Syndiotactic polystyrene: crystallization and melting behaviour

Sossio Cimmino, Emilia Di Pace, Ezio Martuscelli* and Clara Silvestre
Istituto di Ricerche su Tecnologia dei Polimeri e Reologia CNR, Via Toiano 6,
80072 Arco Felice, Napoli, Italy
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The results of an investigation into the isothermal crystallization and thermal behaviour of syndiotactic polystyrene (sPS) are reported. The study was carried out using differential scanning calorimetry, optical microscopy and dilatometry. From the melt, sPS crystallizes according to a spherulite morphology. The spherulite growth rate and overall crystallization rate depend on crystallization temperature and sample preparation. During the crystallization process, segregation of impurities and non-crystallizable molecules at the spherulite growth front was observed. The nucleation rate, probably very fast, hindered the determination of crystallization kinetic parameters for some crystallization temperatures. Comparing the melt crystallization process of sPS with that of isotactic polystyrene (iPS) for the same value of undercooling, sPS crystallizes more rapidly than iPS, indicating the influence of the tacticity of the materials on the crystallization process. The equilibrium melting temperature T_m° was determined and found to be 275°C.

(Keywords: syndiotactic polystyrene; crystallization; melting behaviour)

INTRODUCTION

After success in the stereospecific polymerization of syndiotactic polystyrene (sPS)[1–4] with high degree of stereoregularity, some papers have been published on the structural characterization and properties of this new material[5–8].

Ishihara *et al.*[1] suggested a zig-zag planar structure for crystalline sPS. Guerra *et al.*[5,6] completed the structural analysis, indicating complex polymorphism phenomena for sPS. In fact, depending on the crystallization conditions, four crystalline forms have been obtained. For the samples crystallized from the melt, in particular, two zig-zag planar structures can be obtained (α-form and β-form). The ratio between these two forms is mainly influenced by the premelting temperature, the premelting time and the cooling rate from the premelting temperature to the crystallization temperature. Vittoria *et al.*[7,8] found that some solvents, such as dichloromethane, chloroform and cyclohexane, induce new crystalline forms in fibres, modifying the initial zig-zag planar structure of the chain into helical structures without destroying the orientation of the fibres. The same solvents were found to induce crystallization in glassy sPS. Very recently Greis *et al.*[4] completed the structural characterization, indicating that three sPS macromolecules form clusters of two types of handedness. These clusters, depending on the crystallization rate, can organize in well pronounced superstructures. They reported that the morphology is also dependent on the crystallization conditions. In fact, lamellar crystals were observed to grow from amorphous films annealed for 5 min at 200°C, whereas spherulites occurred for crystallization at lower temperatures. In the case of drawn films, shish-kebab structures were seen.

Syndiotactic polystyrene seems to crystallize very rapidly[4], but so far no precise data have been reported on the kinetics of crystallization and melting behaviour of this polymer.

It is the purpose of this paper to present results on the bulk crystallization from the melt and the glass phase, on the spherulite radial growth rate, as well as the melting behaviour and the morphology of sPS samples, and to compare, where possible, these data with those relative to isotactic polystyrene (iPS), obtained previously by some of us[9].

EXPERIMENTAL

Syndiotactic polystyrene was synthesized by Zambelli *et al.*, using a homogeneous catalyst consisting of a soluble titanium compound[2,3]. The average molecular weights were[10]: $\bar{M}_w = 7.1 \times 10^5$ g mol^{-1}; $\bar{M}_n = 2.3 \times 10^5$ g mol^{-1}.

Thin films of sPS were obtained by pressing the material at 340°C for 5 min and quickly cooling.

Isothermal crystallization and measurements of the radial growth rate of sPS spherulites were investigated using an optical polarizing microscope fitted with an automated hot stage.

The following procedure was utilized: the films were sandwiched between a microscope slide and a cover glass heated at 300°C and kept for 15 min at this temperature. Then the temperature was rapidly lowered to the pre-fixed crystallization temperature (T_c) and the sample allowed to crystallize. The radial growth of an sPS spherulite was monitored during crystallization, taking photomicrographs at appropriate time intervals, t. From the slope of the lines, obtained by plotting radius against time, the spherulite radial growth rate G was derived for any crystallization temperature investigated (238–257°C).

After crystallization, the samples were heated up at 3 K min^{-1}, until birefringence patterns disappeared. The corresponding temperature was taken as the observed optical melting point of sPS (T'_m).

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* To whom correspondence should be addressed

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The overall kinetics of crystallization and the thermal properties of sPS sample were analysed by differential scanning calorimetry (Mettler TA 3000).

