

CRYSTALLIZATION AND MELTING BEHAVIOUR OF A STEREOBLOCK ISOTACTIC POLYPROPYLENE

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ABSTRACT

The crystallization and melting behaviour of a stereoblock isotactic polypropylene were analyzed using the dilatometric method. The samples were crystallized at different temperatures and at each temperature the crystallization kinetics were noted. The melting temperature was obtained as a function of the crystallization temperature according to the Hoffmann and Week equation. The obtained results show that the chain microstructure plays a significant role in the melting behaviour; the effect was related to the crystal thickness, as determined mainly by the length of the stereoregular sequences.

INTRODUCTION

In recent years the use of soluble Ziegler–Natta catalysts has allowed the synthesis of new stereoregular polymers. Among the new possibilities, it was shown [1] that the stereospecific polymerization of propene can be controlled to obtain a stereoblock system in which isotactic sequences are statistically distributed along the chain. The microstructure depends on the block length and distribution; the distribution can be described by a Bernoullian statistical model [2], each block being interrupted at its end by an inversion of configuration which is maintained in the adjacent blocks. The particular chain microstructure, intermediate between that of atactic and isotactic polypropylene, affects the physical behaviour, as reported in a previous paper [3]. The most significant features related to the chain microstructure are low crystallinity, low melting point and mechanical behaviour typical of a thermoplastic elastomer. Also, the crystalline form is determined by the particular microstructure; in fact, the system crystallizes in γ form [3], as observed in sterically disordered polypropylene [4]. It was suggested that crystallization mode, crystal thickness and morphology are ruled mainly by the average length of the stereoregular sequences. In the

present paper, the crystallization and melting behaviour were investigated using the dilatometric method, and the results obtained give further information on the relationships between morphology and chain microstructure.

EXPERIMENTAL

The stereoblock polypropylene was prepared by Zambelli and coworkers, following the synthesis procedure first described by Ewen [1]. The sample was introduced into a glass dilatometric cell, which was sealed and filled with mercury under high vacuum. The filling procedure was carried out by measuring the exact quantity (± 0.1 mg) by weight, and therefore by volume, of polymer and mercury; from these quantities, the volume occupied in the cell was calculated as the sum of the two components. The changes of the mercury level in the calibrated capillary (internal diameter = 0.2 mm) of the cell give the volume changes of the system, and therefore the volume changes of the polymer, knowing the thermal expansion coefficients of mercury and glass: $1.81 \times 10^{-4} \text{ K}^{-1}$ and $9.9 \times 10^{-6} \text{ K}^{-1}$ respectively [5]. The cell was thermostated in an oil bath ($\pm 0.1^\circ \text{C}$) and the mercury level was detected using a cathetometer (to within ± 0.05 mm). The volume of the polymer was measured as a function of time, at constant temperature, in the crystallization experiments, and as a function of temperature, with heating at constant rate ($2^\circ \text{C min}^{-1}$), in the melting experiments.

RESULTS

As previously reported [3], the analyzed sample shows a melting endotherm in the range $40\text{--}80^\circ \text{C}$, as detected by scanning calorimetry with a scan rate of $20^\circ \text{C min}^{-1}$. On this basis the crystallization and melting runs were performed according to the scheme in Fig. 1, where the time and

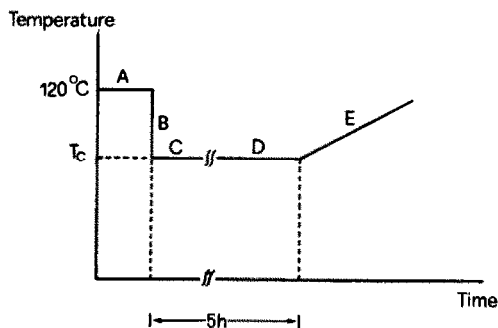


Fig. 1. Scheme of the thermal analysis procedure used to obtain crystallization and melting data. See text.

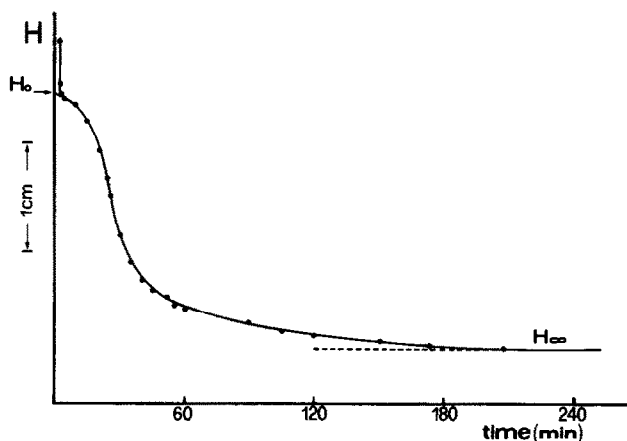


Fig. 2. Crystallization curve. The mercury level H is reported versus time. The plot refers to $T_c = 50^\circ\text{C}$.

