

Shear-induced crystallization of isotactic polypropylene melts: isothermal WAXS experiments with synchrotron radiation

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(Received 28 January 1992; revised 14 August 1992)

It is well known that crystallization nuclei are created in the melt of semicrystalline thermoplastic materials by shearing. Sheared polymer melts have a higher number of crystallization nuclei than quiescent melts at the same crystallization temperature. Two types of isotactic polypropylene with different molecular weight distributions were investigated using special shearing equipment and synchrotron radiation diffraction. The results of our time-resolved WAXS investigations are time-dependent functions of the degree of crystallinity, from which certain parameters such as relaxation time can be determined with the help of a given crystallization model. Even a very small shearing of the melt, after a few seconds, enhances the crystallization of both materials at the temperature of 130 and 135°C. At the same temperatures, quiescent polypropylene melts start to crystallize after approximately 1 h. Without shearing the α -modification prevails, whereas an important volume fraction of the β -modification appears in sheared samples even at low shearing velocities of 4 s^{-1} .

(Keywords: isotactic polypropylene; melt; shear-induced crystallization; synchrotron radiation; degree of crystallinity; crystallization kinetics; WAXS)

INTRODUCTION

Semicrystalline thermoplastic materials such as polypropylene can crystallize in many different ways. The kinetics of crystallization is mainly influenced by material parameters and experimental conditions, of which temperature and shearing rates are the most important. A possible way to describe the kinetics of crystallization is to evaluate a time function from the degree of crystallinity, for example from the well known mechanism of nucleus formation¹⁻³. Many experiments have shown that crystallization occurs mainly from heterogeneous nuclei in polymer melts, especially in polymer processing⁴⁻⁶.

Two important models of crystallization have been suggested: crystallization in quiescent melts^{7,8} and crystallization during shear- or drawing-streams^{9,10}. In the first case, the polymer melt crystallizes in a spherulitic form and produces an isotropic structure^{8,10}. In the second case (shear-induced crystallization) the polymer melt crystallizes as a lamellar anisotropic microstructure^{8,11}. The effect of shear-induced crystallization is well documented in the literature¹²⁻¹⁶ and has been demonstrated by different experimental techniques. Shear-induced nucleus formation in polymer melts depends primarily on the temperature and shearing rate^{8,9,11}. In isothermal shearing experiments we can define an 'induction time', which indicates the beginning of crystallization and which depends on the shearing rate^{8,17}. Two different models of shear-induced crystalliz-

ation are sometimes referred to as 'weak flow' and 'strong flow' in the literature¹⁸.

An important object of this paper is to describe the kinetics of crystallization in terms of a time-dependent degree of crystallinity. The theoretical background is the crystallization model of Eder and Janeschitz-Kriegl^{8,9}. By analogy to Avrami^{1,2}, but for the case of shear-induced crystallization, the following exponential law for the degree of crystallinity at time t is applicable:

$$\zeta(t) = \zeta_{\max} \{1 - \exp[-\Phi_0(t)]\}$$

where ζ_{\max} specifies the maximum degree of crystallinity attained and Φ_0 is a probability function, which considers shear-induced nucleus formation.

For the isothermal case (temperature T_s) and at constant shearing rate $\dot{\gamma}$ (maintained through a certain shearing time t_s), $\Phi_0(t)$ is determined by the following equations, if $t > t_s$:

$$\Phi_0(t) = G \left(1 - \frac{1}{\beta}\right)^4 \times \left[t_s - \tau \left[1 - \exp\left(\frac{-\beta t_s}{\tau}\right) \right] \left\{ \frac{1}{\beta} - \left[1 - \exp\left(\frac{t_s - t}{\tau}\right) \right] \right\} \right]^4$$

