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SHORT COMMUNICATION

C. Feldhüsen
W. Wenig

Molecular fractionation in isotactic polypropylene during isothermal crystallization

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C. Feldhüsen · W. Wenig (✉)
Gerhard-Mercator-Universität
Laboratorium für Angewandte Physik
D-47048 Duisburg
Germany

Abstract The nucleation frequency of isotactic polypropylene shows for certain molecular weight distributions during isothermal crystallization a "stepwise" development of the nuclei as a function of time. The resulting curve can be fitted by a superposition of exponential functions assuming a separate nucleation density for each nucleation step. The multimodal nucleation is discussed as a consequence of molecular fractionation effects during crystallization.

Key words Polypropylene – nucleation – isothermal crystallization – molecular fractionation

Introduction

It is generally observed, that under isothermal conditions the primary nucleation in isotactic polypropylene (PP) is preferentially heterogeneous [1, 2]. The usually measured kinetical parameters like nucleation half-times, crystallization temperatures and crystallization half-times are typical for this mode of nucleation. It has been discussed, that this may be an effect of catalyst residues, but it seems, that already natural impurities are responsible for this behavior [3]. The addition of nucleating agents activates the nucleation further.

Polypropylene is known to develop a multimodal supermolecular morphology, as is often revealed by X-ray measurements. It is clear that already the nucleation effects the morphology through the crystal and spherulitic growth. A careful measurement of the nucleation of iPP reveals under certain conditions a "stepwise" development of the number of nuclei with crystallization time. In this paper the reason for this phenomenon is investigated.

Experimental

We investigated two samples of isotactic polypropylene, one with a molecular weight $M_w = 3.2 \times 10^5$ and $M_n = 4.7 \times 10^4$ ($M_w/M_n = 6, 8$) (sample 1), and a second one with $M_w = 1.92 \times 10^5$ and $M_n = 4.93 \times 10^4$ ($M_w/M_n = 3.89$) (sample 2). The samples were of commercial origin containing the usual additives.

For microscopic investigations, thin films of thickness between 20 μm and 80 μm were produced using a laboratory press.

The nucleation was observed using a Leitz polarization microscope. For this purpose, the samples were placed between glass slides and put in a hotstage. The development of the number of nuclei as a function of time $N(t)$ at constant temperature was monitored on a computer screen and the microscope images were stored on a hard disk for further processing.

Results and discussion

For the sample with the higher molecular weight curves for $N(t)$ were measured that showed several steps. Figure1 shows as an example a curve that reveals at a crystallization temperature of $T_k = 400$ K two nucleation steps. Already this curve cannot be described by a simple exponential function as one usually does with these curves.

Avrami [4] showed, that the volume of a growing nucleus (crystal) is proportional to the total volume

K 020

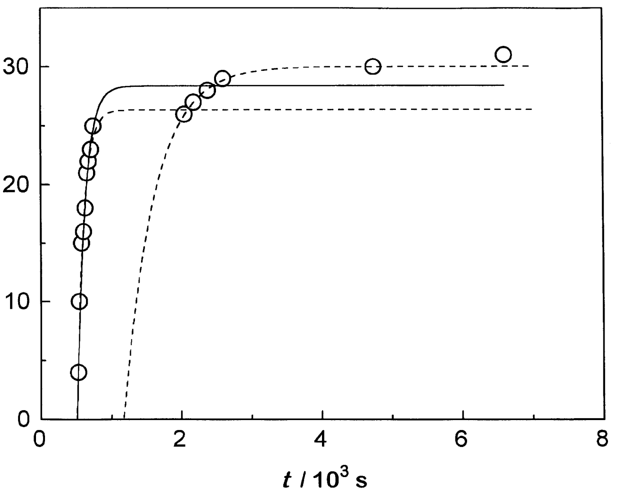

Fig. 1 Nucleation frequency of a thin sample of isotactic polypropylene (sample 1, crystallization temperature $T_k = 400$ K) The dashed lines show the curve fits applying Eq. (7)

