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Joint Effects of Molecular Structure and Processing History on Specific Nucleation of Isotactic Polypropylene

Lenka Chvátalová,[†] Jana Navrátilová,[†] Roman Čermák,*[,†] Miroslav Raab,[‡] and Martin Obadal[§]

[†]*Faculty of Technology, Department of Polymer Engineering, Tomas Bata University in Zlín, nám. T. G. Masaryka 275, 762 72 Zlín, Czech Republic,* [‡]*Institute of Macromolecular Chemistry, AS CR, v. v. i., Heyrovského nám. 2, 162 06 Prague, Czech Republic, and* [§]*Borealis Polyolefine GmbH, St.-Peter-Strasse 25, 4021 Linz, Austria*

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ABSTRACT: The interrelation between specific β-nucleation, thermal history, and molecular weight of isotactic polypropylene (PP) has been investigated by wide-angle X-ray scattering, differential scanning calorimetry, and scanning electron microscopy. Samples with a broad range of molecular weight (M_w), from 240 000 to 1 300 000, allowed to examine the effect of PP molecular structure on the nucleation sensitivity. *N, N′*-Dicyclohexylnaphthalene-2,6-dicarboxamide (NU 100) was introduced in the concentrations of 0, 0.01, and 0.03 wt % as a β-specific nucleating agent into neat PP. Specimens were then processed via compression molding at various processing temperatures and times. Samples containing 0.01 wt % of NU 100 showed a dramatic decrease of nucleation activity into β-phase with increasing M_w, processing time, and temperature. This effect was ascribed to a partial solubility of nucleator in PP melt and a competition between heterogeneous β-nucleation and self α-nucleation.

Introduction

Controlling supermolecular structure of polymorphic semicrystalline polymers is a smart way of tailoring their properties. In particular, in the case of isotactic polypropylene (PP) several crystallographic phases have been recognized, the monoclinic α and trigonal β having practical relevance. During past decades a considerable amount of knowledge has been collected on the formation and transformation of the β-phase.[1−7] This crystallographic modification of this important commodity polymer shows superior toughness and drawability but slightly lower stiffness as compared to the more common α-phase.[2,8−13] Moreover, PP containing predominantly β-phase within the crystalline portion of the material is significantly less sensitive to UV-irradiation as revealed Kotek et al. and Obadal et al.[14−16] Specific nucleation caused by an addition of β-nucleating agent is an efficient way of introducing the β-phase into the polymer.[2−5] Nucleating agents are generally low molecular mass organic or inorganic substances added to polymers, before or during processing.[17] The commercial β-nucleator *N,N′*-dicyclohexylnaphthalene-2,6-dicarboxamide (NU 100) was used in many studies.[10,14−26] Recently, the action of this nucleator, known under the trade name NJ Star NU 100, has been comprehensively described by Varga and Menyhard.[18]

These authors revealed three important features of this organic substance: *First*, the dual effect of this nucleator has been documented; it can also initiate the formation of certain amount of α crystallites. Nevertheless, the β-phase finally prevails owing to its higher crystallization rate. *Second*, NU 100 is a crystalline material and can dissolve in polypropylene melt. *Third*, the nucleating activity of NU 100 is exhibited only by solid crystalline particles. Individually dissolved molecules do not show any nucleating effect during solidification of PP from the melt. In this context a question arises whether the critical concentration of the nucleator of 0.03 wt % as described by Kotek et al.[19] is generally valid.

One can expect that thermal conditions and processing history can play an important role here. Indeed, the influence of processing parameters on the morphology and properties of injection-molded parts from β-nucleated PP has been described by e.g. Cermak et al.[20,21] However, heterogeneous nucleation reflects a mutual interaction between segments of a polymer chain and a solid inclusion. Obviously, the effect of polymer molecular structure can be expected. The goal of the present study is to examine the effect of PP molecular weight on the sensitivity to specific nucleation. For this purpose, polypropylene samples with a broad range of molecular weights have been chosen. The nucleation has then been followed at various processing conditions and nucleator concentrations. This approach should open a new insight into the mechanism of specific nucleation process and, at the same time, bring about practical instructions important for optimizing processing technology.

