Rheol Acta (2006) 45: 793–801
DOI 10.1007/s00397-005-0082-y

ORIGINAL CONTRIBUTION

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Large strain requirements for shear-induced crystallization of isotactic polypropylene

Received: 13 January 2005
Accepted: 28 December 2005

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Abstract We studied strain effects on the crystallization of a series of isotactic polypropylenes (iPP) of various molecular weights using rheology, rheo-optical measurements, differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (WAXD). The samples were pre-sheared and then crystallized both at the same temperature. Transmitted light intensity measurements demonstrate that the effect of pre-shear on crystallization rate keeps increasing with strain up to surprisingly large strain levels, much beyond strains that are required to reach steady shear flow (at given *We*). Crystal orientation sets in at a total strain of about $\gamma_0 = 600$ or higher. WAXD and DSC measurements corroborated the light transmission results. Total shear strains $\gamma_0 = 200$ to 1000 were applied to the iPP samples at the beginning of a crystallization experiment, after the samples had reached the crystallization temperature of 145°C (under-cooled state). A constant Weissenberg number *We*=1 (*We* is defined as the product of shear rate and a relaxation time) was maintained for all pre-shearing of this study. *We*=1 corresponds to the onset of shear thinning in steady shear. Deborah number values were low, *De*<<1, indicating that steady shear flow had been reached in all pre-shearing runs (*De* is defined as the ratio of relaxation time to pre-shearing time). Further studies are needed at high *We* as there are indications that strain requirements are much reduced at high *We*. A fundamental understanding is still missing.

Keywords Shear-induced crystallization · Strain criterion · Weissenberg number · Isotactic polypropylene

Introduction

Semicrystalline polymers are understood to crystallize in two main steps: first, the formation of nuclei and, subsequently, the growth of crystals. Shear flow has been shown to accelerate or even induce crystallization (Pennings et al. 1970; Mackley and Keller 1973; Wolkowicz 1978; Keller and Kolnaar 1997; Jerschow and Janeschitz-Kriegl 1996; Vleeshouwers and Meijer 1996; Kumuraswamy et al. 1999, 2002; Wassner and Maier 2000; Pogodina et al. 2001; Seki et al. 2002; Acierno et al. 2003; Elmoumni et al. 2003; van Meerveld et al. 2004). Flow induces molecular orientation and, thus, increases the molecular size, lowers the entropy, and pre-arranges molecular strands for the ordered crystal morphology.

The effect of shear is largest on the rate of *nucleation* (Wunderlich 1970; Janeschitz-Kriegl et al. 2003), which can be increased by several orders of magnitude. The molecular orientation leads to an effective change of the melt free energy that directly increases the rate of nucleation (Hoffman and Lauritzen 1961). Flow has been assumed to affect nucleation through bundles of highly oriented chains or chain segments (Keller and Kolnaar 1997; Janeschitz-Kriegl et al. 2003). Large molecules contribute significantly more than small molecules (Keller and Kolnaar 1997; Kumaraswamy et al. 2002; Seki et al.

2002; Elmoumni et al. 2005). It remains unclear whether large strains, large stress, or both are required for a large rate of nucleation.

In comparison, little is known about the effect of shear on the *crystal growth rate*. Shearing above *We*=1 (see below) reduces the density of molecular entanglements. Fewer entanglements might increase crystal growth rates due to increased molecular mobility and might also increase the final crystallinity because of defect reduction in the melt before crystallization. However, even if shear may change the growth rate only slightly, it alters the structure of the nuclei and, thus, templates the preferred direction of crystal growth and possibly the crystal habit. Molecularly ordered regions serve as primary nuclei for the crystallization and, if the order is high enough, lead to shish–kebab morphology, which consists of highly oriented chains (shish) that serve as nuclei for the epitaxial crystal growth of chain-folded lamellae (kebab) (Eder and Janeschitz-Kriegl 1997; Keller and Kolnaar 1997).

The Weissenberg number (*We*), the dimensionless product of a characteristic relaxation time and the shear rate,

$$We = \dot{\gamma}\lambda_i \tag{1}$$

was proposed as an important measure of flow effects on crystallization (Acierno et al. 2003; Elmoumni et al. 2003; van Meerveld et al. 2004). Such rheological classification allows to correlate experimental observations of flow-induced nucleation and flow-induced spherulite to shish–kebab structure transition. The choice of characteristic time is not obvious. The characteristic relaxation time λ_i is chosen here as the inverse of the crossover frequency of G' and G'' as measured in a linear viscoelastic experiment at 145°C. The *We* criterion was found to be useful as long as the strain was kept constant for a range of experiments.