$(1 - V(t))$ of the untransformed material in the observed sample. Considering the growth of the total transformable volume during a time interval dt, we find that the increase of the transformed volume dV relates to the theoretical increase of a free volume, dV_f, like the volume $(1 - V(t))$ to the total volume (:=1)

$$\frac{\mathrm{d}V(t)}{\mathrm{d}V_f(t)} = \frac{1 - V(t)}{1} = 1 - V(t) \; . \tag{1}$$

Integration yields

$$V(t) = 1 - \exp[-V_f(t)] \quad \text{(Avrami equation)} \; . \tag{2}$$

Relating the nucleation parameters to the unit volume (model of Avrami, e.g. Tobin relates the parameters to the unit area [13]), and choosing an exponential function for the decrease of the number of activated nuclei, one gets

$$\frac{\mathrm{d}N'}{\mathrm{d}t} = -\alpha N'(t) = -\alpha M \exp(-\alpha t) \; , \tag{3}$$

where N' is the number of nonactivated nuclei at time t, α the probability of activation and M the total number of nuclei after completion of the nucleation (nucleation density).

From this equation we get the number of nuclei to be activated at time t

$$N'(t) = M \exp(-\alpha t) \tag{4}$$

and the number of already growing nuclei at time t that is the nucleation frequency per unit of transformed volume:

$$N(t) = M(1 - \exp(-\alpha t)) \; . \tag{5}$$

Within the temperature range chosen, the nucleation of all samples appeared to be (preferentially) heterogeneous, which can be proved by the corresponding Avrami exponents. However, the nucleation frequency cannot be calculated by a single exponential function according to Eq. (5), but rather through a linear superposition of i functions (5). Because each function is shifted on the time scale, we apply these functions in the form

$$N_i(t) = M_i[1 - \exp(\alpha_i(t_i - t))] \; , \quad i = 1, \ldots, n \; , \tag{6}$$

where i is equal to the number of nucleation processes.

The functions (6) are consecutively fitted to the experimental curves where the ith function is shifted along the ordianate in such a way, that its zero level matches the asymptote value of the $(i - 1)$th function (proportional to the shifts of the induction times). Thus, for the calculation of the ith function, the asymptotic values for all numbers of nuclei of all preceding exponential functions are added

$$N_i(t) = M_{i-(i+1)} + \cdots + M_{i-1} + M_i[1 - \exp(\alpha_i(t_i - t))] \; . \tag{7}$$

The sum of the asymptotic values yields the maximum number of nuclei in the observed volume

$$\sum_{i=1}^{n} M_i = M \; . \tag{8}$$

The induction time, $t_{0,i}$, of the ith function is yielded from the intersection of $N(t_i - t)$, describing the ith nucleation process, and the asymptote of the $(i - 1)$-st nucleation. All experimentally measured curves could be well represented by a superposition of curves of type (7).

A fit of an experimental curve using Eq. (7) is demonstrated in Fig. 1 (dashed lines). The figure shows that two individual nucleation processes can be resolved. From the fits, we get for the induction times $t_{0,1} = 502$ s for the first fit, and $t_{0,2} = 2098$ s for the second fit. The activation probabilities amount to $\alpha_1 = 9.8 \times 10^{-3}\,\mathrm{s}^{-1}$ for the first fit, and $\alpha_2 = 2.3 \times 10^{-3}\,\mathrm{s}^{-1}$ for the second. The asymptotes yield $M_1 = 26$ and $M_2 = 4$. Fitting the curve in a "conventional" way (one fit for the whole curve), one gets $t_0 = 504$ s, $\alpha = 9 \times 10^{-3}\,\mathrm{s}^{-1}$ and $M = 28$. A manual counting of the nuclei in the observation field of the microscope yields $M = 32$. We see, that this evaluation is dominated by the first step of the nucleation, neglecting the second step almost completely.