Experimental Section

Ten samples of PP homopolymer with various molecular weight supplied by the Borealis group were used as a starting material throughout this study. The molecular characteristics of the samples are summarized in Table 1. The following characteristics are given: weight-average molecular weight (M_w), numeric-average molecular weight (M_n), polydispersity index (PDI), and melt flow index (MFI). The molecular parameters (M_w, M_n, and PDI) were obtained from GPC equipped with a light-scattering detector. The MFI values were measured at 230 °C, 2.16 kg in accordance with ISO 1133.

The specific nucleating agent *N,N′*-dicyclohexylnaphthalene-2,6-dicarboxamide was supplied by Rika Int., Manchester, Great Britain, as NJ Star NU 100. The nucleator concentration was 0, 0.01, and 0.03 wt %. Nucleator was homogenously dispersed into

*Corresponding author: e-mail cermak@ft.utb.cz; Ph +420 576 031 323; Fax +420 576 032 733.

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Table 1. Molecular Characteristics of PP Samples

no.	sample	M_w	M_n	PDI	MFI [g/10 min]
1	BE52	1 300 000	320 000	4.0	0.3
2	HB205TF	830 000	300 000	2.8	1.0
3	HD601CF	570 000	170 000	3.5	8.0
4	HE125MO	490 000	130 000	3.8	12.0
5	HF136MO	410 000	170 000	2.5	20.0
6	HG455FB	360 000	150 000	2.4	27.0
7	HK060AE	330 000	86 000	3.7	125.0
8	HL504FB	290 000	85 000	3.4	450.0
9	HL508FB	280 000	60 000	4.9	800.0
10	HL512FB	240 000	55 000	4.5	1200.0

Table 2. Processing Conditions of Compression Molding

set	pressing temp [°C]	pressing time [min]	cooling temp [°C]	cooling time [min]
1	210	6	60	6
2	200	20	60	6
3	210	20	60	6
4	220	20	60	6

PP pellets using 0.30 wt % of paraffin oil. The mixture was then processed in a Brabender twin-screw extruder. The processing conditions were as follows: screw speed 55 min^{-1}; temperatures of barrel zones 190, 200, and 210 °C. From the prepared materials plates of thickness of ~0.5 mm were compression-molded. Four sets of processing conditions, differing in pressing temperature and time, were applied, as shown in Table 2. After the pressing in the hot press, cooling of the sheets was performed in the cold press set up to the temperature of 60 °C. During 1 min the temperature increased to 72 °C, and within the next 5 min the temperature dropped to 64 °C (~2 °C/min). Subsequently, specimens were examined by wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC).

The amount and composition of the crystalline portion were determined by wide-angle X-ray scattering. An X′Pert PRO, PANalytical diffractometer equipped with Cu Kα and Bragg−Brentano geometry was employed in reflection mode. Crystallinity was calculated as a ratio of the integral intensities diffracted by a crystalline part and total integral intensities. The relative content (K) of the β-phase within the crystalline portion of the material was calculated according to Turner-Jones et al.:[3]

$$K = H_b/(H_{a1}+H_{a2}+H_{a3}+H_b) \quad (1)$$

where H_{a1}, H_{a2}, and H_{a3} are the intensities of α-diffraction peaks corresponding to angles 2θ = 14.2°, 17.0°, and 18.8°, respectively, and H_b is the intensity of the β-peak at 2θ = 16.2°.

Melting behavior of the specimens was measured by a Perkin-Elmer Pyris 1 differential scanning calorimeter. Cylindrical specimens with a diameter of 4 mm were cut from the prepared plates using a hole-puncher. The specimens with a mass of ~6 mg were inserted into standard aluminum pans and heated from 50 °C up to 190 °C with heating rate of 10 °C/min. The measurements were performed under nitrogen atmosphere (20 mL/s).

