereoregularities in this T_c range. In the present study the B-H5 sample with 0.1 wt % Ca-Pim was crystallized at 135°C and then annealed at 150°C for 1 h (Fig. 10). This hypothesis should also be excluded because a single and very sharp melting

peak was recorded after the thermal treatment. It does not refer to two different crystalline fractions whose structural perfection processes at 150°C should have resulted in different levels of perfection.

Other researchers¹⁶⁻¹⁹ explained the high temperature peak duplication of α -iPP as a new form of recrystallization. They etched the samples with nitric acid to inhibit the lamellar thickening; thus, they proved that only one crystal fraction is formed in the T_c region that serves as a distinct and very sharp melting peak situated somewhere between the peaks of the original untreated samples. They considered that the recrystallization proceeds between two α modifications (α_1 and α_2) whose structures were revealed by Hikosaka and Seto.²¹ The recrystallization was also proved by structural studies and the effect of heating rate on the relative intensity of melting peaks.^{16,17} It was established¹⁸ that the rate of the perfecting processes were higher than that of the rearrangement processes of the samples crystallized at $T_c < 112^\circ\text{C}$. The annealing processes at sufficiently high sample temperatures led to a high melting temperature and very sharp melting peak that were accompanied by significant structural changes resulting in an α_2 structure.¹⁹

As previously shown, such a recrystallization may occur for the high temperature melting peak widening of β -iPP. In an attempt to answer this question, B-H5 with 0.1 wt % Ca-Sub was crystallized at 135°C and then melted at heating rates between 2.5 and 20°C/min. If a higher melting peak is generated by recrystallization, the relative area should increase with a decrease in the heating rate because the sample has a longer time for recrystallization. The melting traces for this investigation are shown in Figure 11. (It should be noted that the power unit of the curves recorded at different heating rates was divided by the heating rate in order to make the peak areas comparable.) The melting peak recorded at a 2.5°C/min heating rate does not widen significantly. With an increase in the heating rate, the shoulder of the melting peak becomes more pronounced. This suggests that recrystallization occurs, although at a much faster rate than that observed in the case of $T_c < 115^\circ\text{C}$. Further measurements were conducted with the sample crystallized at 135°C and then annealed at 150°C for 1 h. The DSC melting trial at a heating rate of 10°C/min (Fig. 10) revealed a single and very sharp high temperature melting peak, which proved that, similar to α -iPP,¹⁹ considerable structure perfection took place during annealing.

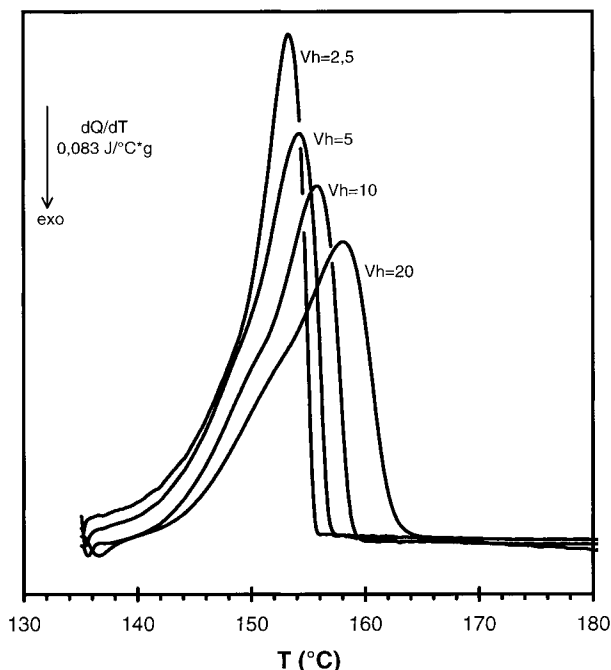


Figure 11 The effect of the heating rate on the high temperature peak widening of the B-H5 (0.1 wt % Ca-Sub) sample crystallized at $T_c = 135^\circ\text{C}$.