The isothermal crystallization process was studied using two different procedures: (1) The samples were heated up from room temperature to 340°C, kept at this temperature for 10 min under nitrogen and rapidly cooled to the desired crystallization temperature, T_c. (2) The samples were heated up from room temperature to the crystallization temperature, T_c.

The samples were allowed to crystallize at T_c independently of thermal treatment. The heat evolved during the isothermal crystallization was recorded as a function of time.

The weight fraction of the material crystallized at time t, X_t, was determined by the relation:

$$X_t = \frac{\int_0^t (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t}{\int_0^\infty (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t} \qquad (1)$$

where the first integral is the heat generated at time t and the second is the total heat generated up to the end of the crystallization process.

RESULTS AND DISCUSSION

Spherulite radial growth rate

Syndiotactic polystyrene crystallizes from the melt according to a spherulite morphology (see *Figure 1*). The dimensions of the spherulites are very sensitive to the moulding temperature and time. For samples obtained as described in the 'Experimental' section, the radius of the spherulites at the end of the crystallization process ranges between 30 and 80 μm.

In *Figure 2* the variation of the spherulite radius with time is reported for different crystallization temperatures. For any T_c it is evident that the experimental points are aligned on straight lines only for crystallization times that are not very long. This result can be explained by assuming that, during crystallization, the impurities present in the material are rejected outside the borders of the growing crystals, and their concentration increases with time, in agreement with Keith and Padden[11]. Depending on T_c and nucleation rate, there will be a time after which the concentration of impurities is high enough to influence, in a detectable way, the spherulite growth rate, disturbing the transport in the melt of the crystallizable molecules to the spherulites. From the slopes of the straight lines at short crystallization times, the spherulite growth rate G has been calculated. The plot of G as a function of crystallization temperature is reported in *Figure 3*. Note that, owing to the high nucleation rate, it was impossible experimentally to obtain G for T_c lower than 238°C. In the range of T_c studied, G decreases exponentially with crystallization temperature, indicating that, according to the kinetic theory of polymer crystallization, the phenomenon controlling crystallization is mainly the formation of nuclei of a critical size.

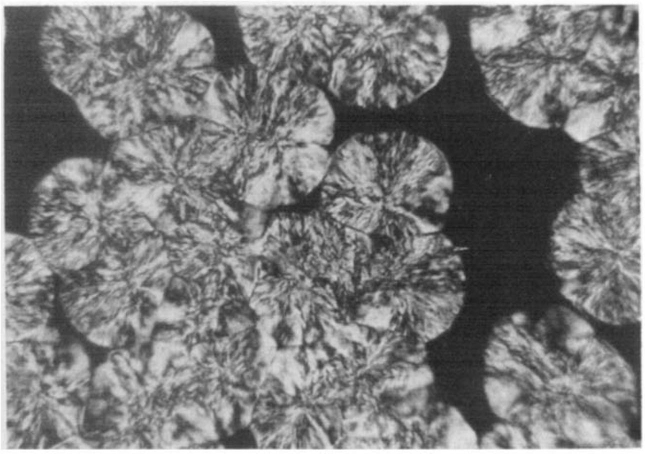

Figure 1 Optical micrograph (crossed polars) of sPS spherulites crystallized at 250°C

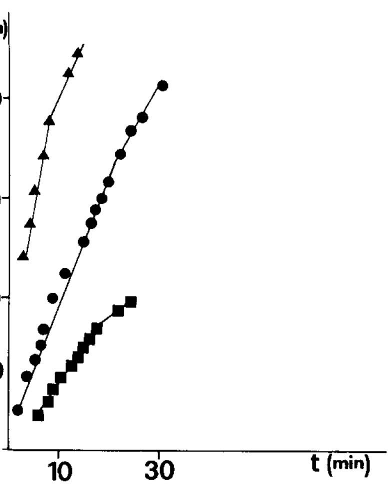

Figure 2 Radius r of spherulite as a function of time t for different crystallization temperatures T_c. T_c = 240 (▲), 248 (●) and 250°C (■)

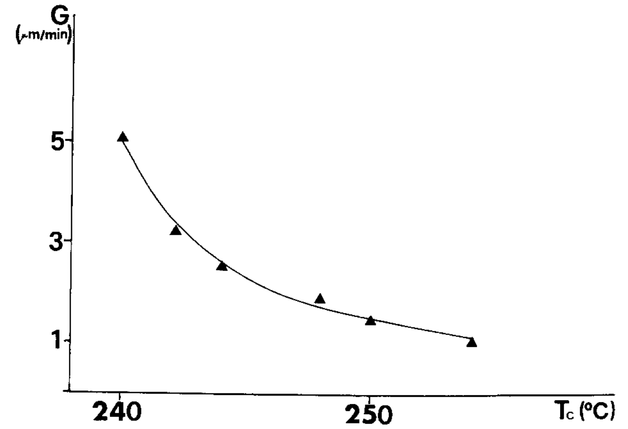

Figure 3 Spherulite growth rate G *versus* crystallization temperature T_c

Comparing the values of G for sPS with those for iPS[9] at the same undercooling ($T_m^\circ - T_c$) (see *Table 1*), it is possible to note that the spherulite growth rate in sPS is more than one order of magnitude higher than in iPS. Because the two samples present the same value of T_g[12] and both are of high molecular weight, this result could indicate that the tacticity of a polymer greatly influences its crystallization process.