Morphology of the specimens was directly documented by a Phillips XL30 ESEM scanning electron microscope (SEM) using secondary electron detector. The compression-molded plates were cryo-fractured under liquid nitrogen; fracture surfaces were then exposed to a permanganic etching (1% $KMnO_4$ in concentrated H_3PO_4) and finally sputtered with a gold−palladium alloy.

Results and Discussion

Effect of Molecular Weight and Specific Nucleation. The X-ray data have shown that the overall crystallinity was ~65%, and no γ-phase was present at all the specimens. The content of the β-phase however is a function of nucleator content, processing condition, and molecular weight. In Figures 1−4 results for specimens processed under the processing setup 1 are presented. The content of the β-phase in non-nucleated specimens is virtually zero nearly in all samples. Only the material with the highest M_w shows a small β-reflection at 2θ = 16.2° (Figure 1). On the other hand, the material with 0.03 wt % of nucleating agent crystallizes predominantly into the β-phase; the values reach more than 90%. The specimens prepared with 0.01 wt % of nucleator

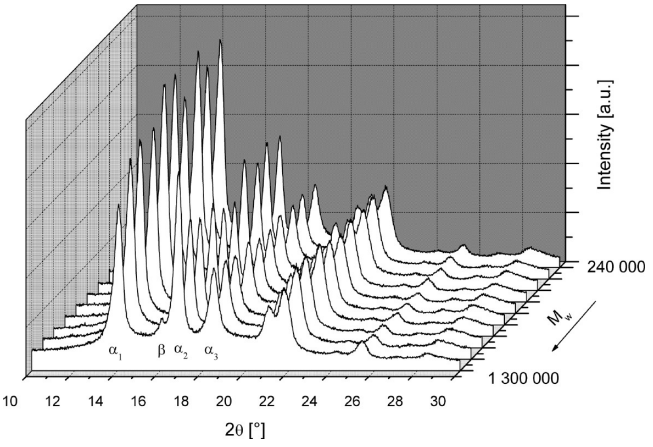

Figure 1. X-ray diffraction patterns of the neat PP specimens compression-molded at temperature of 210 °C for 6 min.

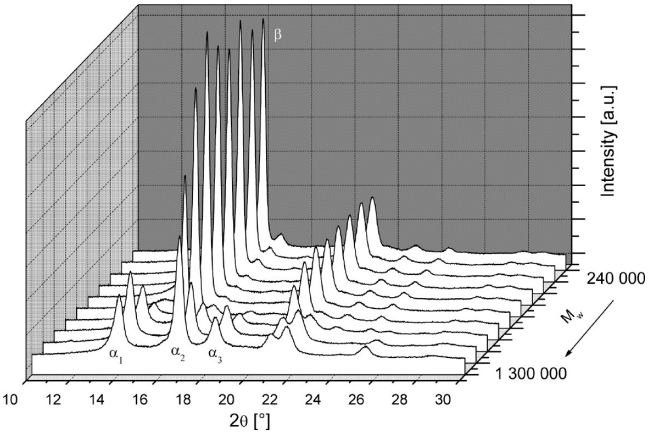

Figure 2. X-ray diffraction patterns of the PP specimens containing 0.01 wt % of nucleator compression-molded at temperature of 210 °C for 6 min.

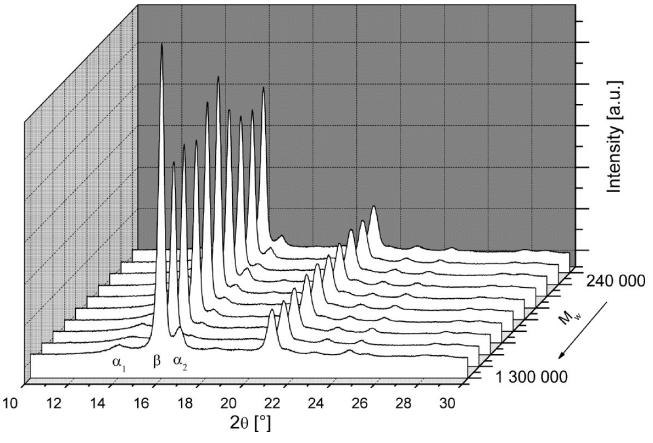

Figure 3. X-ray diffraction patterns of the PP specimens containing 0.03 wt % of nucleator compression-molded at temperature of 210 °C for 6 min.