WAXS studies carried out on samples crystallized at 130, 135, and 140°C and on those crystallized at 135°C and annealed at 150°C showed the same spectra. Only the relative intensity of the β_1 and β_2 reflection peaks had changed. The order parameter S introduced by Zhou et al.²² is defined as

$$S = H_{\beta_2} / (H_{\beta_1} + H_{\beta_2}) \quad (1)$$

where H_{β_1} and H_{β_2} are the height of the reflection peaks of β_1 and β_2 , respectively (see Fig. 12). The order parameter denotes the order of chain packing in the chain direction. The higher the S value, the more ordered the crystalline structure. In this respect, the S value increases both with the T_c above 135°C , and as the result of annealing at sufficiently high temperatures. The S values for T_c values of 130 and 135°C are nearly the same, although the DSC heating runs reveal different melting features. This suggests that the difference between the melting features of the samples were not caused by the difference in chain packing order. The high S value connected with a T_c of 140°C suggests a higher order level. Enhanced peak duplication was also observed in this sample. Nevertheless, the very high melting peak of the annealed sample and its moderate S value compared to those of the sample crystallized at

140°C suggest that the order parameter is not in strict correlation with the melting temperature of β -iPP. In other words, the extent of the structural rearrangements during the annealing process that result in an increase in the chain packing order are limited by the original crystallization temperature. Furthermore, other structural changes or lamellar thickening might play a significant role in the increase in the melting temperature. This also explains the increase of T_m with T_c in this region, assuming that the increase in the chain packing order results in an increase in the melting temperature.

Recently, modulated DSC was used by Karger-Kocsis and Shang²³ for the study of the melting features and $\beta\alpha$ recrystallization of β -iPP. Similar measurements for $\beta\beta'$ recrystallization are underway in our laboratory.

Supermolecular and Lamella Structure of β -Nucleated Samples

Based on the extensive investigation of the structure of the β -nucleated homopolymer and random and block copolymers, the character of the supermolecular structures were not influenced by either the polymer type or the additive type. During the thin film crystallization of the β -nucleated samples, especially at higher temperatures (T_c

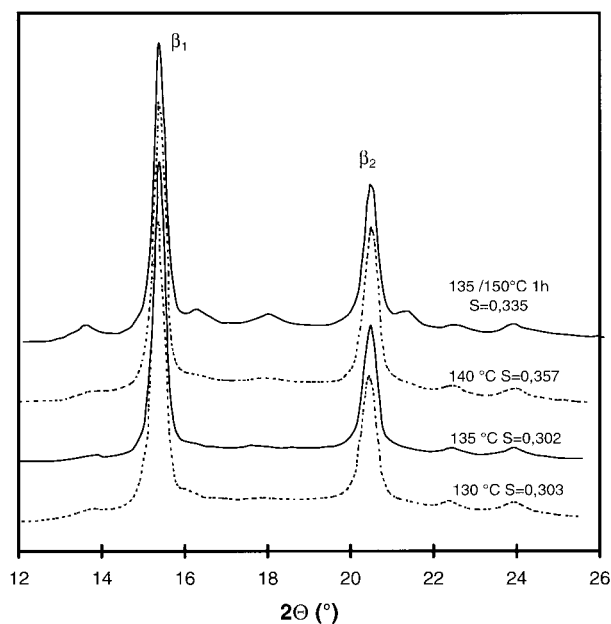
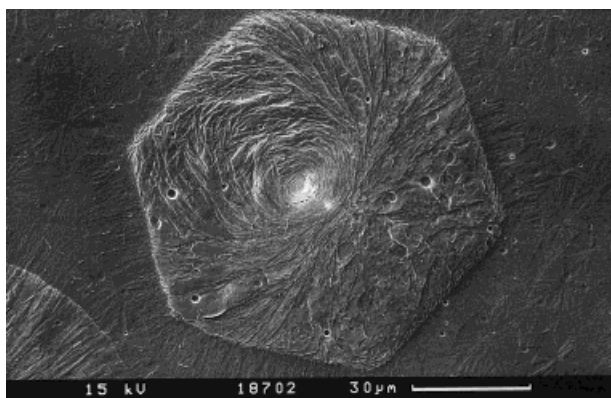
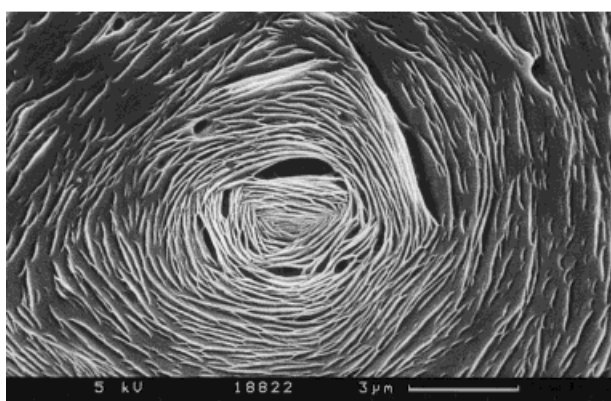


Figure 12 WAXS traces of the B-H5 (0.1 wt % Ca-Sub) sample crystallized isothermally at 130, 135, and 140°C and that crystallized at 135°C and then annealed at 150°C .