temperature scales are completely arbitrary. In stage A the sample is maintained at 120°C (well above the melting point) for 30 min, then in stage B it is rapidly quenched at the chosen crystallization temperature T_c , and the crystallization process is monitored as a function of time (stage C). Regardless of the crystallization time, the sample is maintained at T_c up to 5 h (stage D). After stage D the sample is heated at 2°C min^{-1} to detect the melting point (stage E). In Fig. 2 a typical crystallization curve is reported. The mercury level H is reported versus the time t . In the figure two values, H_∞ and H_0 , are indicated; H_∞ and H_0 are the mercury levels detected at the final equilibrium and at the initial stage of the experiment (obtained using an extrapolation method). The curve refers to $T_c = 50^\circ\text{C}$. In Fig. 3 a melting plot is reported as H vs. T ; the curve refers to a sample crystallized at 40°C and covers heating from 40°C to the melting. As shown in Fig. 3, it is possible to measure a lower melting point (point A) and an upper melting point (point B), and therefore a melting range. Moreover, the extrapolation of the two straight lines to 25°C gives the mercury level for a hypothetical sample which is completely amorphous (point l), and for the actual crystallized sample (point s). Since the mass of polymer in the cell is known, the changes of polymer volume and density can be easily obtained from the difference in the level of mercury. Assuming the density of amorphous polypropylene as 0.856 g cm^{-3} at 25°C [6], the density of the crystallized sample can be derived. It is well known that, from the density, a mass crystallinity can be calculated as

$$x_c = d_c(d - d_a) / d(d_c - d_a)$$

where d_a and d_c are the densities of completely amorphous and completely crystalline samples, and d is the density of the analyzed sample. As reported, $d_a = 0.856\text{ g cm}^{-3}$, while $d_c = 0.946\text{ g cm}^{-3}$ for the γ form [6].

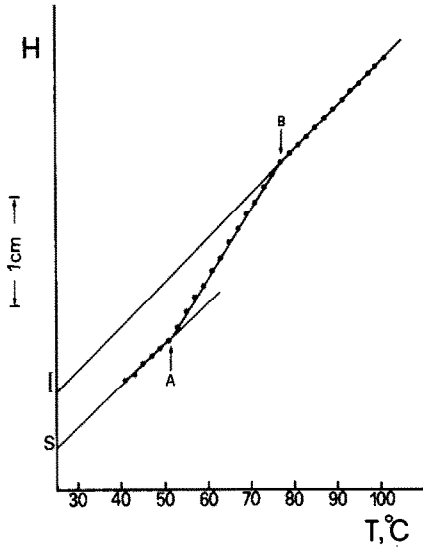


Fig. 3. Melting curve obtained by heating at 2° min^{-1} . A and B refer to the lower and upper melting; l and s indicate the extrapolated values for liquid and solid polymer respectively.

Therefore, from each experiment performed according to Fig. 1, it is possible to obtain the crystallization kinetics, the lower and upper melting points and the crystallinity.

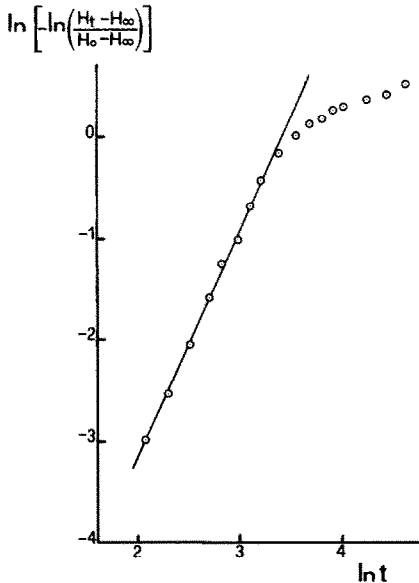


Fig. 4. Avrami plot relative to the crystallization detected at 50°C .

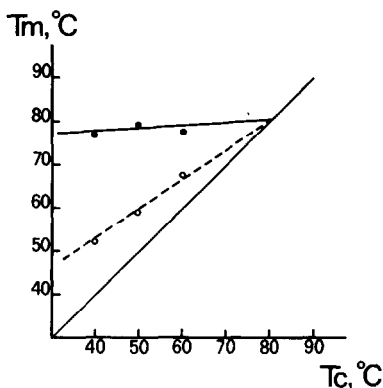


Fig. 5. Hoffmann and Week plot. The melting temperature is reported versus the crystallization temperature. (○) Lower melting; (●) upper melting.

In Fig. 4 an Avrami plot [7] is reported, which also refers to the crystallization at 50°C shown in Fig. 2. The function

$$\ln[-\ln(H_t - H_\infty)/(H_0 - H_\infty)]$$

is plotted versus $\ln t$. H_t is the mercury level at time t , while H_0 and H_∞ are defined in Fig. 2. The slope of the straight line gives n , the Avrami coefficient [7], and the obtained values are $n = 2.04$, 2.14 and 2.15 at $T_c = 40^\circ$, 50° and 60° C respectively. It is important to note that n was also obtained after reducing the temperatures of stage A (see Fig. 1) to 95 and 85°C and crystallizing at 50°C; the values calculated for n were 1.10 and 0.41 respectively. In Fig. 5 the lower and upper melting points are reported versus the crystallization temperature, according to the Hoffmann and Week method [8]. The melting temperature T_m extrapolated to the condition $T_m = T_c$ is 81°C for both cases. The calculated crystallinity is 14.8, 4.9 and 5.1% at $T_c = 40^\circ$, 50° and 60° C respectively.