where

$$\beta = 1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_a}\right)^2$$

and

$$G = 2g_x g_y g_z g_n$$

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In this equation material parameters such as relaxation time (τ), critical shearing rate ($\dot{\gamma}_a$) and the product (G) of crystal growth velocities (g_x, g_y, g_z) and nucleating velocity (g_n) are adapted. These are strongly dependent on the shearing temperature (T_s). These parameters can be estimated from the experimental data for the corresponding experimental conditions. Therefore the main interest in our experiments was the analysis of polymer melts submitted to shearing with very small velocities of approximately 10 s^{-1} compared with the usual conditions that occur during extrusion, injection moulding, calendaring and similar methods¹⁹. For this purpose an extensometer was equipped with a shearing unit, based on the measuring principle of Maxwell and co-workers^{13,17}, which makes real-time X-ray diffraction possible during the drawing of polymer melts.

EXPERIMENTAL

Two kinds of isotactic polypropylene (it-PP) samples, KS10 and PT55 (Daplen KS10 and Daplen PT55 from Petrochemie Danubia, Linz, Austria), were used to investigate the influence of molecular weight distribution on crystallization kinetics^{20–22}. KS10 and PT55 are typical of injection moulding grades of it-PP with wide and narrow molecular weight distributions, respectively (Table 1). Both material types were produced without additives or filling materials, which could act as nucleating agents. We prepared samples with isotropic structure by compression moulding in the form of foils 0.5 mm thick.

For the examination of the kinetics of crystallization the foils were melted and X-ray diffraction patterns were taken during cooling. The cooling process was stopped for shearing experiments and the temperature kept constant. Wide angle X-ray scattering (WAXS) experiments using synchrotron radiation were carried out at DESY (Deutsches Elektronen Synchrotron, Hamburg) on the so-called 'polymer beamline'. This beamline uses the X-ray spectrum of the synchrotron radiation from DORIS (Double Ring Storage device). After monochromatization, X-rays with wavelength of 0.154 nm are available. A description of the beamline and the instrumentation is given by Elsner *et al.*²³.

In the shearing experiments, an extensometer designed by Bratich *et al.*²⁴ was equipped with an additional shearing unit (Figure 1). This consisted essentially of two plates (poly(ethylene terephthalate) (PET) foils) holding the sample between them²⁵. They could be rotated against each other so that the melt was sheared during drawing. A Gabriel detector system (a run time wire counter with multichannel registration) recorded X-ray diffraction patterns every 5 s. In principle, any shearing velocity in the wide range of $0\text{--}40 \text{ s}^{-1}$ can be selected in this experiment. For constant drawing velocities the

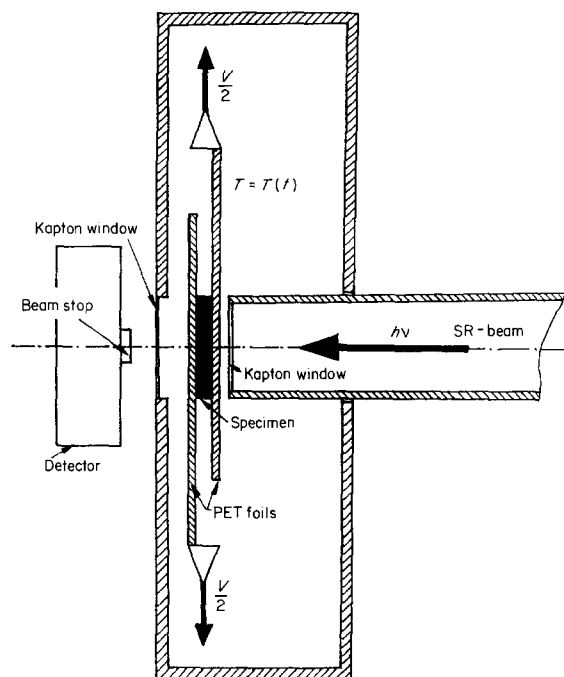


Figure 1 Extensometer and shearing unit (schematic)

