Non-isothermal crystallization kinetics of poly(*p*-phenylene sulphide)

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The non-isothermal crystallization kinetics of poly(*p*-phenylene sulphide) (PPS) were studied. Linear PPS of selected molecular weights and branched PPS were investigated. The theory of Ozawa for non-isothermal crystallization was used to analyse the differential scanning calorimetry data. All the samples studied followed this theory and allowed the calculation of the Avrami exponent under non-isothermal conditions. The values of the Avrami exponent determined by the Ozawa equation were in good agreement with our earlier reported values obtained by means of isothermal methods.

(Keywords: crystallization; kinetics; non-isothermal; Ozawa; poly(*p*-phenylene sulphide))

INTRODUCTION

In previous reports, the crystallization behaviour of PPS was studied by isothermal methods. The effects of molecular weight, branching agent content and chemical nature of the end group counter-atom on the kinetic parameters were studied by means of the Avrami equation and crystal growth rates[1,2]. However, from a technological point of view, the non-isothermal crystallization behaviour of polymers is of great importance because most of the processing techniques occur under non-isothermal conditions. In addition, isothermal measurements are often restricted to narrow temperature ranges because the response time of the measuring instrument becomes comparable to the overall time for crystallization. Consequently, non-isothermal experiments can be complementary to the understanding of the crystallization behaviour of polymers. Therefore, this manuscript will address the study of the non-isothermal crystallization of PPS, to complement the isothermal data discussed in previous publications[1,2]. We discuss the different methods available to study the non-isothermal crystallization of polymers so that we can stress the criteria for the selection of the method utilized in the present report. Following this discussion, the kinetic parameters of PPS will be determined by a non-isothermal method and compared with those obtained by the more conventional isothermal techniques.

METHODS

Only a few methods have been developed to study the kinetics of non-isothermal crystallization[3–5]. The theory of those pertinent to this study will be briefly reviewed here. The first to be discussed is the theory of Ziabicki[3] which assumes that the crystallization of polymers can be represented by first order kinetics,

$$\frac{dx}{dt} = (1-x)K(T) \tag{1}$$

where x represents the normalized crystalline content and $K(T)$ is a rate constant dependent on temperature. Furthermore, it is assumed that the shape of plots of rate constant *versus* temperature is represented by a Gaussian function[6]. These assumptions allow the calculation of C, a parameter known as the kinetic crystallizability,

$$C = \int_{T_g}^{T_m} K(T)\,dT = (\pi/\ln 2)^{1/2} K_{max} D/2 \tag{2}$$

where K_{max} is the value of K corresponding to the maximum of the crystallization exotherm, D is the width of the crystallization exotherm at half height, and T_m and T_g have the usual meaning. The kinetic crystallizability characterizes the degree of crystallization per unit cooling rate obtained over the crystallization range $T_m - T_g$. Consequently, it characterizes the kinetics of non-isothermal crystallization. The parameter C would then serve as a comparative measure of the crystallizability of various materials when non-isothermal crystallization occurs. In particular, the higher C is, the larger the degree of crystallinity is at the same cooling rate. Moreover, the higher C is, the higher is the cooling rate necessary to quench a melt to the glassy state without appreciable crystallization in the course of cooling. As examples, Ziabicki[3] indicated that polymers such as isotactic polystyrene with $C = 0.15$ and poly(ethylene terephthalate) (PET) with $C = 0.53–1.0$ can only crystallize upon slow cooling. However, polymers such as nylon 6,6 with $C = 133$ and isotactic polypropylene with $C = 33$ can still crystallize upon rapid cooling. This theory was utilized by others to study the non-isothermal crystallization of PET by differential scanning calorimetry (d.s.c.)[6], and to investigate the crystallization of PET/polycarbonate (PC) blends[7]. However, the kinetic crystallizability does not allow a direct comparison with kinetic parameters determined by other more conventional methods. Therefore, this method was not used in the present study.