Bulk crystallization

Typical crystallization isotherms obtained by plotting X_t *versus* time are shown in *Figure 4* for samples crystallized isothermally from the melt and the glass state. From these curves the half-time of crystallization $\tau_{1/2}$, defined as the time required for half of the final crystallinity to develop, was obtained. The variation of

Table 1 Spherulite growth rate G for iPS and sPS for the same undercooling ΔT

	G (μm min^{-1})	
ΔT (°C)	iPS	sPS
35	6.0×10^{-2}	5.0
25	4.5×10^{-2}	1.8

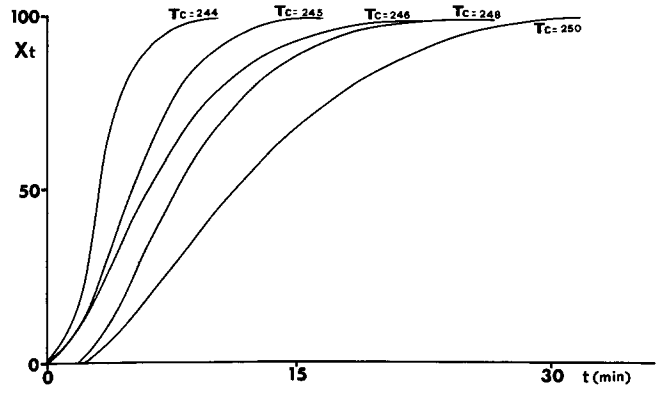

Figure 4 Crystallization isotherms of sPS crystallized at different crystallization temperatures

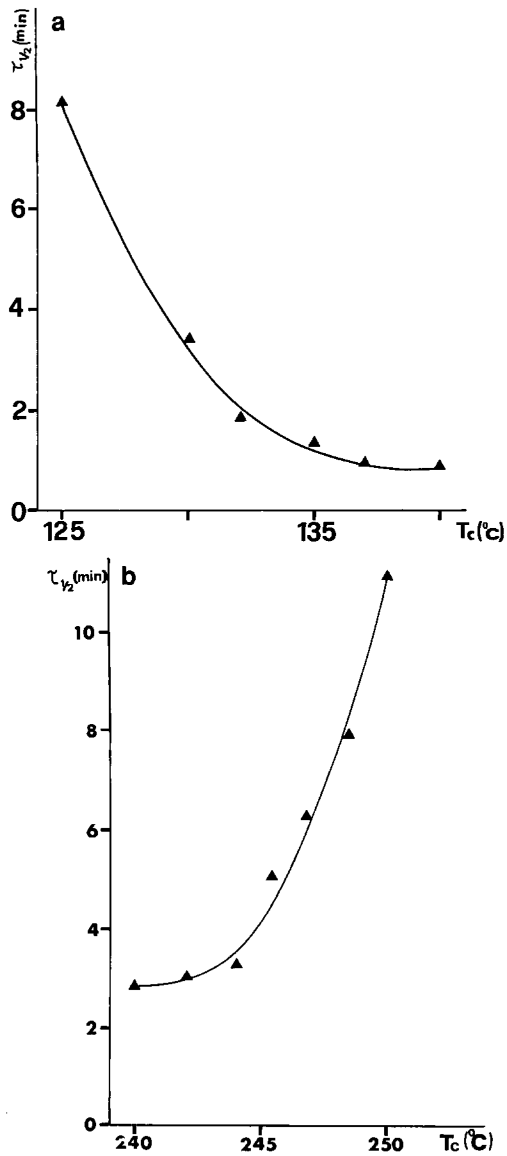

Figure 5 Half-time of crystallization $\tau_{1/2}$ as a function of T_c for samples crystallized from (a) the glass and (b) the melt state

$\tau_{1/2}$ with temperature is reported for samples crystallized from the glass in *Figure 5a* and from the melt state in *Figure 5b*. From these figures it is evident that $\tau_{1/2}$ is strongly dependent on temperature. For temperatures between 140 and 240°C, it was impossible to follow the crystallization process isothermally, because of the high nucleation rate presented by the material.