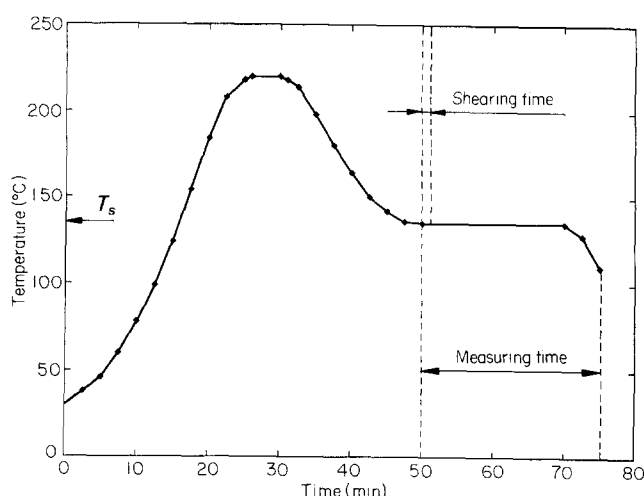


Figure 2 Heating and cooling programme for sample

shearing rate was also constant over the cross-section of the specimen. Two drawing velocities were used corresponding to shearing rates of 4 and 12 s^{-1} . The samples were drawn over 120 mm. After the preheating phase the samples were kept at constant temperatures by a stream of hot air in a closed metal box surrounding the extensometer. At the appropriate temperature, shearing was started by rotating the plates holding the samples against each other.

Shearing experiments with PP were carried out at temperatures of 130 and 135°C . At these temperatures quiescent PP melts crystallize in spherulitic form only after approximately 1 h. The heat treatment was divided into two stages: preheating at constant temperature of 210°C , and cooling at a constant rate of 5°C min^{-1} to the chosen shear temperature. During the preheating phase the number of crystallization nuclei (athermal nuclei) was reduced to a minimum. The heating and cooling programme is shown in Figure 2.

Table 1 Material data^a

Material	MFI (g/10 min)	M_w (g mol^{-1})	M_w/M_n	T_m ($^\circ\text{C}$)
KS10	8.0	290 000	5.7	171
PT55	18.6	160 000	2.5	171

^aMFI, melt flow index 230/21.19N (DIN 53 735); M_w , weight-average molecular weight; M_n , number-average molecular weight; T_m , melting point