This study focuses on the melt state before crystallization and on its effect on the crystallization itself. Due to the dominating effect of shear on primary nucleation, any flow-induced molecular orientation and stretch is assumed to be most important at the very onset of the crystallization process when nuclei are formed. For that purpose, Janeschitz-Kriegl's group (Liedauer et al. 1993) has proposed an experimental procedure at which the sample temperature is lowered to generate an under-cooled state and then the sample is sheared for a short time. The rapid shearing strain that is imposed on the material at the very onset of the experiment determines the initial condition for the crystallization process. The actual crystallization occurs without adding any more flow. The magnitude of the shear strain is varied in this study, and it is found to be a dominating parameter for classifying the crystallization behavior.

Table 1 Characteristics of samples utilized to study the effects of strain on the crystallization of iPP

Sample	M_w (kg/mol)	M_n (kg/mol)	M_w/M_n	λ_i (s)
iPP171	171	40.4	4.2	0.055
iPP300	300	51.8	5.8	0.217
iPP350	350	85.8	4.1	0.630

The characteristic relaxation time λ_i of iPP samples at 145°C determined from Fig. 1

Strain as a possible parameter for shear-induced crystallization has not been studied much. Vleeshouwers and Meijer (1996) pre-sheared an isotactic polypropylenes (iPP) in the supercooled state (T_x=138°C) and found that longer and longer pre-shearing gave shorter and shorter crystallization times until the pre-shearing began to overlap with the growth of spherulites. The shear conditions were fairly mild and accumulated strains of up to $\gamma = 1{,}000$ kept reducing the crystallization time.

At similar experimental conditions, Li and de Jeu (2003) found that pre-shearing at comparatively small strain (γ = 15) already gave rise to oriented precursors for crystallization (bundles with smectic ordering) of an iPP that contains nucleating agent. In situ structural studies by simultaneous small-angle X-ray scattering and wide-angle X-ray diffraction (WAXD) allowed the detection. No mention was made of the effect that a larger strain might have.

Chai et al. (2004) explored the effect of thermomechanical history on the crystallization of polyethylene (PE) melts. As model processing history, the PE samples were pre-sheared above crystallization temperature (T=190, 170, and 150°C) and then held quiescently for some prescribed relaxation time at elevated temperature. After that waiting time, the samples were rapidly quenched to T_x=90°C and held there for isothermal crystallization. For a metallocene PE (mPE) of narrow molecular weight distribution, the pre-shearing history had no effect on the crystallization. For a Ziegler–Natta PE of broad molecular weight distribution and some long chain branching, the effect of the pre-shearing (even after some relaxation) was substantial. Very large strains were necessary to scan the effect to its fullest.

There were other indications that the magnitude of the strain has a large effect in addition to the *We* value. When exploring shear effects at high *We* values, our WAXD and differential scanning calorimetry (DSC) measurements were carried out on samples that had been sheared between two concentric disks. For that flow geometry, the strain rate (and automatically the *We* values) increases linearly with the radial position in the sample. The corresponding inhomogeneous strains also increase radially. Thus, in these experiments, the effects of both strain rate and total strain were found to be coupled.

In the following, we will decouple the effects of strain and strain rate by choosing a constant *We* value (*We*=1) and increase the total shear strains $\gamma_0 = 200,\ 400, 600, 800,$ and 1,000. The value of *We*=1 was chosen as shear effects in rheology (shear thinning) become important at about

We=1. *We*=1 was achieved by applying a constant shear rate, $\dot{\gamma} = We/\lambda_i$, over time t_s. The strain λ_0 was applied to the samples as soon as the experimental temperature T_x was reached. After pre-shearing, the actual crystallization was intended to occur without flow. The experiments focused on the evolving crystal fraction and on crystal orientation due to the pre-shearing.

Experimental

Materials

The slow crystallization of iPP makes it a useful model material for crystallization studies. In the following experiments, three experimental grades of isotactic Ziegler–Natta polypropylene (of ExxonMobil) with various molecular weights (M_w) were used (see Table 1). The DSC melting has its maximum at about 165°C. The sample properties were described in an earlier paper (Elmoumni et al. 2003).Symp 365–382

Pre-shearing protocol

In crystallization experiments, after melting at 220°C for 10 min, the samples were cooled to the experimental temperature, T_x=145°C which is substantially below T_m, and held for isothermal crystallization in the Linkam hot-stage to monitor the structure growth. As soon as the sample reached experimental temperature, T_x (after a cooling time of about 3 min), total strains of γ=200, 400, 600, 800, or 1,000 were applied while maintaining a Weissenberg number value of 1. For a constant *We*, the shearing time $t_s = \gamma\lambda/\ We$ depends on the strain only. Table 2 is a list of the corresponding shear rates and shearing times.