Asking for the reasons of this behavior, a number of explanations can be found in the literature. Keith and Padden [5] investigated fractionation and segregation phenomena in polypropylene in the presence of impurities. They found an effect on the spherulitic growth and size distribution. Mandelkern [6] found an influence of molecular-weight-dependent entanglements on nucleation

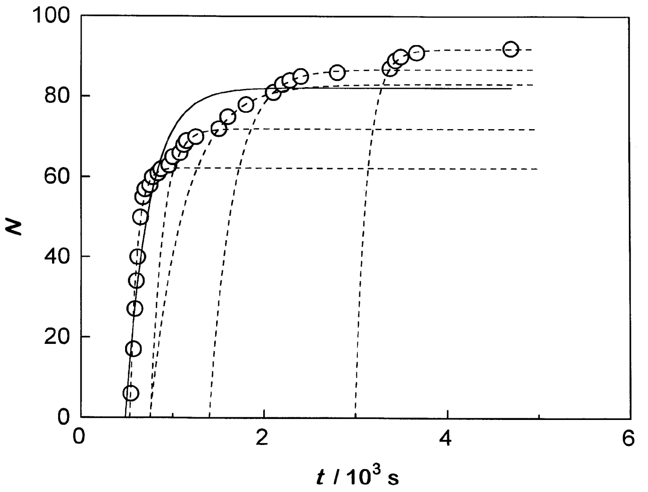

Fig. 2 Nucleation frequency of sample 1 at $T_k = 411$ K. Five nucleation processes can be resolved

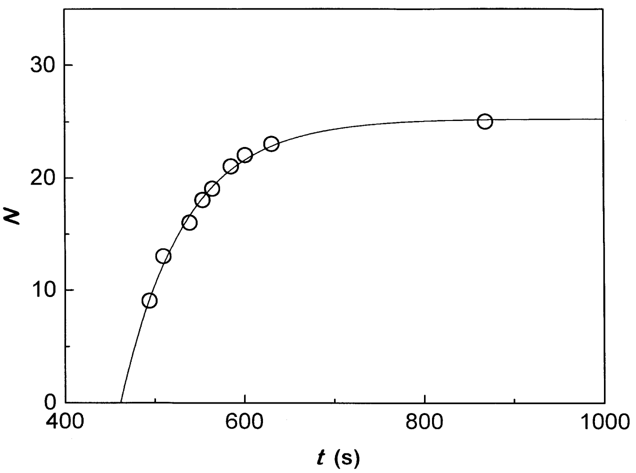

Fig. 3 Nucleation frequency of sample 2 ($T_k = 411$ K)

and crystallization kinetics. Wunderlich [7] reported an influence of molecular weight on the crystallization kinetics. The higher molecular weight fraction crystallizes first, the lower fractions follow later. This fractionation should depend on the supercooling. Hoffmann [8] calculated the critical molecular weight for the secondary nucleation on an infinitely extended substrate and explained a molecular-weight-dependent fractionation for this model system. Other authors confirmed these results in principle [9–11]. Fatou [12] found, that in systems showing fractionation, the crystallization rate is proportional to the nucleation rate and depends at constant crystallization temperature on the chain length.

Assuming molecular fractionation, sample 1 should exhibit an increased stepwise nucleation at higher crystallization temperatures, because then the nucleation half times are much higher giving the system more time to fractionate. Figure 2 confirms this by showing five nucleation steps for sample 1 crystallized at $T_k = 411$ K. We see that the curves $N_i(t)$ shift with time consecutively to higher induction times. This is in good accordance with the literature [12] and reflects the fact, that the thicker lamellae crystallize first followed by the thinner ones.

A further proof should be the measurement of a sample having a lower molecular weight distribution. Figure 3 shows the nucleation of sample 2, which exhibits a smaller average molecular weight and a narrower MWD. This sample nucleates in a conventional way not exhibiting any nucleation steps.

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