DISCUSSION

The obtained results can be explained by considering the microstructure of the analyzed system, characterized by a block-like distribution of stereoregular sequences. The average length of the sequences is of the order of a few monomer units [1]. The change of absolute configuration which interrupts each block is a steric defect hindering the crystallization process and the growth of thick crystals, as suggested in a previous paper [3]. The current theories on polymer crystallization [9] directly relate the melting temperature T_m to the crystal thickness $\langle l \rangle$. Quantitative relationships of T_m versus $\langle l \rangle$ are available, albeit with some restrictions and approximations. Such a correlation has been recently described [10] for an elastomeric isotactic

polypropylene obtained using a different stereospecific catalyst. On this basis one can consider the data in Fig. 5, where the lower and the upper melting are reported as a function of the crystallization temperature. As predicted by the Hoffmann and Week theory [8], the melting temperature increases on increasing T_c ; the effect, which is significant for the lower melting point, is very weak for the upper one. The visible consequence is a restriction of the melting range, which is about 25 degrees for $T_c = 40^\circ\text{C}$ and drops to 10 degrees for $T_c = 60^\circ\text{C}$. The amplitude of the melting range is a measure of the distribution of crystal dimensions. At the lower temperature, the melting of smaller crystals occurs, and Fig. 5 indicates that the fraction of smaller crystals decreases on increasing T_c ; however, this expected phenomenon does not affect the upper limit of the melting range which, as observed, is practically constant on increasing T_c . This limit is the consequence of the microstructural limit related to the maximum length of the stereoregular sequences. The crystallization temperature dictates the sequences able to crystallize and, as T_c increases, the shorter sequences are excluded from the crystallization process. Therefore, on increasing T_c , the population of the sequences able to crystallize decreases and the crystallinity decreases, as observed. The crystallinity, which is $\approx 14\%$ for $T_c = 40^\circ\text{C}$, drops to $\approx 5\%$ for $T_c = 60^\circ\text{C}$. Also the melting temperature obtained by extrapolating to the condition $T_m = T_c$ reflects the microstructure of the analyzed system. This upper limit can be assumed as the melting point of crystals having dimensions determined by the maximum observable length of stereoregular sequences. One can try to calculate this thickness limit. The following equation [9]

$$T_m = T_m^0(1 - 2\sigma_e/\langle l \rangle \Delta H_m^0)$$

gives T_m as a function of the crystal thickness $\langle l \rangle$. Considering the upper limit 81°C , and giving to σ_e , ΔH_m^0 and T_m^0 the values 100 mJ m^{-2} , 154 MJ m^{-3} and 460.7 K respectively, as reported by Wunderlich and co-workers [11], one obtains $\langle l \rangle = 5.6 \text{ nm}$. Since the repeat distance along the polypropylene helix is 0.65 nm per three monomer units [6], one obtains 26 units contained in the thickest crystal allowed by the chain microstructure. This is too high for the analyzed system [1]. Considering the average melting temperature given by the maximum of the melting endotherm obtained by differential thermal analysis, 60°C [3], the obtained $\langle l \rangle$ value is 4.7 nm , corresponding to ≈ 21 units, which is still too high. However, one must consider that σ_e refers to chain folding surfaces, and the used thermodynamic parameters ΔH_m^0 and T_m^0 refer to the α form. In the analysed system chain folding is improbable [3], and the observed crystalline form is the γ form [3], for which precise ΔH_m^0 and T_m^0 values are not reported. Particularly relevant is the aspect regarding chain folding; in fact, in the absence of folding surfaces, 100 mJ m^{-2} largely overestimates the actual surface energy. It is known that in lamellar crystals the energy of the lateral surfaces is

about 5 mJ m^{-2} . In the analyzed system the energy is probably intermediate between these two values. It is interesting to note that, assuming σ_c of the order of 30 mJ m^{-2} , one obtains about eight units along the crystal thickness as the upper limit. This limit agrees well with the chain microstructure [1], and 30 mJ m^{-2} can be a reasonable estimate of the actual average surface energy. However, one can conclude that the calculated number of monomer units along the crystal thickness must be considered as approximate, but that the obtained results do not disagree with the model. Further support to the model can be found in the kinetic data. The Avrami coefficient excludes a tridimensional crystal growing as suggested in the previous paper [3]. For $n = 2$ a fibrillar or ribbon-like growth with thermal nucleation can be suggested [7]. The presence of thermal nucleation seems to be confirmed by the values of n observed on decreasing the temperature of stage A (see Fig. 1). A linear or bidimensional growth model is the natural consequence of the chain microstructure, which does not allow the growing of complex morphological units, such as spherulites or circular lamellae.

To conclude, one can observe that the obtained results give a satisfactory picture of the relationships between chain microstructure and the morphological organization as deducible from the thermal behaviour.

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