If one defines the Deborah number with the shearing time, $De = \lambda_i/t_s$, then the corresponding Deborah number is extremely small for all experiments of this study, *De*<<1. This means that steady shearing conditions were amply reached during pre-shearing (all experiments).

Table 2 Shearing conditions for the three samples

We=1				
Sample		iPP171	iPP300	iPP350
$\dot{\gamma}$(s^{-1})		18.2	4.6	1.6
γ	200	11	44	125
	400	22	87	252
	600	33	130	375
	800	44	174	500
	1,000	55	217	625
		t_s (s)		

For maintaining *We*=1, different shear rates $\dot{\gamma}$ are required for the three samples. The corresponding shearing times t_s belong to a prescribed strain γ as listed on the left side of the table

Techniques and instruments

The rheological experiments were performed on molten samples using the time-resolved rheometry technique (Mours and Winter 1994) with a rotational rheometer (Stresstech of ATS RheoSystems) equipped with cone-plate fixtures (diameter 25 mm, 4° angle). Samples were melted directly in the rheometer at 220°C for 10 min to erase previous strain and temperature histories. Small amplitude oscillatory shear was started as soon as the experimental temperature was reached. Cyclic frequency sweeps were performed at temperatures between 220 and 140°C (at ΔT=20 K intervals) in the frequency window between 0.01 and 10 rad/s (5 points per decade). The shear strain amplitude was 0.04 (ensuring sufficiently high torque values) while remaining in the linear viscoelastic range. Master curves (Fig. 1) were generated at a crystallization temperature of 145°C, and characteristic relaxation times λ_i for the intersect of G' and G'' were obtained and summarized in Table 1 (Elmoumni et al. 2003).

Growing spherulites and threads get observed under a universal polarizing microscope (Carl Zeiss, model ZPU01). For transmittance measurements in a self-built rheo-optical setup (Pogodina et al. 2001), light from a 10-mW He–Ne (wavelength of 632.8 nm) laser passes through the sample onto a polarizing beam splitter with its axis at −45° to the flow direction. Two detectors measure the intensity of light through crossed and parallel polarizers.

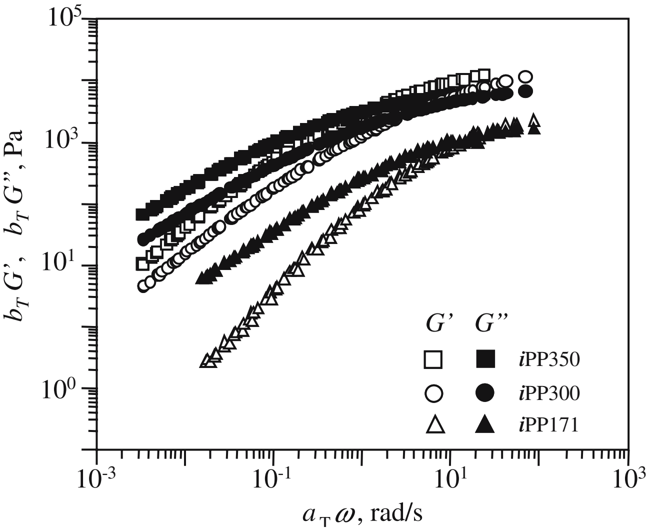

Fig. 1 Melt rheology of iPP samples. Storage modulus G' and loss modulus G'' of iPP samples shifted to 145°C. The activation energies for the three samples are E/R=423, 115, and 475 K with Vogel temperatures T_v=312, 1,230, and 304 K, respectively, for iPP171, iPP300, and iPP350

The sum of these two intensities represents the total light transmitted through the sample. The total intensity, normalized by the intensity of light transmitted initially through the molten sample, decreases as crystallites form and scatter light. To quantitatively describe the crystallization kinetics, a transmittance half time, $\tau_{1/2}$, was introduced. It is defined as the time where the normalized transmitted light intensity has reduced to half its initial value.

Both microscope and rheo-optical setups were equipped with a shearing hot-stage (CSS 450 of Linkam Scientific Instruments). For shearing, a disc-shaped sample of 200-μm thickness is held between concentric discs. The shear rate increases linearly with distance from the center; however, the shear rate is constant in the light path, which is normal to the disk.

