

Crystallization Kinetics of Polyphenylene Sulfide*

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Synopsis

The crystallization kinetics of unfilled and glass-reinforced grades of polyphenylene sulfide has been investigated by using differential scanning calorimetry. The maximum rate of crystallization is observed at about 170°C. From the crystallization data, it is recommended that the molding parameters should be so specified that the polymer spends 10–15 s over the temperature range of 155–190°C during cooling, before demolding, in order to ensure stable morphology of the molded part. The glass fibers have an accelerating influence on crystallization resulting in a 15–25% reduction in crystallization time. The kinetic data have been interpreted by using Avrami analysis followed by a discussion of the possible crystallization mechanisms.

INTRODUCTION

Polyphenylene sulfide (PPS) is a versatile engineering plastic with an unusual combination of properties such as high chemical resistance, excellent thermal stability, and good mechanical properties. It can be compounded with various fillers and fibers, thereby extending its property spectrum and applications potential. The polymer in the compounded form exhibits good melt processibility and is widely used in making injection-molded components of complex shapes for engineering applications. Typical molded components of PPS include pump impellers, ball valves, gears, wear rings, electrical sockets, battery, and telephone components etc.

In the case of semicrystalline polymers such as PPS, the mechanical properties, and dimensional stability of the molded part are governed by the morphology of the polymer, as formed during the molding cycle. Therefore, injection molding of precision engineering components with close tolerances requires a thorough knowledge of the crystallization behavior of the polymer. Information concerning the crystallization time and extent of crystallization as a function of temperature is critical for specifying the molding parameters such as the mold temperature and demolding time. There is little published literature on the crystallization kinetics of PPS, although Tabor et al.¹ has reported the crystal structure details, and Brady² has discussed in depth the effects of processing conditions on crystallinity and properties of the molded parts.

The kinetics of polymer crystallization can be studied by a number of techniques such as dilatometry,^{3,4} polarized light microscopy,⁵⁻⁷ and differ-

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TABLE I
Thermal Characterization of PPS Samples^a

Observation no.	Grade	T_m (°C)	ΔH_f (cal/g)	T_c (°C)	ΔH_c (cal/g)	ΔH_{rc} (cal/g)
1	R-4	278	7.8 ^b	235	7.9 ^b	—
2	R-4 (annealed)	282	9.6 ^b	—	—	—
3	R-4 (quenched)	280	7.0 ^b	—	—	4.6 ^b
4	V-1	280	10.5	229	10.3	—
5	V-1 (annealed)	285	12.3	—	—	—

^a ΔH_f = heat of fusion (heating mode), ΔH_c = heat of crystallization (cooling mode), ΔH_{rc} = heat of recrystallization (heating mode), T_m = melting peak temperature, and T_c = crystallization peak temperature.

^b The values of ΔH_c have been corrected for 40% fiber glass content.

ential scanning calorimetry^{6,8,9} (DSC). Pratt and Hobbs have reported a comparative study of crystallization rates by using DSC and microscopy. Difference in crystallization half times ($t_{1/2}$) of PBT and PET were noted between the two techniques, although similar $t_{1/2}$ values were obtained for isotactic PP. A direct comparison of DSC with dilatometry has been made by Booth and Hay.⁹

In general, DSC is not as sensitive as precision dilatometry, and it also cannot accurately detect secondary crystallization. However, it is a useful tool for defining molding guidelines with microsamples, as it allows estimating crystallization time over a range of temperatures in a short time.

The present work reports kinetic data on the crystallization of unfilled and glass fiber reinforced grades of PPS over a temperature range of 110–250°C. The technique of differential scanning calorimetry has been used for the investigation. The kinetic data have been interpreted by using Avrami analysis followed by discussion of the possible crystallization mechanisms.

EXPERIMENTAL

Two grades of Ryton polyphenylene sulfide, R-4 and V-1, manufactured by Philips Petroleum Co. were used for the investigation. Ryton R-4 is a pelletized resin containing 40% glass fibers and is used for injection molding. Ryton V-1 is an unfilled powder resin recommended for use in compression molding and slurry coating. The amount of glass fibers in R-4 was confirmed from the fractional residue of the sample in thermogravimetric analysis (TGA).