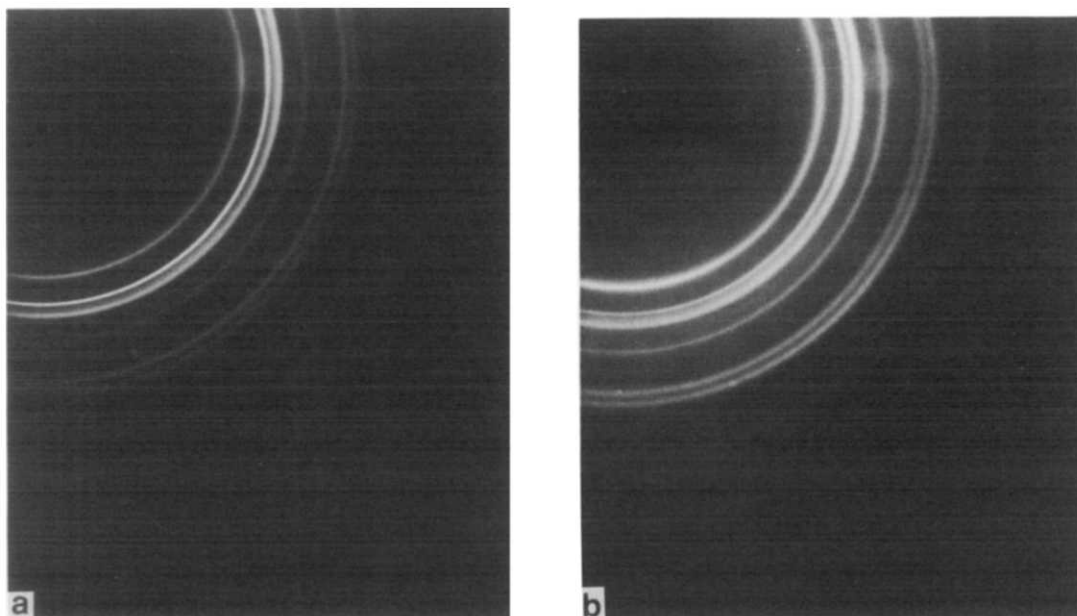


Figure 3 Diffraction patterns on film of (a) PP-PT55 and (b) PP-KS10

RESULTS AND DISCUSSION

The two samples of PP were subjected to very small shearing velocities. The samples have a nearly isotropic structure on shearing at rates of $4\text{--}12\text{ s}^{-1}$. X-ray diffraction patterns of both materials showed closed rings (Figure 3), so that measurements with a one-dimensional detector system were possible, but only at small shearing rates.

The temperatures of 130 and 135°C were chosen so that no spherulitic crystallization would take place within several minutes. Both PP samples crystallize in the α -modification isothermal at temperatures of 130 and 135°C and during cooling at $5\text{--}40^\circ\text{C min}^{-1}$. Diffraction patterns obtained from the quiescent melts of PT55 are shown in Figure 4.

Both materials KS10 and PT55 have similar kinetics of crystallization for the quiescent melt, but in the case of shear-induced crystallization there are some differences. The change of entropy of the melt, as a consequence of shearing, enhances nucleation and crystal growth rates in the shear direction. As the experimental results show, this effect depends strongly on the molecular weight distribution.

Diffraction patterns recorded during shearing of KS10 are shown in Figure 5. These show that at small shearing rates a significant volume fraction (approximately 15%) of the β -modification is present. We determined the degree of crystallinity according to Ruland^{26,27}. With the help of time-resolved WAXS studies we can measure the degree of crystallinity as a function of time for each shearing experiment. As a result, the following parameters such as relaxation time (τ), critical shearing rate ($\dot{\gamma}_a$) and the product (G) of crystal growth velocities ($g_x g_y g_z$) and nucleating velocity (g_n) were estimated (Table 2). In this connection it is worth mentioning that the different structure of crystals (spherulitic, fibrillar or lamellar) is only considered indirectly in the value of the degree of crystallinity.

The curve of the crystallinity versus time in Figure 6 obviously suggests that the crystallinity of polymer melts

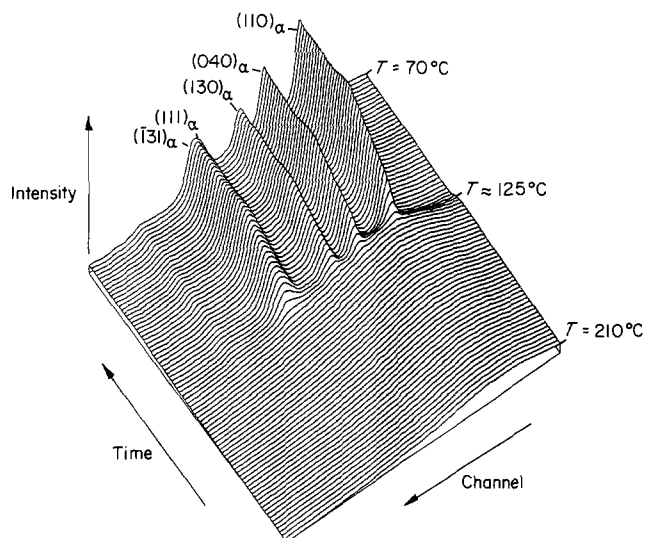


Figure 4 WAXS diagrams versus measuring time for spherulitic crystallization of PT55