The final iPP structure formed was evaluated with WAXD using a flat plate Statton camera with Ni-filtered CuKα radiation. Samples were heated from room temperature to 200°C at a rate of 5 K/min in a differential scanning calorimeter (Q1000 of TA instruments) to obtain thermograms.

Results

Transmittance

Crystallization kinetics was monitored using transmitted light intensity measurements. Figure 2 shows the evolution of normalized transmitted light intensity of the three samples at increasing strain conditions. The normalized intensity maintains its full value during the induction period where nuclei are formed. Only after some crystal growth did crystals become large enough to scatter the light passing through the sample so that transmitted light intensity decays gradually. It is evident from Fig. 2 that the decay in light intensity shifts to shorter times as the strain of pre-shearing is increased.

This study uses the transmission half time, $\tau_{1/2}$, defined above as characteristic crystallization time. Due to the accelerated crystallization, a dramatic decrease in $\tau_{1/2}$ is observed with increasing total strain for each of the samples (see Fig. 3). This is attributed to the increased number density of scatterers that grow from the nuclei created by the shear-induced orientation. Large strain values are required (γ=600 and beyond) before the strain effects seem to level off.

For comparison, several experiments were conducted at *We*=0.5. It was found there that even larger shear strains are required to generate a strong effect (strains of 800 and above). It is expected, vice versa, that the transition will occur at lower strain value if shearing at high *We* numbers were applied. However, high *We* experiments could not be performed due to equipment limitations.

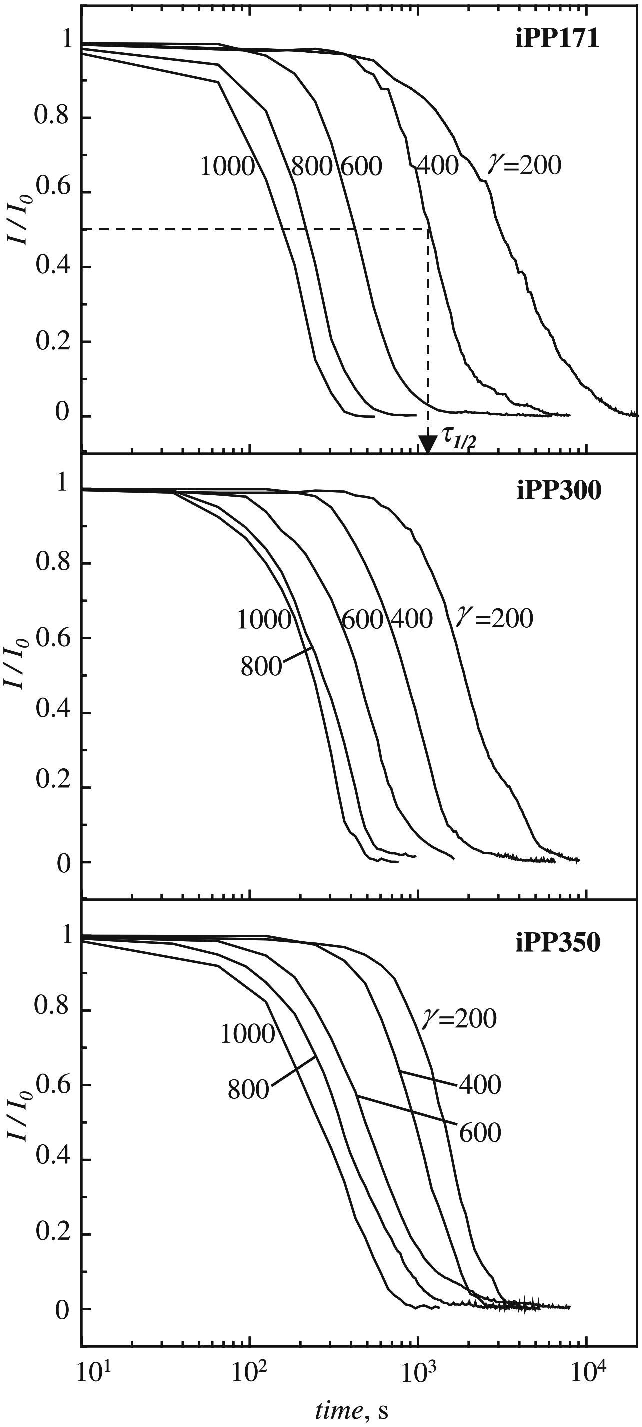

Fig. 2 Evolution of normalized transmitted light intensity of the three samples at increasing conditions