The thermal characterization of the starting samples and the crystallization studies were carried out using the Perkin-Elmer DSC-2 Differential Scanning Calorimeter. Calibration of the equipment for temperature scale and heat of fusion was done using Indium as the standard material with a melting point of 156.8°C and the heat of fusion of 6.79 cal/g. The sample weights were in the range of 5–7 mg. Thermal characterization data on the PPS grades R-4 and V-1, obtained at 10°C/min heating and cooling rates, are given in Table I and the DSC scans are shown in Figure 1.

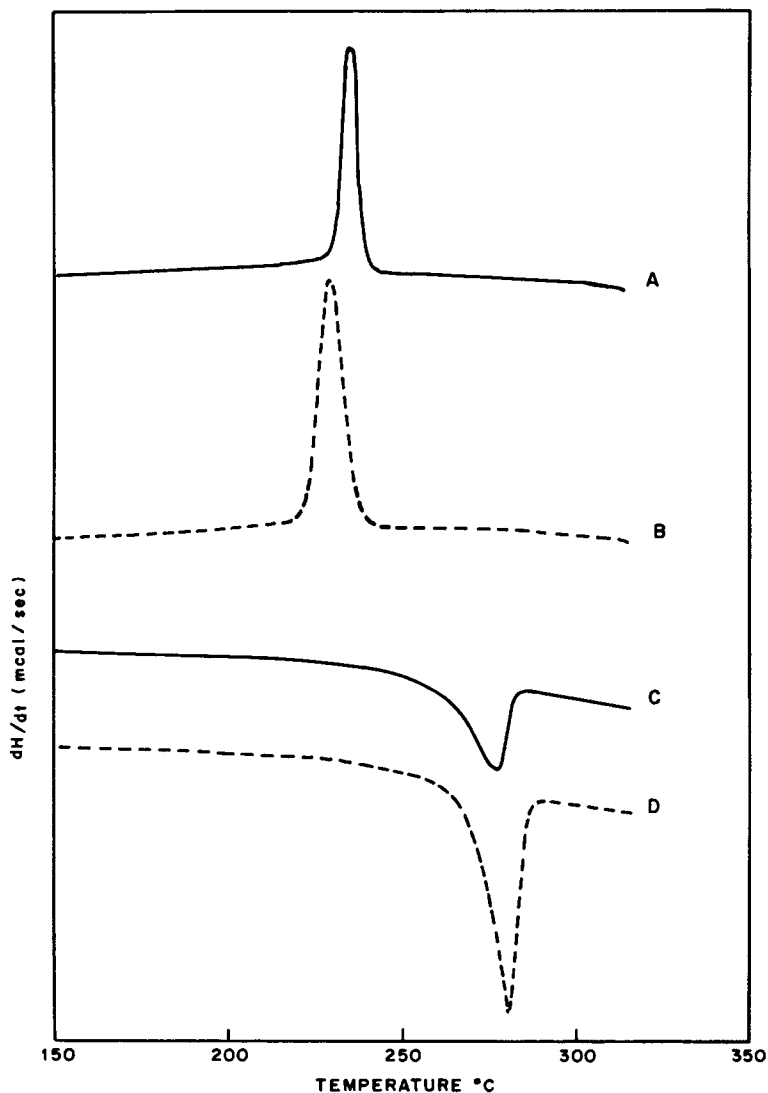


Fig. 1. DSC scans for PPS samples Ryton R-4 (—) and V-1 (---): (A, B) cooling scans; (C, D) heating scans.

In order to obtain the crystallization isotherms, isothermal DSC scans were obtained over a range of crystallization temperatures. For semicrystalline polymers, the rate of crystallization goes through a maximum (minimum crystallization time) at intermediate temperatures between the glass transition temperature; T_g and the melting point; T_m .

Therefore, the range of interest for PPS is 90–280°C. Crystallization isotherms in the high temperature region beyond the temperature of maximum crystallization rate were obtained via DSC scans in the cooling mode. The weighed sample of the polymer was heated to 350°C at 10°C/min and held at this temperature for 10 min to destroy residual nuclei. The sample was then cooled at 160°C/min to the predetermined temperature of crystallization, T_c , at which the crystallization peak was recorded against time