Harnisch and Muschik[4] developed a method to determine the Avrami exponent from non-isothermal

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d.s.c. experiments. The method derives from the well known Avrami equation,

$$X(t)=1-\exp(-Kt^{n}) \qquad (3)$$

where $X(t)$ is the crystalline fraction, K is a rate constant dependent on temperature, and n is the Avrami exponent. By rearranging the Avrami equation, and assuming the enthalpy of the transformation is independent of temperature, Harnisch and Muschik[4] derived the following equation to determine the Avrami exponent,

$$n=1+\left(\ln\frac{\dot{x}_1}{1-x_1}-\ln\frac{\dot{x}_2}{1-x_2}\right)\Big/\ln(\phi_2/\phi_1) \qquad (4)$$

at $T=T_c$, where $x_i(T)$ is calculated by integrating partial areas of the d.s.c. exotherm, $\dot{x}_i(t)$, the derivative of x, represents the $\mathrm{d}H/\mathrm{d}T$ value of the exothermic curve, and ϕ_i's are the heating or cooling rates used in the experiments. This equation has been successfully used to determine n in polyethylene and polypropylene. Their values compared well with those determined isothermally[4,8]. However, the method presents some possible limitations. The Avrami equation must be applicable and the enthalpy of the transformation must be independent of temperature in the temperature range of analysis. In addition, the heat of fusion of the polymer needs to be known to correct the values of x, because polymers are not 100% crystalline. This last limitation precluded the use of this method for PPS because the heat of fusion of 100% crystalline PPS has not been determined.

A third and rather simple method to determine the Avrami exponent from non-isothermal d.s.c. experiments was developed by Ozawa[5] as an extension of the theory of Evans for isothermal crystallization[9]. The Ozawa model assumes that crystallization occurs under a constant cooling rate ϕ, and that crystallization originates from a distribution of nuclei that grow as spherulites with constant radial growth rate at a given temperature. Through these assumptions, Ozawa derived an expression for the volume fraction of untransformed material,

$$\begin{aligned}&1-x(T)\\&\quad=\exp\left\{-\frac{4\pi}{\phi^3}\int_{T^0_m}^{T}N(\theta)[U(T)-U(\theta)]^2G(\theta)\,\mathrm{d}(\theta)\right\} \qquad (5)\end{aligned}$$

where $x(T)$ is the volume fraction of growing spherulites at temperature T, ϕ is the constant cooling rate, $N(\theta)$ is the nucleation density, i.e. the number of nuclei per unit volume activated between temperatures T^0_m and θ, T^0_m is the equilibrium melting temperature, $G(\theta)$ is the spherulite radial growth rate and $U(T)$ is a function of $G(\theta)$, $U(T)=\int_{T^0_m}^{T}G(\theta)\,\mathrm{d}\theta$. Amongst other terms, equation (5) depends on the type of nucleation that takes place during crystallization. Therefore, *instantaneous* nucleation and nucleation *sporadic* in time have to be considered. In the former case, the nucleation density $N(\theta)$ is independent of time, and equation (5) only depends on the temperature θ. Consequently, $N(\theta)$ is independent of the cooling rate ϕ. Taking the logarithm on both sides of equation (5) two times at a constant temperature, it follows that

$$\ln\{-\ln[1-x(T)]\}=\chi_{\mathrm{inst}}-3\ln|\phi| \qquad (6)$$

where the constant χ_{inst}, called the cooling crystallization function, is defined as

$$\ln 4\pi+\ln\left|\int_{T^0_m}^{T}N(\theta)[U(T)-U(\theta)]^2G(\theta)\,\mathrm{d}\theta\right|$$

For *sporadic* nucleation, the nucleation density, $N(\theta)$, is a function of time and temperature. As a consequence, $N(\theta)$ has to be assumed to follow a predetermined function of time. For example, $N(\theta)$ is usually assumed to be proportional to time, i.e. the nuclei appear at a constant rate per unit volume, $\dot{N}(\theta)$. If this is the case, at a given temperature, equation (5) can be written as

$$\ln\{-\ln[1-x(t)]\}=\chi_{\mathrm{spor}}-4\ln|\phi| \qquad (7)$$

defining χ_{spor} as

$$\ln 4\pi+\ln\left|\int_{T^0_m}^{T}\left[\int_{T^0_m}^{\theta}\dot{N}(u)\,\mathrm{d}u\right][U(T)-U(\theta)]^2G(\theta)\,\mathrm{d}\theta\right|$$