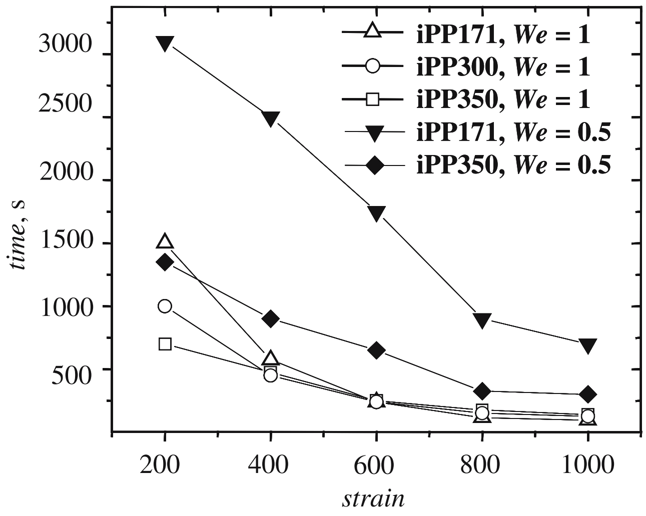

Fig. 3 Crystallization half time as a function of total strain for all iPP samples

Optical microscopy

Optical micrographs of iPP171 at increasing strains are shown in Fig. 4. At strains of 400 and below, the number of nuclei is substantially increased, but crystal growth is still in the form of spherulites. The number of spherulites seems to be determined by the pre-shearing, but it does not increase from thereon. The crystal growth rate is uniform so that the radius $R(t)$ is practically the same for all spherulites. An increase in nucleus density is observed at higher pre-shearing strains. The micrographs in Fig. 4 (iPP171) shows a spherulitic structure up to a strain value of 400, while at higher strains, a transition from spherulitic to elongated structure is observed.

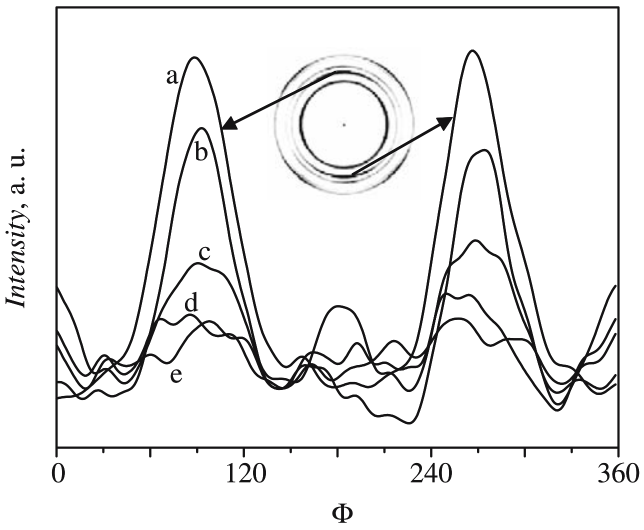

Fig. 5 Azimutal scans of the 040 crystalline plane of ZNiPP171 at increasing total strains **a** γ=1,000, **b** γ=800, **c** γ=600, **d** γ=400, and **e** γ=200. WAXD pattern for **a** γ=1,000 is illustrated *inside* the graph (flow in horizontal direction)

Wide angle X-ray diffraction

Wide angle X-ray diffraction was performed on the cooled samples after completion of crystallization (see Fig. 5). The monoclinic lattice structure (Lotz and Wittmann 1996) for α-crystals of isotactic polypropylene, with lattice constants a=6.6 Å, b=20.78 Å, and c=6.5 Å and a tilt angle β=99.6°, gives rise to the main reflections from the crystallographic planes (110), (040), (130), (111), and (041). The first three of these crystallographic planes are parallel to the chain axis, which can align with the flow direction. The patterns