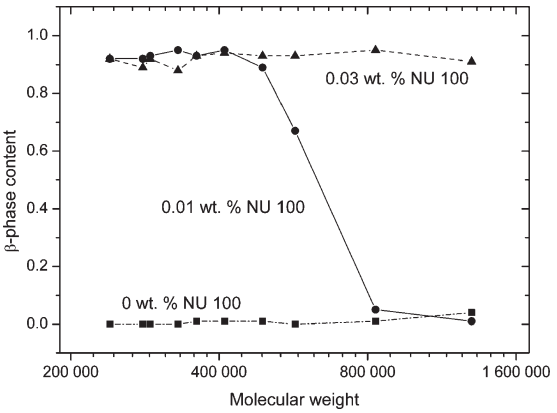

Figure 4. Dependence of β-phase content on M_w of the specimens compression-molded at temperature of 210 °C for 6 min.

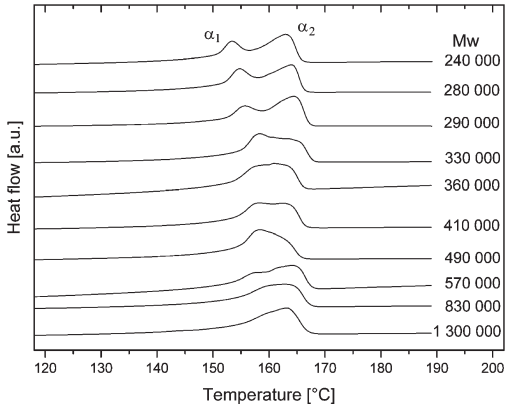

Figure 5. Melting thermograms of the neat specimens compression-molded at temperature of 210 °C for 6 min.

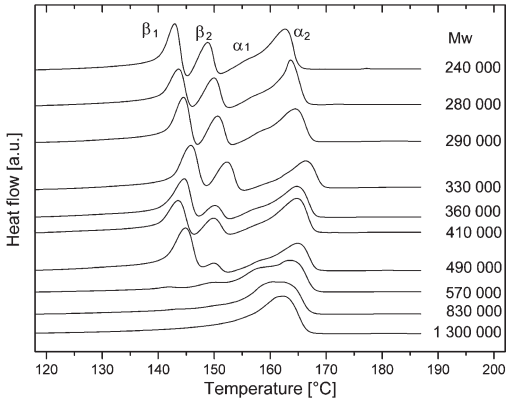

Figure 6. Melting thermograms of the specimens with 0.01 wt % NU 100 compression-molded at temperature of 210 °C for 6 min.

show a strong dependence on molecular weight. A dramatic change of the β-phase content appears between the lowest and highest M_w; in a relatively narrow M_w window the values drop from 0.91 to 0.04.

The effect of molecular weight on the phase structure is also manifested by the DSC thermograms (Figures 5−7). Again, no β-phase was detected for non-nucleated specimens. The effect of molecular weight is expressed in the different shape of the α-melting peaks: twin peak for lower M_w and single maximum for the highest M_w. Rather complicated melting profiles occur with the nucleated specimens. For the lower nucleator concentration (0.01 wt %) the

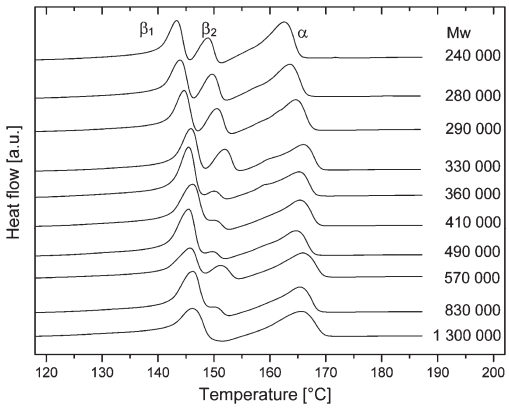

Figure 7. Melting thermograms of the specimens with 0.03 wt % NU 100 compression-molded at temperature of 210 °C for 6 min.