In a general form, equations (6) and (7) can be written as follows

$$\ln\{-\ln[1-x(t)]\}=\chi-n\ln|\phi| \qquad (8)$$

at $T=$ constant, where n represents the well known Avrami exponent and x represents the cooling crystallizatin function. Consequently, equation (8) allows the determination of the Avrami exponent in terms of the cooling rate and the fraction of crystallized material.

Two factors were neglected by Ozawa in the derivation of equation (8). The slow secondary (post-Avrami) crystallization was not considered. This can lower the values of the Avrami exponent determined. However, because the crystallization process occurs under non-isothermal conditions, the slow secondary crystallization would be virtually nonexistent as the temperature decreases. The other factor disregarded in equation (8) is the fold length of the polymer chain.

The fold length is a function of the crystallization temperature. If changes in fold length depend upon the temperature during dynamic crystallization, then, the fold length should be considered in the derivation of equation (8). In most instances, this factor does not seem to have a noticeable effect. Ozawa[5] used this equation to study the non-isothermal crystallization of PET. He found that PET followed equation (8) and the values of n were in agreement with those obtained isothermally. Polypropylene also followed the Ozawa equation over the cooling rate range of 0.5°C/min to 10°C/min (ref. 10). The Avrami exponents found seemed to be in fair agreement with values determined isothermally. Eders and Wlochowicz[10] also reported that the cooling crystallization function (χ) followed an exponential function of temperature. However, Monasse *et al.*[11,12] observed that the Avrami exponent of polypropylene was a function of temperature. These authors reported that n decreased from 4 at 107–116°C to about 3 at 122–129°C, with intermediate values in the 116–122°C temperature range. This variation of n was attributed to a change in the nucleation behaviour. At low temperatures, nucleation was sporadic in time, whereas at high temperatures, nucleation was instantaneous. Optical microscopy confirmed this hypothesis[11,12]. The Ozawa equation has been also used to study the non-isothermal crystallization of polyamide 6 from the glassy state[13]. The crystallization process of polyamide 6 seemed to follow the Ozawa equation, i.e. straight lines were obtained when $\ln\{-\ln[1-x(t)]\}$ was plotted as a function of $\ln|\phi|$. The Avrami exponent, however, decreased continuously from 1.8 to 0.5 over the narrow temperature range from 56°C to 66°C.

Contrary to all the cases presented, equation (8) did not conform to non-isothermal crystallization data of polyethylene[10]. Eder and Wlochowicz[10] attributed the deviation from the Ozawa equation to factors such as secondary crystallization, dependence of lamellar thickness on crystallization temperature, and occurrence of both sporadic and predetermined nucleation. However, it is worth commenting again that secondary crystallization would not be expected to be an important factor in the non-isothermal crystallization of PPS, it was observed that secondary crystallization did not have an important contribution to the crystallinity of PPS[1]. Similarly, the occurrence of sporadic and predetermined nucleation would not affect the validity of Ozawa's equation. It would only affect the value of the Avrami exponent.

Due to the simplicity of the method of Ozawa to analyse the non-isothermal data, and the ease of comparison of the parameters obtained with those determined from isothermal experiments, equation (8) was used to analyse the non-isothermal crystallization of PPS.

EXPERIMENTAL

The materials used in this study comprised PPS with various molecular weights and branching agent content, as listed in *Table 1*. The results obtained for these samples can be directly compared with the values determined from isothermal experiments[1,2].

A Perkin Elmer DSC-4 was used for the thermal treatment and data gathering. The sample crystallizations were performed at constant cooling rate after being held in the molten state at 320°C for 4 min. As discussed before[1,2], the short residence time in the melt was used to avoid curing reactions. The crystallization exotherms were recorded at selected cooling rates: 2.5, 10, 15, 20, 25, 30, 35, 40°C/min.