(a)



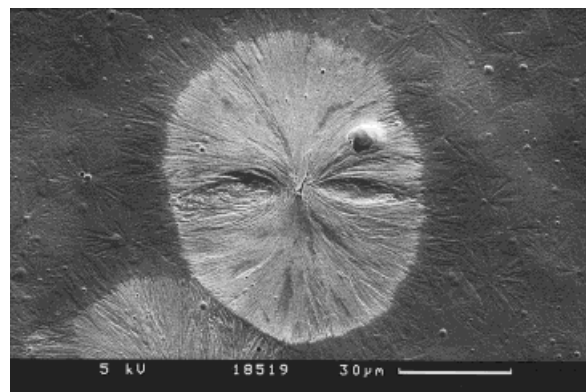
(b)

Figure 13 SEM micrographs taken of (a) β -hexagonite and (b) its magnified center; $T_c = 141^\circ\text{C}$; 0.1 wt % Ca-Pim.

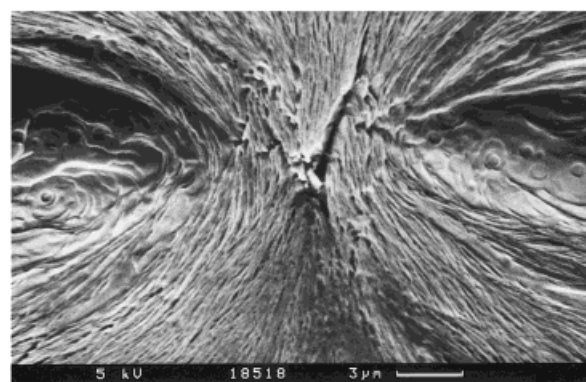
= $130\text{--}145^\circ\text{C}$), a hedritic structure formed that is visible at the optical microscopic level. Hedrites are polygonal formations consisting of clusters of folded chain lamellar crystallites.²⁴ They are considered as an intermediate structure between the polymeric single crystals and the spherulites. In β -nucleated samples, hexagonal β -hedrites called hexagonites are produced. SEM records (Fig. 13) reveal that β -hexagonites are constructed by lamellar crystallites lying on their plates approximately in the plane of the sample. The folded chains are perpendicular to the plane of the lamellae, which continue to branch during crystal growth. Lamellae formed due to branching gradually leave the plane of the hexagonite at a continuously increasing angle to this plane as the growth progresses. Lamellae situated near the center of the hexagonite tend to leave the plane first. The high-resolution image of the hexagonite center in Figure 13(b) demonstrates this process.

Note that the lamellae are located about the central axis of the hexagonite and resemble a flower-cup arrangement. Due to the symmetry, a similar arrangement of lamellae may also be formed below the plane of the hexagonite.

When the plane of the hexagonite is perpendicular to the plane of the sample, the lamellae appear first as rod-shaped crystallites (needle crystals), which then transform into an oval shape (ovalite) structure. According to the SEM records in Figure 14, the lamellae stand on their edges (i.e., perpendicular to the plane of the sample). The formation of the ovalite is induced by the lamellar crystallites standing on edge along the sample plane of symmetry. In the case of such a steric configuration of the initial hexagonite, no steric barrier exists for the lamellar growth and branching in the directions perpendicular to the plane of the hexagonite. It should be emphasized that the mechanism of development of the two formations (hexagonite and ovalite) in Figures 13



(a)



(b)

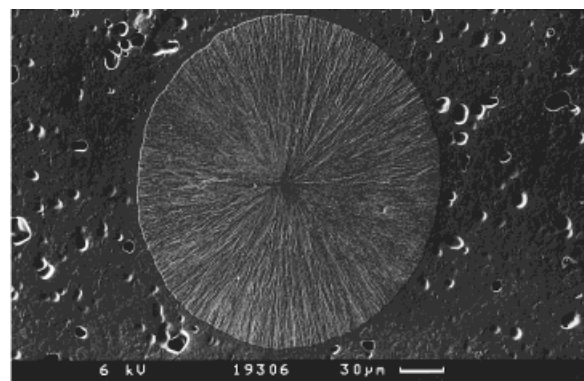
Figure 14 SEM micrographs on an ovalite developed from (a) a needle crystal (hexagonite standing on edge) and (b) a structural detail; $T_c = 141^\circ\text{C}$; 0.1 wt % Ca-Pim.

and 14 is entirely identical. The apparent differences in the construction of the two formations derive from the fact that the very same object is seen from two different (perpendicular) directions. Other structures, such as deformed hexagonites or nonsymmetrical ovalites, can be observed in the sample. Deformed hexagonites also develop from a hedrite, but the plane of the hexagonite encloses a certain axis between 0 and 90° from the plane of view.