β-melting peak disappears with increasing M_w. In the medium M_w range three different peaks can be observed, indicating $\beta \rightarrow \alpha$ recrystallization.[1,2] Specimens containing the "critical" nucleator concentration (0.03 wt %) show distinct β-melting peaks in the whole M_w range. Nevertheless, a double melting β-peak appears in the lower M_w range. These results correlate well with the WAXS data.

Scanning electron microscopy shows the higher structural level of the morphology, namely the detailed lamellar structure and spherulite shape. The fracture surfaces presented in Figure 8 show a distinct difference between α- and β-lamellar structure: smooth crack surface of material containing predominantly α-phase reflects fine lamellar structure (Figure 8, left). On the other hand, a distinctly rough surface structure of the PP rich in β-phase is a manifestation of thick sheaf-like lamellae (Figure 8, right). Scanning electron microscopy has also shown an interesting encounter of α- and β-structure in one material (Figure 8, middle). This is exactly the specimen exhibiting both α- and β-morphology by X-ray diffraction and DSC. Here electron microscopy shows that α- and β-phases coexist in one specimen but are divided in space at virtually macroscopic level.

Effect of Molecular Weight and Processing. The joint effect of processing conditions (temperature history during compression-molding) and the molecular weight on the β-phase content is presented in Figures 9−12. Here the data for specimens with the lower nucleator content (0.01 wt %) are given. It is shown unambiguously that particularly these materials with low nucleation are very sensitive to the thermal history. The processing temperature (T_p) plays here a crucial role: for low T_p (200 °C) the nucleator concentration 0.01 wt % is sufficient for the virtually complete crystallization into the β-phase. On the other hand, for T_p 220 °C the nucleation activity practically vanishes. For intermediate processing temperature (T_p 210 °C) a transition from high to very low nucleation activity is observed, in dependence on the M_w. At the same time, a distinct effect of processing time is clearly demonstrated. Prolonged processing time (from 6 to 20 min) distinctly limits the nucleation activity.

The distinct effect of processing temperature on the supermolecular structure of nucleated PP is directly documented on SEM micrographs for samples with intermediate molecular weight (Figure 13). Material processed at lower temperature, 200 °C (left), shows complete β-morphology, high processing temperature, 220 °C (right), induced formation of α-spherulites solely, and material processed at 210 °C (middle) shows a coexistence of both crystallographic modifications. Similar morphology variation (caused by nucleator concentration) has been presented in Figure 8.

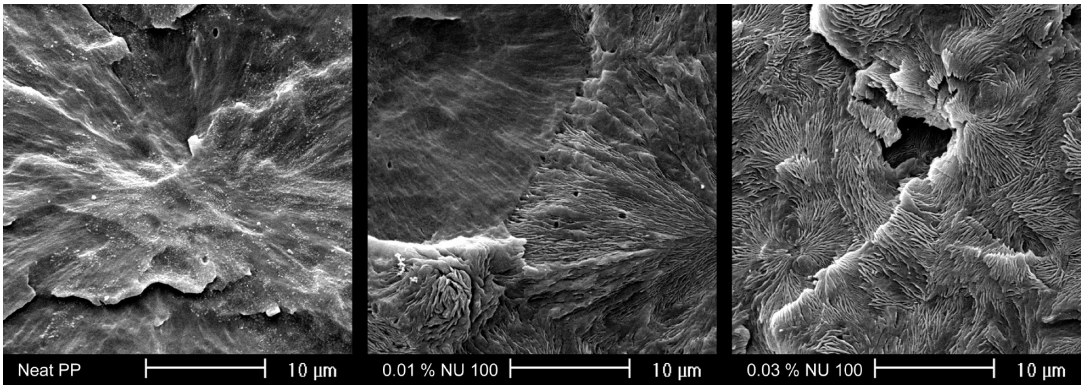

Figure 8. SEM images of PP with M_w 570 000 containing various amounts of nucleator (0, 0.01, and 0.03 wt %) processed under the condition 1 (210 °C, 6 min).