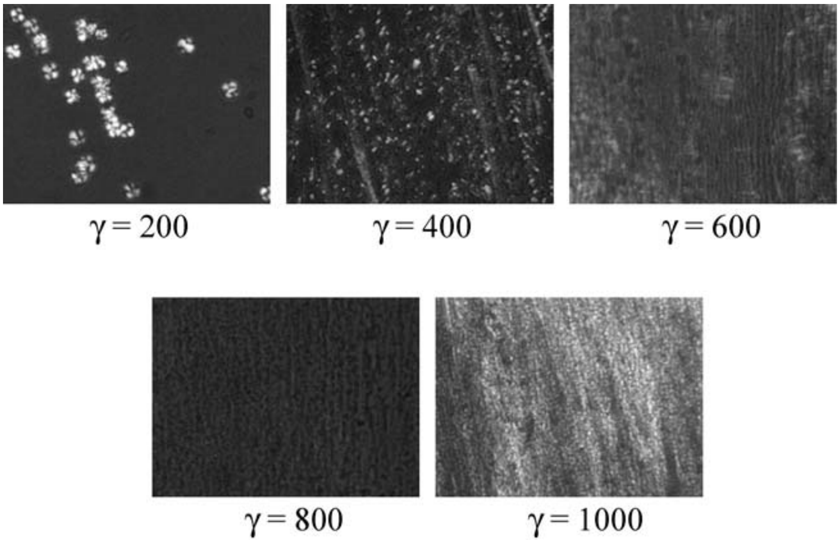

Fig. 4 Optical micrographs of iPP171 at increasing total strains

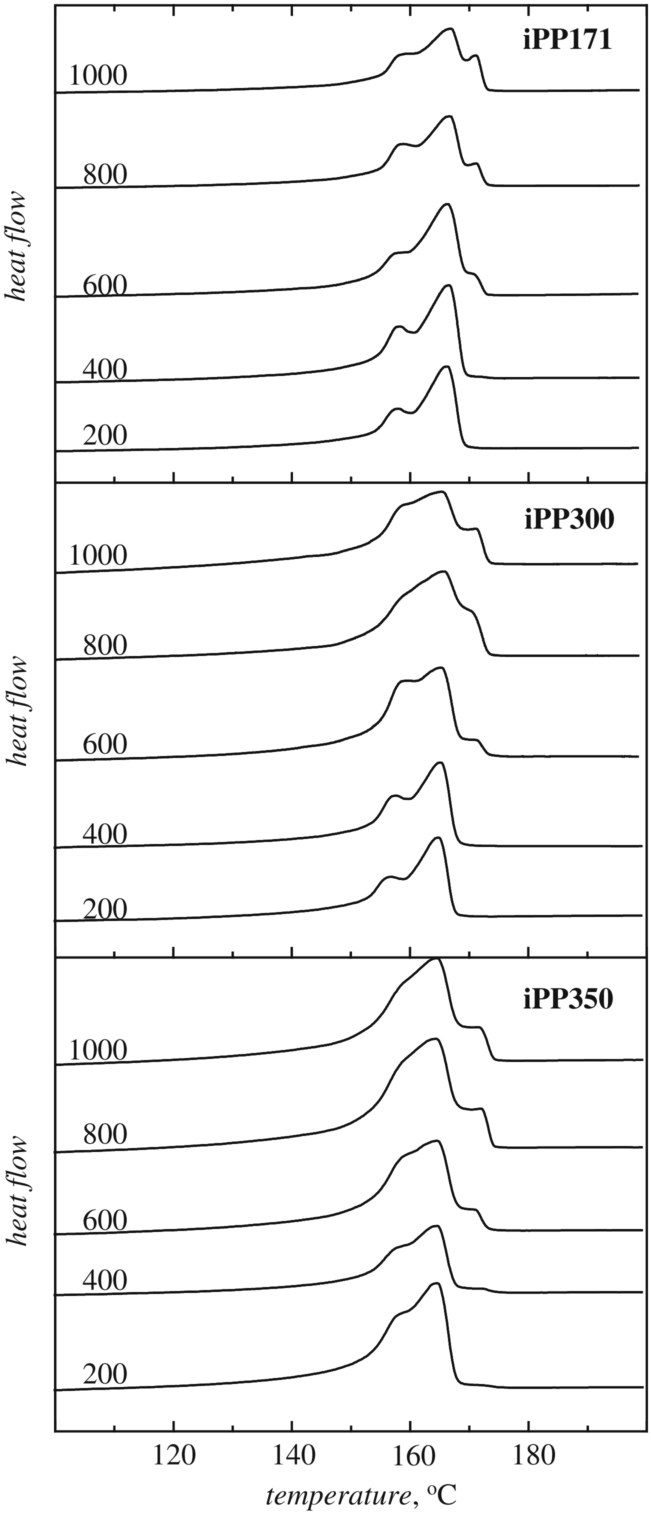

Fig. 6 DSC thermograms of all three iPP samples at increasing total strains

are, in fact, composed of two composite patterns, each corresponding to (1) the chain-extended fibrils aligned parallel to the flow direction and (2) the chain-folded lamellae (kebab) overgrowth that adopt a helical growth habit in a direction perpendicular to the nucleating fibril.