RESULTS AND DISCUSSION

Due to the non-isothermal nature of the experiments, the temperature scale must consider a correction for the temperature lag existing between the sample and the calorimeter furnace. This temperature lag comprises the thermal gradient inside the sample and the temperature lag between the bottom of the sample and the calorimeter furnace. The former term was previously calculated for a 0.3 mm thick polypropylene sample during an 80°C/min cooling by Monasse and Haudin[12]. These authors estimated a 1°C maximum thermal gradient under those conditions. Assuming that a similar value would be obtained for PPS, and comparing it with the measured temperature lag between sample bottom and calorimeter furnace (10.8°C), the thermal gradient inside the sample can be neglected. Therefore, a temperature calibration as a function of cooling rate is required. This was achieved by calibrating the d.s.c. with an indium standard at various scanning rates.

Table 1 Characteristics of samples used to study the non-isothermal crystallization kinetics of PPS. The polydispersity ratio is in the order of 1.4–1.7. The values were measured by g.p.c. in α-chloronaphthalene at 210°C. These values seem low for PPS if synthesized by a step growth polymerization reaction that would lead to a polydispersity ratio of 2[14].

Sample designation	$\langle M_w \rangle$	Branching agent content
PPS24	24 000	none
PPS49	49 000	none
PPS63	63 000	none
PPS13	75 000	low level
PPS20	65 000	high level

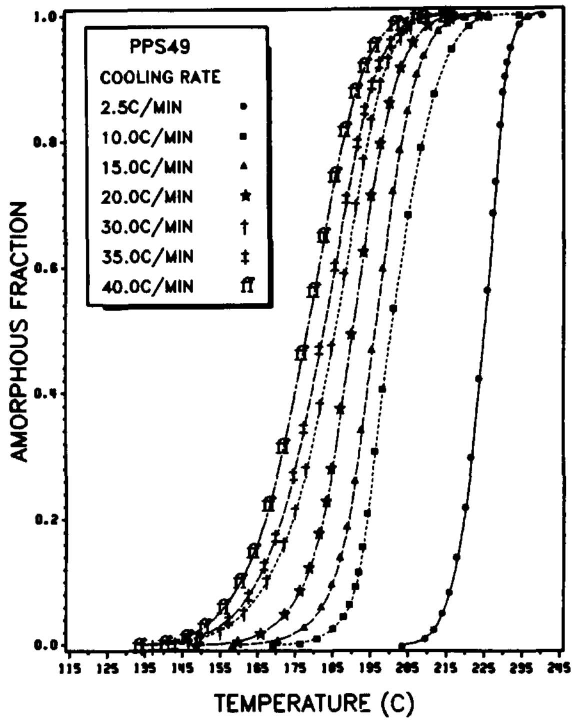

Figure 1 Plot of amorphous fraction as a function of temperature for PPS49 crystallized non-isothermally at various cooling rates

The data treatment, then, involves calculating $x(T)$ from the measurement of partial areas of the exotherms obtained upon cooling crystallization. In addition, the partial areas are normalized by specimen mass and cooling rate to allow comparison between the different curves. The calculated amorphous fraction $[1 - x(T)]$ is plotted as a function of temperature for the different cooling rates as shown in *Figure 1* for PPS49. Values of the amorphous fraction at a given temperature are taken from these plots at each cooling rate. Then, the double logarithm of the amorphous fraction $\ln\{-\ln[1 - x(t)]\}$ at constant temperature is plotted as a function of the cooling rate. If equation (8) is valid, the curve corresponding to each temperature should be a straight line. The slope provides the Avrami exponent and the intercept determines the value of the cooling crystallization function.