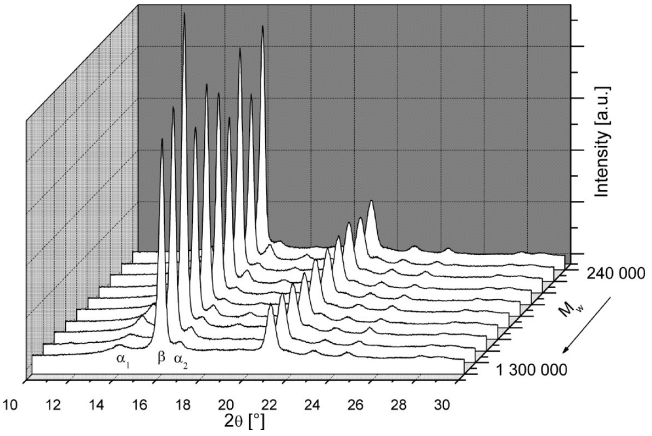

Figure 9. X-ray diffraction patterns of the specimens containing 0.01 wt % NU 100 processed at temperature of 200 °C.

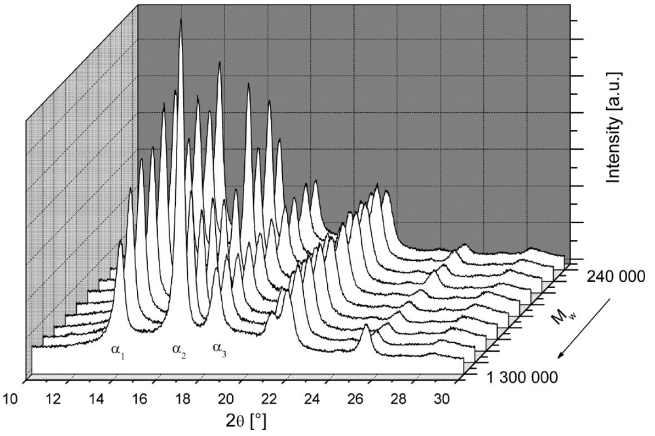

Figure 11. X-ray diffraction patterns of the specimens containing 0.01 wt % NU 100 processed at temperature of 220 °C.

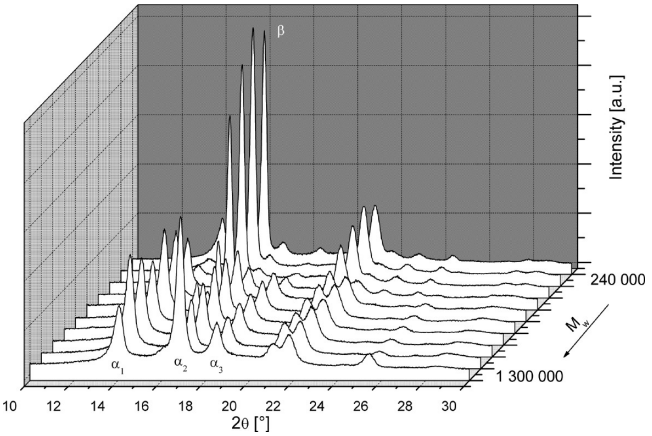

Figure 10. X-ray diffraction patterns of the specimens containing 0.01 wt % NU 100 processed at temperature of 210 °C.

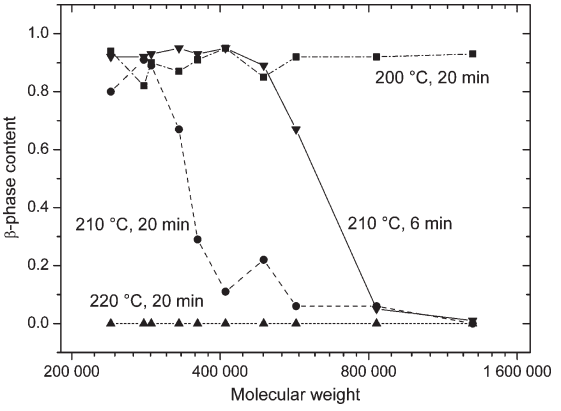

Figure 12. Dependence of β-phase content on M_w of the specimens containing 0.01 wt % NU 100 processed at various temperatures.