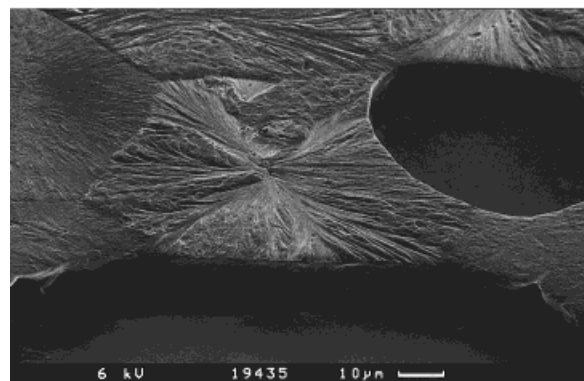
Bulk crystallization where no steric hindrance exists leads to randomization in the growth due to the branching of the lamellae and thus the transition of the hedritic structure into spherulitic. However, the injection molded β -nucleated samples reveal that the centers (20–30 μm) of the β -spherulites formed in this manner remain hedritic.²⁵ In contrast to the α -spherulites, the spherically symmetrical arrangement of the lamellae at the midpoint of the β -spherulites is missing. The SEM image in Figure 15(a) reveals that the structure of the α -spherulites is very compact and composed of fibrillar crystallites with a spherically symmetrical order. The lesser restrained steric arrangement and the branches of the lamellae of the β -spherulites are illustrated by the essential 3-dimensional SEM records on the structure of a β -spherulite that has grown next to an air bubble [Fig. 15(b,c)]. This allows us to see two perpendicular sections of the same structure.

CONCLUSION

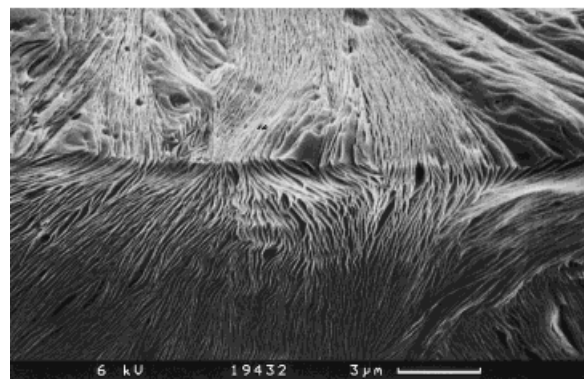
Calcium salts of pimelic and suberic acids are highly active, thermally stable β -nucleating agents. In their presence, isotactic homopolymers and random and block copolymers of propylene crystallize almost purely in β modification, even at a low concentration. Ca-Sub proved to be the most effective β -nucleating agent found in the literature to date. In the presence of Ca-Sub the iPP crystallized in pure β form up to a temperature of $\sim 140^\circ\text{C}$. These additives caused significant changes in crystallization, melting characteristics, and structure of the polymers. The degree of crystallinity of the β -nucleated samples was markedly higher than that of the α modification. Similar features were found for the melting behavior of α - and β -iPP crystallized isothermally in a wide temperature range. The widening of the high temperature melting peak of β -iPP was first studied in a wide crystallization temperature range. Structural and DSC studies suggested



(a)



(b)



(c)

Figure 15 SEM micrographs showing the different compactnesses of α - and β -iPP: (a) β -spherulite formed at 141°C , (b) β -spherulite formed in the surroundings of an air bubble at 141°C , and (c) the section line of its upper and side planes.

that, similar to the α -iPP crystallized at high T_c , recrystallization of β -iPP occurs in melting runs. The supermolecular structure of the β -nucleated samples was studied at the lamellar level. Independent of the polymer type, hedrites were formed as a precursor to the formation of

β -spherulites during the initial stages of crystallization. The characteristic features of the lamellar arrangement of the β modification were independent of the type of β -nucleating agent.

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