In Fig. 5, azimuthal scans of the 040 crystalline plane of iPP171 at increased strains were taken. Two distinct peaks appear at strains about 600 and higher. These arise from the oriented chain segments in the structure. Because the chains are parallel to the flow axis, these planes are also parallel to the sample axis and, therefore, must reflect X-ray intensity at right angles to the flow direction. The reflections obtained are isotropic up to a strain of 400 and lead to the conclusion that molecular orientation is too weak to affect the orientation of the final crystals.

Differential scanning calorimetry

The morphological differences of iPP samples at increasing strains shows up in DSC thermograms, at a heating rate of 5 K/min (Fig. 6). Sections of the sheared samples were cut and thermograms were measured. The sheared samples with strains of 600 and higher melt with two peaks, one at a temperature ~171°C that can be attributed to the melting of the chain extended component (Somani et al. 2002, Elmoumni et al. 2003) and the other at around 166°C corresponding to the nominal melting of the un-oriented spherulites consisting of chain-folded lamellae. The extra peak is not present in the thermograms of the sheared samples with strains of 400 and lower.

Discussion

The growth of polymeric crystals affects the entire range of physical properties. In this study, we use the reduction of light transmission to half its original value, the transmission half time $\tau_{1/2}$, as a characteristic crystallization time. Earlier experiments on iPP crystallization had shown that the $\tau_{1/2}$ correlates well with characteristic crystallization times from light scattering and from rheology. $\tau_{1/2}$ is easy to measure, even at high crystallization rate.

For this study, it helps to distinguish between the Deborah number, *De*, and the Weissenberg number, *We*. Following the original suggestion (Reiner 1964), *De* is defined here as the ratio of material time, λ, to shearing time, t_s. The pre-shearing time exceeds the longest relaxation time by far ($De \ll 1$), which means that steady shear flow is reached in all pre-shearing experiments. Different from *De*, the Weissenberg number is a measure of the strain that occurs during a shearing time that is equal to the longest relaxation time. *We* applies to steady state and to transient flow conditions as well. $We=1$ locates, for instance, the (broad) transition from zero-shear-rate viscosity behavior to shear thinning at steady shearing conditions. At the onset of nonlinearity, the shearing conditions are still fairly mild, which has the advantage that crystallization is still relatively slow, thereby leaving ample time for measurements. This is the main reason why *We*=1 was chosen for this study.

A disadvantage of the slow shearing is the relatively long shearing time that is required for introducing large strains. The pre-shearing time, t_s, should be short compared to the crystallization time. Otherwise, crystals already grow during the "pre-shearing". With this criterion ($t_s << \tau_{1/2}$), all experiments with iPP171 are allowed (compare t_s data in Table 2 with $\tau_{1/2}$ of Fig. 3). For iPP300, experiments up to $\gamma_0 = 400$ might be fine, and for iPP350, only the $\gamma_0 = 200$ should be considered. In this study, most of the analysis of structure focuses on the iPP171 experiments where the pre-shearing process occurred before the crystal growth.

The order in the large-strain iPP171 samples shows that there is no threshold stress that needs to be overcome for generating ordered crystals. However, the few experiments with varied *We* suggest that the strain that is necessary for generating alignment (at some level) will be reduced when shearing at high *We* (i.e., high stress). Further studies are required to explore this phenomenon.

There is a basic difference between samples that were pre-sheared with $\gamma_0 = 400$ (and below) and samples that were sheared further. The magnitude of the applied strain was found to substantially affect the crystallization dynamics and the final iPP morphology. Pre-shear at $\gamma_0 = 400$ (and below) increases the nucleation density, but optical micrographs and isotropic WAXD patterns indicate spherulitic crystal growth and un-oriented crystals in the final samples. Primary nuclei are mostly generated at the onset and less during the crystal growth period. In comparison, a pre-shear of $\gamma_0 = 600$ (and higher) increases the nucleation density further. This reduces the crystallization time by substantial amounts. In addition, strings appear in the optical micrograph, which is an expression of elongated "spherulite" structure. Crystals in the final samples are oriented as demonstrated by WAXD. The new crystal structure expresses itself in new melting transitions (DSC experiments).

