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SHORT COMMUNICATION

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Crystallization of s-polypropylene: a qualitative change in the kinetics induced by the temperature of the melt

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Abstract The crystallization of syndiotactic polypropylene (sPP) can be strongly affected by the temperature of the melt prior to cooling to the crystallization temperature. We observed, for a commercial sample, a variation in the form of the crystallization isotherm that cannot be explained simply on the basis of a changing number of growing hedrites.

Introduction

If a semi-crystalline polymer is melted and then recrystallized, memory effects can show up, in the sense that the time required for the second crystallization is found to vary with the temperature of the melt and the time during which the sample is kept in the molten stage (compare, for example, [1, 2]). Crystallization times tend to reduce as the melt temperature is lowered and the period of melting is shortened. Most authors explain this memory effect by assuming a persistence of nuclei in the melt, expressed by the popular term of ‘‘self seeding’’. One might also envisage a further effect, when considering that on crystallizing a polymer system the entanglements become concentrated in the amorphous regions and that the reestablishment of a uniform entanglement distribution, as it corresponds to an equilibrated melt, needs some time.

So far, in the large majority of works the memory effect is discussed in terms of observed changes of the halftime of crystallization only. When we came across the phenomenon in a recent study of the crystallization behavior of syndiotactic polypropylene (sPP) we found this simple approach to be insufficient. A discussion in terms of the halftime of crystallization would only be justified if the variation with the temperature of the melt and the period of storage simply leads to a shift of the crystallization isotherm along the t -axis, without a change in the curve shape. Our observations, however, were different, as we found, in fact, quite remarkable changes in the curve form that showed up in consistent manner.

Experimental

Samples

The sample of sPP used in the studies was a commercial brand supplied by FINA Oil, Brussels. It has 83% syndiotactic pentades and a molar mass $M_w = 6\times10^4$ gmol^{-1}($M_w/M_n = 4$). We had used this material previously in investigations of the deformation behavior that also included a structural characterization [3].

Dilatometry

Structure formation at various crystallization temperatures was studied with a mercury filled dilatometer. Crystallizations were started by rapidly transferring the dilatometer from one (oil-filled) thermostat, set at the chosen melt temperature T_m, to another, preset at the crystallization temperature T_c. Thermal equilibrium was generally reached within one minute. Absolute values of the change in the specific volume were obtained after a calibration.

Results and discussion

Dilatometry

Fig. 1 shows various crystallization isotherms as obtained in the dilatometer. The decrease with time of the specific volume, $\Delta v(t) = v_0 - v(t)$, is presented in log-log-plots for one crystallization temperature, $T_c = 105$ °C, and for various temperatures T_m of the melt. The sample was always kept for 20 minutes at T_m before it was cooled rapidly to the crystallization temperature.

Curves show that for melt temperatures above 161 °C we always obtained the same result, whereas for temperatures below this critical value the crystallization isotherms altered. One observes not just a change in time but also in the curve shape. There was a further observation: as long as T_m was below 161 °C, then even for annealing times of many hours the limiting curve found for the higher temperatures was not reached. On the other hand, for temperatures above the critical value the establishment of the equilibrium always occurs in a rapid manner.

With the knowledge of the existence of two different melt temperature ranges, separated by the critical temperature of 161 °C, we selected 150 °C and 180 °C as two representative cases and varied the crystallization temperature T_c. The crystallization isotherms obtained for four different crystallization temperatures between 105 °C and 120 °C are shown in Fig. 2. One observes systematic shifts for both types of curves together. Hence, for a fixed melt temperature a variation of the crystallization temperatures leads to the well-known shift of the crystallization isotherm along the t -axis.

The isotherms found for the two different melts follow different power laws and therefore differ qualitatively, indicating a change in the process of structure evolution. In the initial stages, the exponent in the law

$$\Delta v \sim t^m \qquad (1)$$

is $m = 3$ for a melt temperature above 161 °C, and much larger, around $m = 5.5$, for melt temperatures below this critical value.

We, therefore obtained a clear result: a critical temperature of the melt exists, in this case 161 °C, which separates two different ranges. For $T_m > 161$ °C the same kinetics of crystallization is always observed after cooling to some T_c; for $T_m < 161$ °C the kinetics changes qualitatively (not just in the sense of a variation of the characteristic time). The high temperature melt can be called "equilibrated", and the low temperature melt, which keeps some memory of the former semi-crystalline state, called "structured". It is an interesting finding that the time during which a sample is kept in the molten state plays only a minor role. Is there further meaning behind the critical temperature? It may be an accidental coincidence, but the critical temperature of 161 °C agrees with the equilibrium melting point $T_f^\infty$of the sample under study, as obtained in previous work by an extrapolation of measured melting points based on the Gibbs-Thomson equation [3].