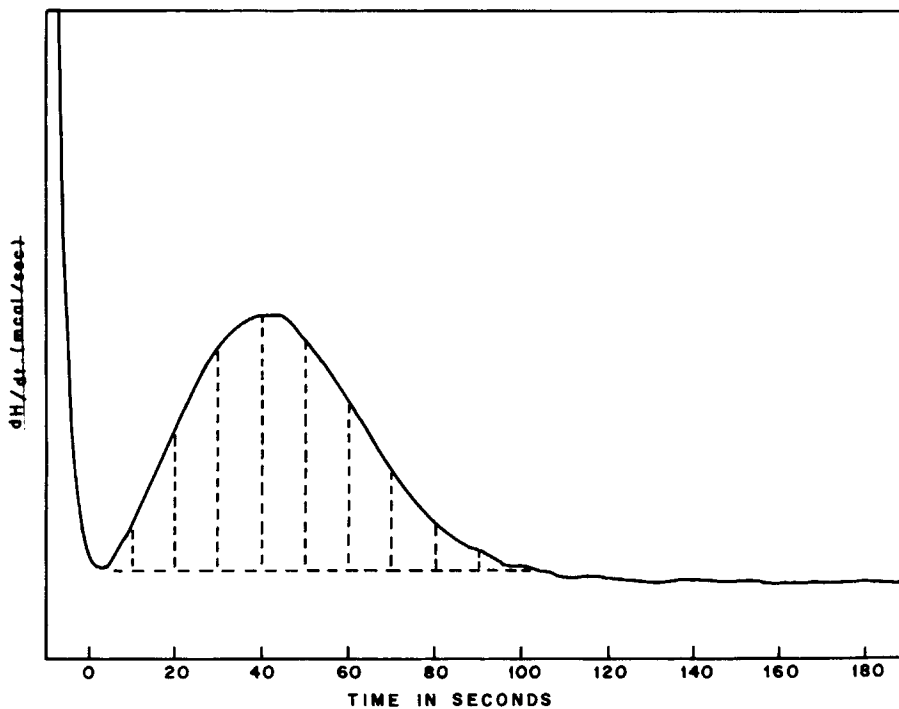


Fig. 2. A typical isothermal crystallization peak at 235°C (Ryton V-1).

base (Figure 2). The extent of crystallization completed at a fixed time was determined from point-by-point area measurements of the crystallization peak, assuming that the fractional crystallization at a given time is proportional to the ratio of the crystallization peak area up to that time, to

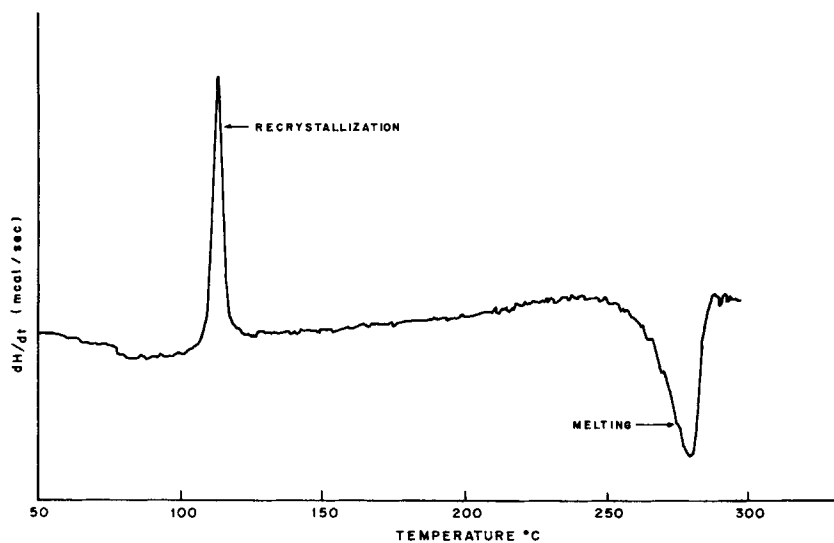


Fig. 3. DSC scan of quenched sample (Ryton R-4).

the total peak area. That is, the weight fraction X_t of material that is crystallized at time t is given by

$$X_t = \int_0^t \left(\frac{dH}{dt} \right) dt \bigg/ \int_0^\infty \frac{dH}{dt} dt \quad (1)$$

where dH/dt is the rate of evolution of heat as a function of time.

By following the above procedure in cooling mode crystallization isotherms (X_t vs. $\log t$ curves) were obtained over a temperature range from 250°C to 215°C. It was not possible to obtain the crystallization data below 215°C. in the cooling mode, because of the very fast crystallization of the sample being cooled even before the desired crystallization temperature was reached.