Figure 1 presents plots of the amorphous fraction as a function of temperature for PPS49 crystallized non-isothermally at various cooling rates. The effect of the different cooling rates is observed in these plots corresponding to PPS49. The higher the cooling rate, the lower the temperature range at which the crystallization occurs. At each cooling rate, crystallization takes place at temperatures above the point of maximum crystallization rate (~180°C). Therefore, the transformation is controlled by nucleation. At slow cooling rates, there is sufficient time to activate nuclei at higher temperatures. On the contrary, at faster cooling rates, the activation of nuclei occurs at lower temperatures. Consequently, crystallization nucleates at higher temperatures when the polymer samples are cooled at slower scanning rates. *Figure 1* also shows the limits of cooling rates used in this study. The lower limit is 2.5°C/min and the upper one is 40°C/min. The former is determined by the sensitivity of the differential scanning calorimeter utilized. At cooling rates lower than 2.5°C/min, the signal output presents noise due to a lower sensitivity of the calorimeter. Consequently, the data is not accurate. The upper limit is established by the limiting heat transfer. Analysing *Figure 1*, it is observed that the temperature gap between successive curves at different cooling rates decreases as the cooling rate increases. Crystallizations performed at higher cooling rates tend to occur at the same temperature range as those obtained at 40°C/min. This indicates that the higher cooling rates are not effective in lowering the temperature of the onset of crystallization. Another important characteristic of *Figure 1* is the shape of the curves. All the curves of amorphous fraction *versus* temperature have approximately the same shape. This would indicate that only the retardation effect of cooling rate on the crystallization is observed in these curves.

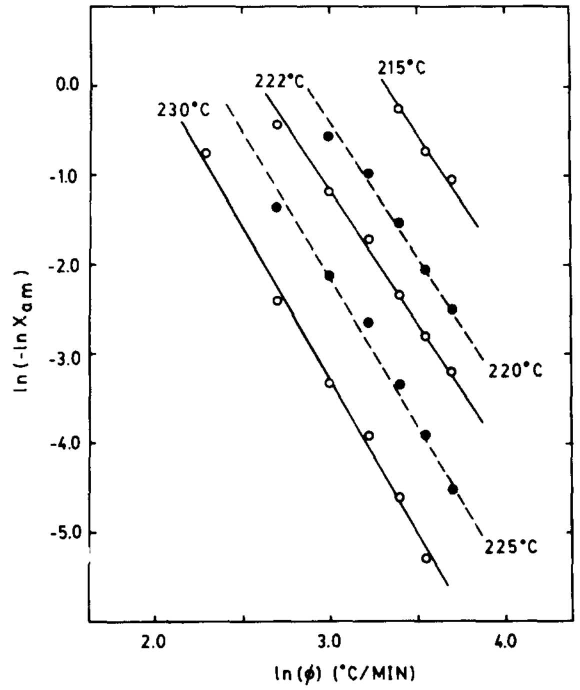

Figure 2 Plot of $\ln\{-\ln[1-x(t)]\}$ as a function of $\ln\phi$ at various temperatures corresponding to PPS24

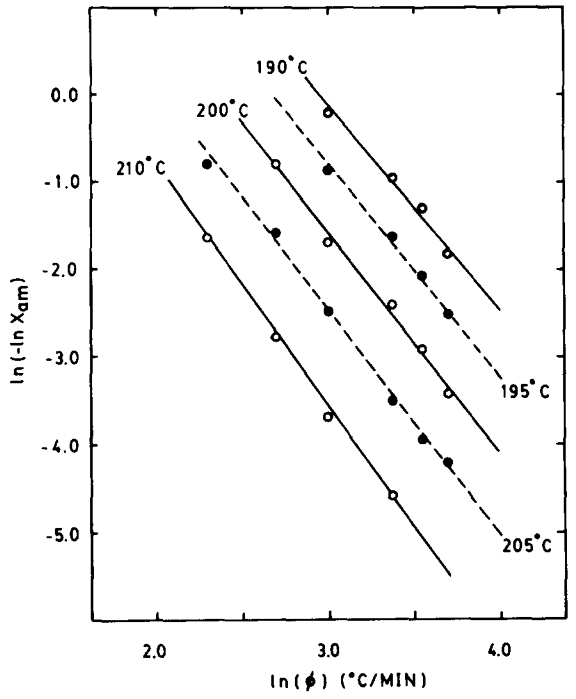

Figure 3 Plot of $\ln\{-\ln[1-x(t)]\}$ as a function of $\ln\phi$ at various temperatures corresponding to PPS49