The above transition at a strain level between $\gamma_0 = 400$ and $\gamma_0 = 600$, to our knowledge, has no obvious correlation with the molecular properties of the polymer. In rheological experiments, typical strains needed for the onset of nonlinear behavior in polymer melts are in the range between $\gamma_c = 0.1$ and 1 and to reach steady state are about $\gamma = 20$ to 40 shearing units. It is quite surprising to have about three-orders-of-magnitude difference in strain between the onsets of nonlinearity and the occurrence of oriented crystals in the final sample. Crystallization seems to be much more sensitive to molecular orientation than rheology; in other words, the shear flow rheologically has long reached steady state after $\gamma_0 = 600$ and the molecules are supposed to be fully oriented, but the effect on the crystal structure is only saturated after a total strain of about $\gamma_0 = 600$ to 1,000. One possible explanation is that the time to reach steady stress in a shear flow can be considered to be much shorter than the time to reach steady-state segmental orientation.

Another reason for the large strain requirement might be a relatively slow rate of nucleation during shear. In comparison, for quiescent crystallization of iPP at a constant crystallization temperature, all nuclei seem to form at once. This has been concluded from the uniform size of the spherulites as observed in the optical microscope. Same age and same growth rate for all spherilites result in the uniform spherulite size of quiescent crystallization. The size of the spherulites in sheared samples, however, is non-uniform. This lets us conclude that not all spherulites were born at the same time (presuming a uniform growth rate). A prolonged shearing (leading to a large strain) will allow longer periods of nucleation until all nuclei that possibly can form at a given *We* value have formed. This hypothesis is worth testing in a follow-up experiment.

The entanglement density at the onset of crystallization might also have a large effect. Shear at *We*=1 is just beginning to reduce the entanglement density (as expressed in the onset of shear thinning). The entanglement state might continue to change even if steady stress conditions are reached during the pre-shearing. Large strains might be required to acquire a steady state of the entanglement structure.

The molecular weight distribution might also be of influence. The mean orientation in the polymer is probably less than the orientation of large chains. Large fluctuations in orientation are expected due to the broad distribution of molecular weights (Mackley et al. 1975; Bashir et al. 1984; Seki et al. 2002; Elmoumni et al. 2005; Hsiao et al. 2005). Large strain experiments on model polymers are required for exploring the effects of changing the distribution (narrow distribution and addition of high molecular weight component) and molecular architecture.

Our observations agree with the earlier findings of Vleeshouwers and Meijer (1996) and Chai et al. (2004) but also raise major questions. It remains unclear how universally valid the findings are as one of the samples of Chai et al. (mPE) showed little sensitivity to large pre-shearing. The large effect of strain on crystallization agrees well with the observations of Li and de Jeu (2003) of ordered structure during shearing in the under-cooled state. However, these oriented precursor structures were found to appear at small strain ($\gamma = 15$), while much larger strains are required to generate ordered morphology in the final sample.

Conclusions

The most important rheological criteria for flow-induced crystallization in iPP appear to be the Weissenberg number and the imposed strain of the short-time shearing experiment. A surprisingly large strain in the order of $\gamma_0 = 600$ is required not only to effect the rate of crystallization but also to have full impact on crystallization morphology.

For a constant Weissenberg number (*We*=1, a value near the onset of shear thinning), strains at or below $\gamma_0 = 400$ already increase the crystallization rate by substantial amounts. Strains at or below $\gamma_0 = 400$ still lead to a spherulitic crystalline structure while strains of $\gamma_0 = 600$ or higher produce oriented morphology. WAXD and DSC corroborated these findings by the appearance of high intensity arcs in the 040 reflections and melting peak at 171°C, respectively. It is remarkable that no threshold stress has to be exceeded in order to generate aligned crystal structure. The only prerequisite for alignment is a sufficiently large strain during preshearing.

The shearing conditions at *We*=1 are fairly mild (when compared to polymer processing). Large strains require a relatively long time t_s. For satisfying the short shearing protocol as described in the "Introduction", t_s should be substantially smaller than $\tau_{1/2}$. This is only satisfied for the sample of lowest molecular weight. The higher molecular weight samples develop substantial crystallinity during shearing already. Further studies at higher shear rate are required so that preshearing and crystal growth are clearly separated. Shearing at higher rates is also important as it involves higher *We* values. Then, we can check the proposal that, at large *We*, smaller strains will be sufficient to affect nucleation and oriented crystal growth.

Acknowledgements We are grateful to the Petroleum Research Fund (PRF 41891-AC7) and NSF-MRSEC (DMR-0213695) for financial support of this work. The anonymous review was conducted with Dr. Martin Laun as member of the editorial board of Rheologica Acta.

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