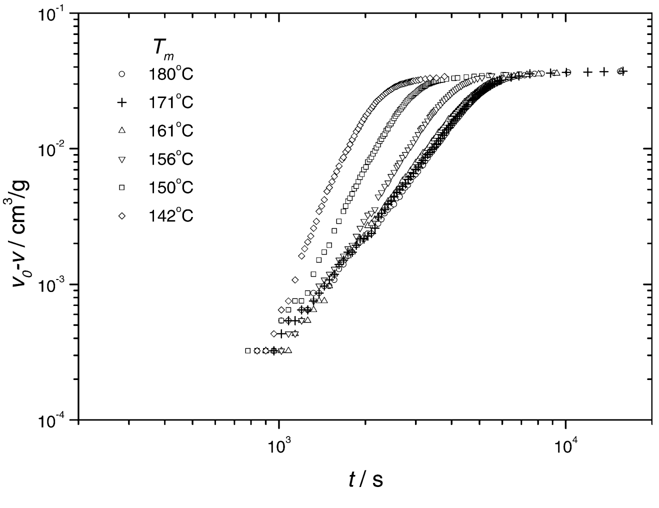

Fig. 1 sPP: Kinetics of isothermal crystallization at $T_c = 105$ °C as observed in a dilatometer for different temperatures T_m of the melt prior to cooling (v : specific volume, v_0 : specific volume of the melt at T_c)

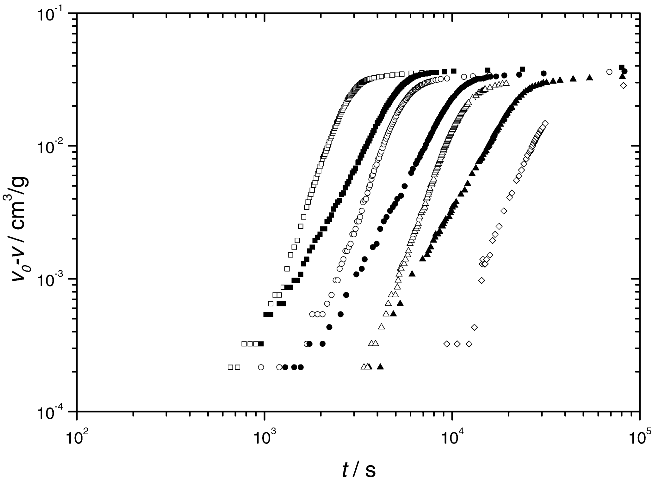

Fig. 2 sPP: Dilatometric registration of the kinetics of crystallization at $T_c = 105$ °C (*squares*), 110 °C (*circles*), 115 °C (*triangles*) and 120 °C (*lozenges*). For the first three T_c values, measurements were carried out for two melt temperatures, T_m = 150 °C (*open symbols*) and 180 °C (*symbols filled*), but for the highest T_c only for 150 °C

An initial increase of the crystallinity according to a power-law

$$\Delta v \sim t^3 \qquad (2)$$

as it is observed for the crystallization out of the equilibrated melt indicates a 3D-growth with constant rate for a fixed number of objects with an invariant inner structure. In the case of sPP these objects resemble hedrites much more than spherulites [4, 5, 6].

Crystallization from a structured melt proceeds in a qualitatively different manner, as is demonstrated by the different power law

$$\Delta v \sim t^5 \qquad (3)$$

describing the initial stages. Such behaviour is indicative of a sequential building-up of the hedrite's inner structure. They begin in an open form with large distances between the first growing "dominant" lamellae. Subsequently, the space is filled continuously by later growing "subsidiary" lamellae, using the names introduced by Bassett after corresponding TEM-observations [7].

The development of the crystallinity in the initial stages where all objects are isolated can be described as

$$\Delta v = n[v_{\mathrm{h}}(t) - v_{\mathrm{m}}](gt)^3 \qquad (4)$$

with

Δv : change in the specific volume of the system
$v_{\mathrm{h}}(t)$: specific volume of the hedrite (time-dependent)
v_{m} : specific volume of the melt
g : linear growth rate of the hedrites

The observed power of five would imply that

$$v_{\mathrm{h}}(t) - v_{\mathrm{m}} \sim t^2 \qquad (5)$$

as a consequence of the in-filling processes.

Indeed, such in-filling processes have often been observed, in particular in recent times with the aid of atomic force microscopes [8]. The experiments cover only a factor of two in time, which would imply an increase by a factor $2^{(5-3)} \approx 4$ in the packing density. This looks reasonable. Hence, what we observe is a change in the structure formation process of the hedrites, from a sequential mode to a growth of filled hedrites with a constant inner structure. Melt memory effects are so far merely exclusively discussed assuming the remaining presence of "seeds", which then act as nuclei. Although this effect certainly exists, it seems to be less important for the system under study.

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