The bulk kinetics of crystallization of sPS were analysed using the Avrami[13] treatment for the kinetics of phase changes. The Avrami equation is written:

$$\log[-\ln(1-X_t)] = \log K_n + n\log(t-t_i) \qquad (2)$$

where n is the Avrami exponent, K is the kinetic rate constant and $(t-t_i)$ is the time of crystallization (t_i is the induction time of nucleation). Both K and n depend on the nucleation and growth mechanism of the crystals.

The experimental data appear to fit the Avrami equation (see *Figure 6*), as for any T_c plots of $\log[-\ln(1-X_t)]$ *versus* $\log(t-t_i)$ are also linear for long crystallization times, indicating that secondary crystallization can be excluded.

The values of n determined from the slopes of the above-mentioned straight lines are in almost all cases non-integer and range between 2 and 3. This result indicates that, during the crystallization process, mixed growth and nucleation mechanisms can occur. Studies are in progress on this subject in order to analyse the nucleation process (rate and mechanism) of the material.

Melting behaviour

The variation of the observed melting temperature with the crystallization temperature is shown in *Figure 7*. In the range of T_c explored, the T'_m of sPS increases almost linearly with T_c according to the Hoffmann equation[14]:

$$T'_m = (1/\gamma)T_c + (1-1/\gamma)T^\circ_m \qquad (3)$$

where T°_m is the equilibrium melting temperature and $\gamma = l/l^*$ is the ratio of the lamellar thickness l to the thickness l^* of the critical nuclei at T_c.

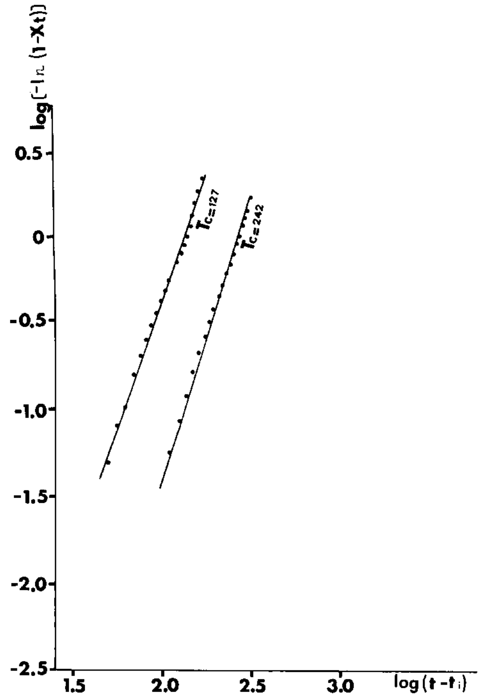

Figure 6 Avrami plots for sPS at different crystallization temperatures

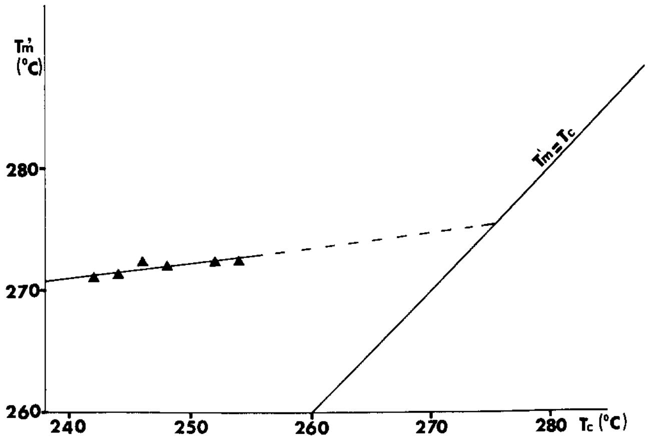

Figure 7 Observed melting temperature *versus* crystallization temperature

According to equation (3) the equilibrium melting temperature can be determined from a plot of T'_m *versus* T_c. Then T°_m is the intercept of the extrapolated T'_m values with the line defined by $T'_m = T_c$. The value of T°_m obtained by this method is 275°C. This value is in very good agreement with that obtained very recently by Caselli and Ravanetti (274°C), using a calorimetric method[15].

CONCLUSIONS

We have characterized the melting behaviour and the crystallization kinetics as a function of crystallization temperature and sample preparation of the novel polymer, syndiotactic polystyrene (sPS). At the end of crystallization the sample is filled with spherulites whose dimension ranges between 30 and 80 μm. The results on the crystallization rate, compared with those obtained by some of us on isotactic polystyrene (iPS), indicates that the crystallization rate of sPS is higher than that of iPS, leading to the conclusion that the configuration of the polymers is one of the parameters to take into account in the definition of the crystallization process.

The Avrami treatment of the experimental data seems to indicate mixed growth and nucleation mechanisms.

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