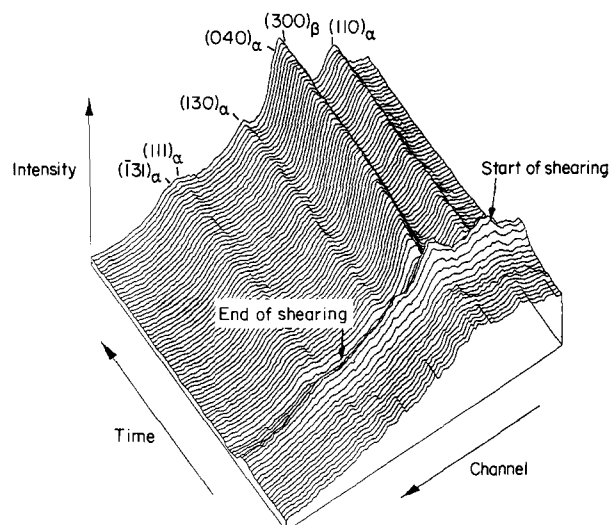


Figure 5 WAXS diagrams versus measuring time for shear-induced crystallization of KS10

is increased by shearing. From Figure 6 it is evident that the induction time (the time before crystallization begins^{8,17}) is shorter for KS10 than for PT55 (Table 3). Shearing produces more nuclei in KS10 melts than in PT55. Besides, the crystal growth rate is essentially higher for KS10, with wide molecular weight distribution, than

Table 2 Crystallization kinetics parameters

Material	T_s (°C)	$\dot{\gamma}$ (s ⁻¹)	t_s (s)	τ (s)	β	$\dot{\gamma}_a$ (s ⁻¹)	G (s ⁻⁴)
KS10	135	4	60	306	10	1.3	3.7×10^{-8}
KS10	130	4	60	365	12	1.2	3.6×10^{-8}
PT55	130	4	60	1084	36	0.7	5.7×10^{-9}
KS10	130	12	20	364	36	2.0	7.7×10^{-8}

Table 3 Induction times for different shearing conditions

Material	Temperature, T_s (°C)	Shearing rate, $\dot{\gamma}$ (s ⁻¹)	Induction time, $t_{1/2}$ (s)
KS10	135	4	80
KS10	130	4	67
KS10	130	12	33
PT55	130	4	123

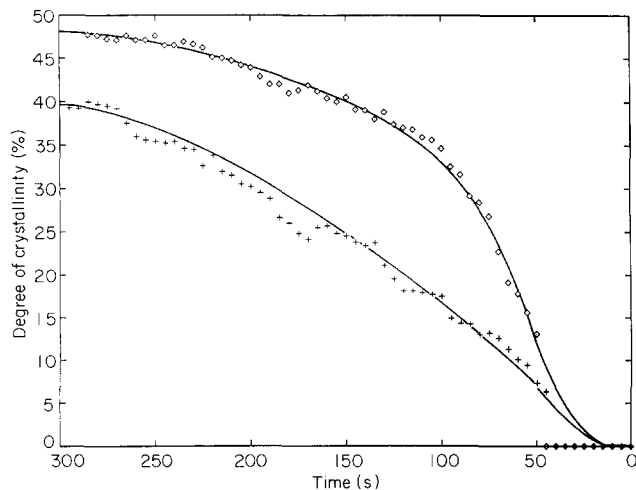


Figure 6 Degree of crystallinity versus measuring time: +, PT55; ◇, KS10. Shearing rate, 4 s⁻¹; crystallization temperature, 130°C