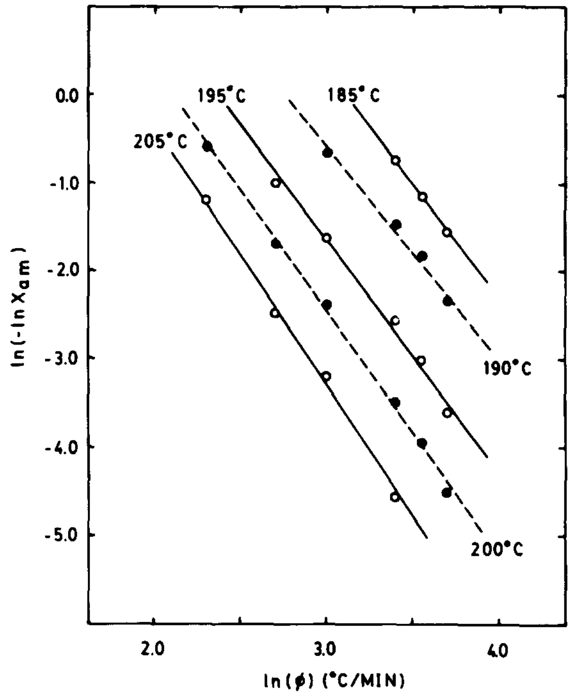

Figure 4 Plot of $\ln\{-\ln[1-x(t)]\}$ as a function of $\ln\phi$ at various temperatures corresponding to PPS63

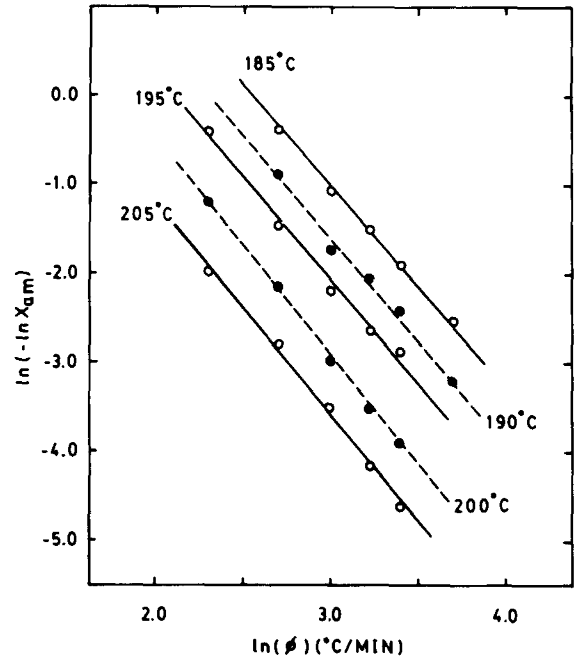

Figure 5 Plot of $\ln\{-\ln[1-x(t)]\}$ as a function of $\ln\phi$ at various temperatures corresponding to PPS13

Figures 2–6 present plots representative of the Ozawa equation (equation 8) for PPS24, PPS49, PPS63, PPS13, and PPS20; i.e. plots of $\ln\{-\ln[1-x(t)]\}$ as a function of $\ln|\phi|$ at constant temperature. If equation (8) is valid, the curve corresponding to each temperature should be a straight line. Indeed, *Figures 2–6* indicate a very good