Obviously, the effects of processing temperature and time can be unambiguously ascribed to dissolution of the nucleator in polymer melt, in agreement with the recent concept of Varga and Menyhard.[18] However, the effect of molecular weight has not been reported yet. According to our knowledge, the pronounced effect of the polymer molecular weight on its sensitivity to specific nucleation is presented here for the first time. In addition, the solubility of nucleator itself cannot offer a plausible explanation, as it should decrease with increasing M_w; the presented data show an opposite trend—decreasing nucleation activity with increasing M_w. An explanation of this effect is not thus straightforward but can be based on the notion of competition between self-nucleation and heterogeneous β-nucleation. Generally, self-nucleation is a process during which the primary nucleation takes place in the melt on its own crystals grown previously. According to Galeski,[27] this nucleation prevails in PP melt. Indeed, the number of the self-nuclei depends on the annealing conditions. In this context, one can expect that also M_w of the polymer can play an important role; the stability of self-nuclei in the melt within annealing at a given temperature should be controlled by the viscosity and diffusion rate of chain segments. Upon annealing, the number of

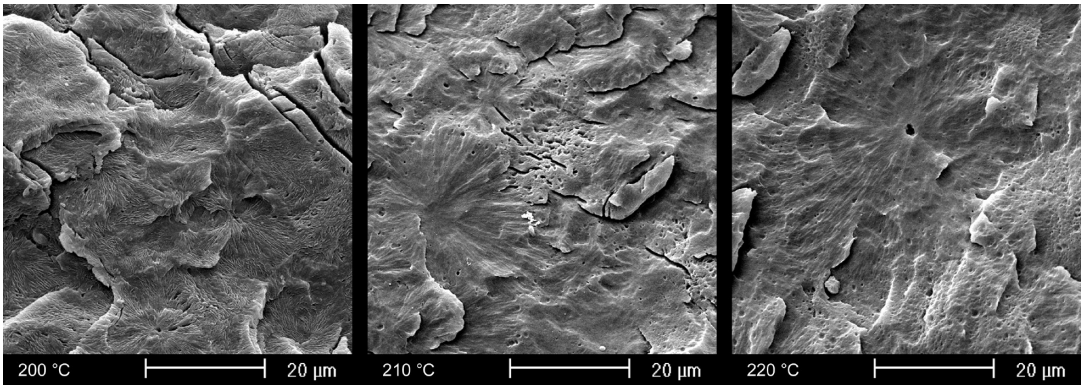

Figure 13. SEM images of PP with M_w 360 000 containing 0.01% NU100 processed under the conditions 2−4 (200, 210, and 220 °C, 20 min).

self-nuclei should be higher in high-M_w systems. Then, the content of the β-form in PP with low amount of β-nucleator should be sensitive to self α-nucleation and decrease with M_w. At this point, it is worth mentioning that some further effects could play an additional role, such as the presence of impurities arising from the catalyst residua or the effect of the length of crystallizing sequences on nucleation and growth rate. A successive study of overall crystallization kinetics would be helpful.

Conclusions

The experimental study has shown combined effects of a specific nucleation, processing parameters, and molecular weight on the resulting morphology of isotactic polypropylene. Samples encompassing a broad range of molecular weight (M_w from 240 000 to 1 300 000) allowed to describe for the first time the effect of molecular structure on nucleation efficiency. For the samples with low nucleator concentration of 0.01 wt % a dramatic decrease of nucleation activity with increasing M_w, and processing time and temperature were documented. This behavior was ascribed to the temperature-dependent solubility of the nucleator in PP melt and a competition between heterogeneous β-nucleation and self-nucleation. The results obtained within this study have important consequences for both polymer physics and plastics technology.

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