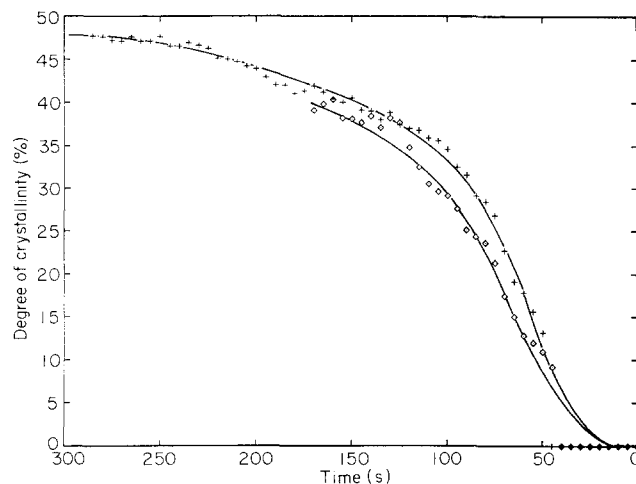


Figure 7 Degree of crystallinity versus measuring time at crystallization temperatures of +, 130 and ◇, 135°C for KS10. Shearing rate 4 s⁻¹

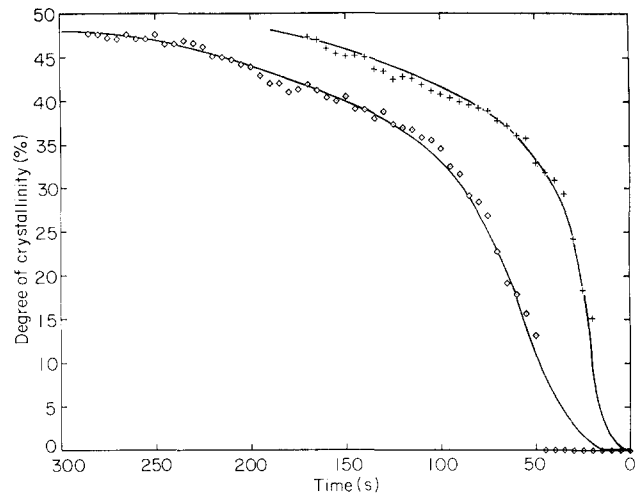


Figure 8 Degree of crystallinity versus measuring time at shearing rates of ◇, 4 and +, 12 s⁻¹ for KS10. Crystallization temperature 130°C

for PT55, which has a narrow molecular weight distribution (Table 2).

Figure 7 compares the crystallinity of sheared KS10 melts at two constant temperatures. The results show that the induction time is shorter at 130°C than at 135°C. At the higher temperature less nuclei develop on shearing. At a constant temperature of 130°C and with shearing rates of 4 and 12 s⁻¹ it was shown that the corresponding induction time diminished with higher shearing velocity (Figure 8).

The volume fraction of the β -modification in the sheared samples can be determined from changes on the diffraction peaks during shearing (Figure 5). For KS10 the ratio of the intensity of the (300) reflection (corresponding to the β -modification) to the intensity of the (110) reflection (from the α -modification) is two to one at 130°C but only four to three at 135°C. The volume fraction of the β -modification grows with decreasing temperature.

CONCLUSIONS

For the experimental procedures described above the crystallization kinetics based on Eder and Janeschitz-Kriegl's model have been applied to melts sheared at up to 40 s⁻¹. In this work we have determined for the first time crystallization rate parameters at selected crystallization conditions (Table 2). It appears that under the same shearing conditions the entropy of the melt of material with wide molecular weight distribution is essentially higher than the entropy of the narrow molecular weight distribution polymer. This fact is obviously related to the induction time, which is lower for KS10 than for PT55 (Table 3).

Finally, it should be mentioned that quiescent PP melts crystallize in α -modification, in the case of isothermal crystallization at temperatures of 130 and 135°C and in the case of cooling experiments at rates of 5–40 K min⁻¹. Even small shearing velocities cause a significant increase of the volume fraction of the β -phase at melt temperatures of 130 and 135°C.

ACKNOWLEDGEMENT

One of the authors (J.M.) gratefully acknowledges the support of B. Heise and M. Bratrich from the University

of Ulm at their synchrotron radiation facility at HASYLAB. This work was sponsored by the Austrian 'Fonds zur Foerderung der wissenschaftlichen Forschung' under contract P7660-TEC.

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