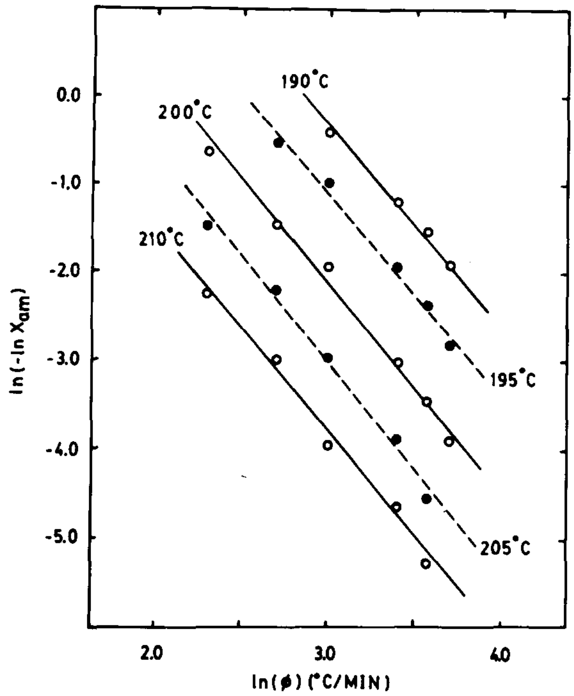

Figure 6 Plot of $\ln\{-\ln[1-x(t)]\}$ as a function of $\ln\phi$ at various temperatures corresponding to PPS20

agreement between the experimental results and the theoretical treatment of Ozawa[5]. In addition, it should be noted that branching does not affect the behaviour of PPS when it is crystallized non-isothermally. Samples PPS13 and PPS20 were synthesized containing the branching agent trichlorobenzene, which presumably introduces long-chain branches. The Ozawa plots corresponding to PPS13 and PPS20 are presented in *Figures 5* and *6*. It is noted that the plots are straight lines, following equation (8). The data corresponding to linear and branched PPS, then, conforms with the theoretical treatment of Ozawa[5]. Consequently, equation (8) can be used to calculate the Avrami exponents of non-isothermally crystallized PPS. As expressed above, the Avrami exponent is the slope of the $\ln\{-\ln[1-x(t)]\}$ *versus* $\ln|\phi|$ curve. The intercept of this straight line provides the cooling crystallization function. For the determination of the Avrami exponent, amorphous volume fractions higher than 0.5 were used. At lower fractions, the effect of impingement and truncation of spherulites can become very important. If impingement and truncation occur, the overall rate of crystallization is decreased and the mechanism of crystallization can change. Ultimately, the value of the Avrami exponent decreases. Therefore, using values of the amorphous fraction higher than 0.5 minimizes the problem mentioned. The values of the Avrami exponent determined by this method are plotted in *Figure 7* as functions of temperature. The Avrami exponent has values between 2.3 and 3.0. In the cases of PPS13 and PPS20, n is equal to 2.4 on average. This value is slightly lower than those obtained isothermally by the method of Avrami (3.0 and 2.8, respectively)[2]. PPS63 has a higher value of n, in the order of 2.8 on average, with no systematic variation with temperature. Furthermore, n is in very good agreement with that determined isothermally (3.0). However, the Avrami exponents determined for PPS24 and PPS49 present an increasing trend with temperature. This trend is more pronounced in PPS24. The Avrami exponent of PPS24 increases from 2.4 at 220°C to 3.0 at 230°C. This phenomenon was not observed when the crystallization of PPS24 was studied isothermally. The latter case showed an Avrami exponent of ≈ 2.5 that was attributed to the presence of sheaf-like superstructures that lower the value of n. These structures were presumed present due to the fast crystallization rate of PPS24 that did not allow their full development into spherulites. A possible explanation of the present experiment is that due to the non-isothermal nature of the experiment, the overall crystallization rate would increase as the temperature is decreasing. If nuclei are distributed in clusters (non-uniformly), then impingement effects may occur regardless of whether the crystalline fraction is smaller than 0.5. Therefore, these localized impingement effects may lower the values of n.

The cooling crystallization function, χ, was also determined for each temperature from the intercept of

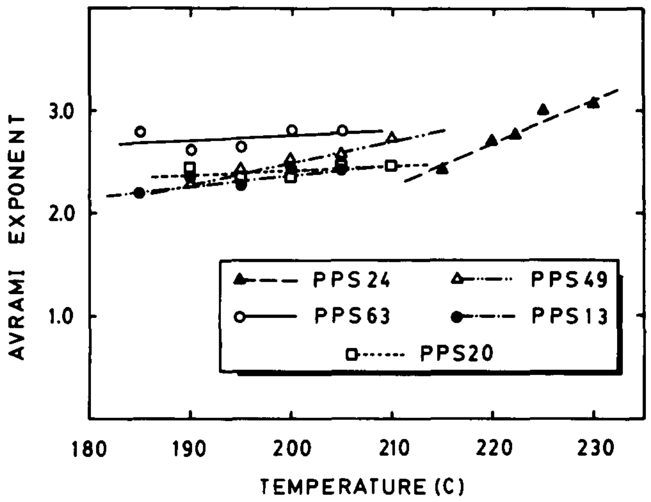

Figure 7 Plot of the Avrami exponent determined from equation (8) as a function of temperature corresponding to various PPS samples

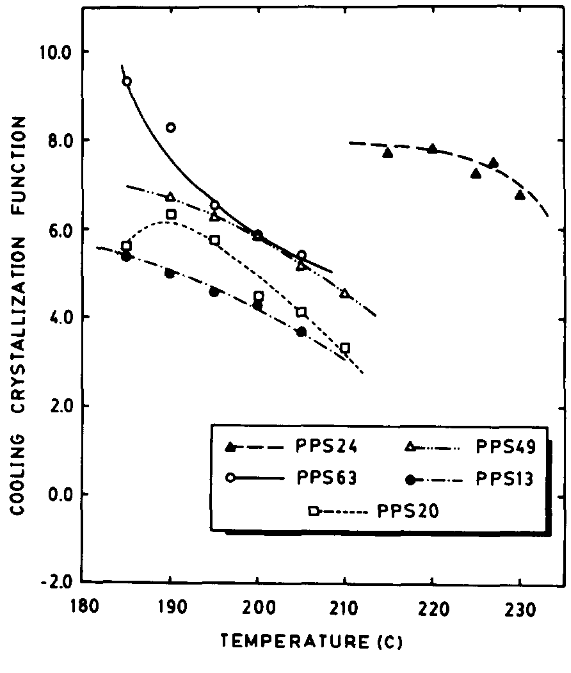

Figure 8 Plot of the cooling crystallization function, χ, as a function of temperature

the plot of $\ln\{-\ln[1-x(t)]\}$ *versus* $\ln|\phi|$. Such values are presented in *Figure 8* as functions of temperature. The values of χ range from 4 to 10 for the PPS samples, showing a decreasing trend with increasing temperature for every polymer sample. These values are in a similar range to those determined for PET by Ozawa (2–15) (ref. 5). Furthermore, the decreasing trend is in agreement with data on PET presented by Ozawa[5]. This author showed that χ decreased with increasing temperature. Polypropylene also presented a similar trend[10]. However, the significance of χ has not been discussed. *Figure 8* shows that the linear PPS samples, PPS24, PPS49 and PPS63, have higher values of χ than the branched samples PPS13 and PPS20, at a given temperature. In addition, considering the decreasing trend, the values corresponding to PPS24 at high temperature are higher than those PPS49 and PPS63 would have. Therefore, we believe that the cooling crystallization function, χ, is related to the overall rate of bulk crystallization in the sense that it may give an indication of how fast the non-isothermal crystallization occurs.

CONCLUSIONS

The theory of Ozawa has been shown to be a good method to analyse data corresponding to non-isothermally crystallized PPS. Equation (8) conformed very well to the d.s.c. data of PPS, allowing the determination of the Avrami exponent. In general, the Avrami exponents determined by this method were in agreement with values obtained by means of isothermal techniques. In addition, the analysis of Ozawa allowed the study of the crystallization behaviour of PPS in a wider temperature range. This indicates that this technique can be a complementary tool for the investigation of the crystallization of polymers.

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