In order to obtain crystallization data over the temperature range between the glass transition temperature and the temperature of maximum crystallization rate, a partially amorphous sample was prepared. The PPS grade R-4 pellets were melted in a melt flow index apparatus at 290°C, and the melt was extruded into a beaker containing water at 25°C. The DSC scan of the resulting quenched sample is shown in Figure 3, which indicates a recrystallization peak at 125°C. From the heats of recrystallization and fusion (Table I) of the quenched sample, it is apparent that the quenched sample is not fully amorphous and the residual crystallites would influence

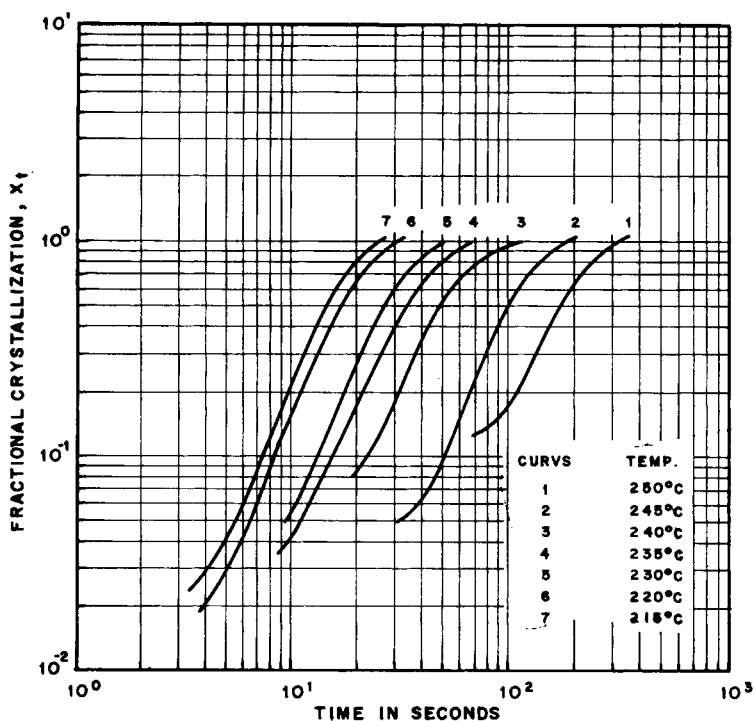


Fig. 4. Crystallization isotherms of Ryton R-4 (cooling mode). Temperature (°C): (1) 250; (2) 245; (3) 240; (4) 235; (5) 230; (6) 220; (7) 215.

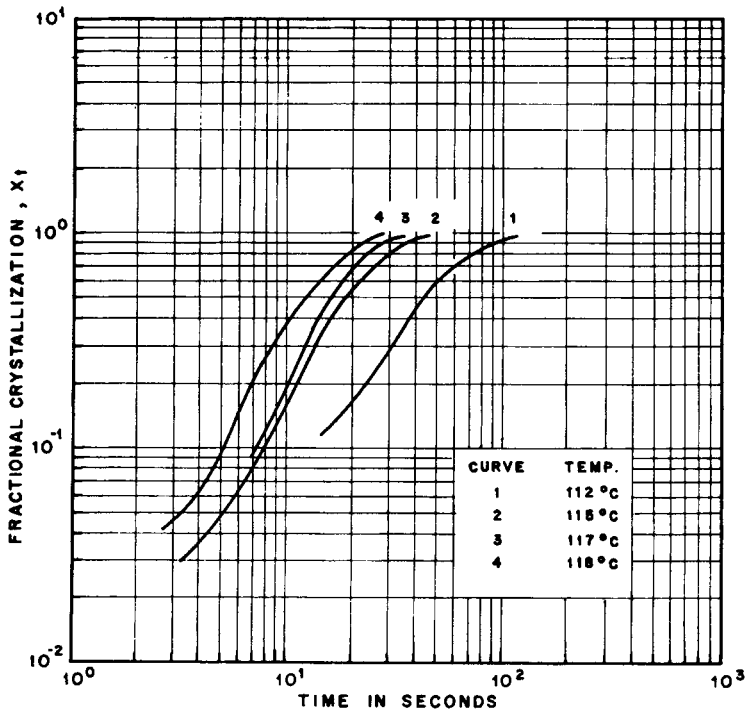


Fig. 5. Crystallization isotherms of Ryton R-4 (heating mode). Temperature (°C): (1) 112; (2) 115; (3) 117; (4) 118.

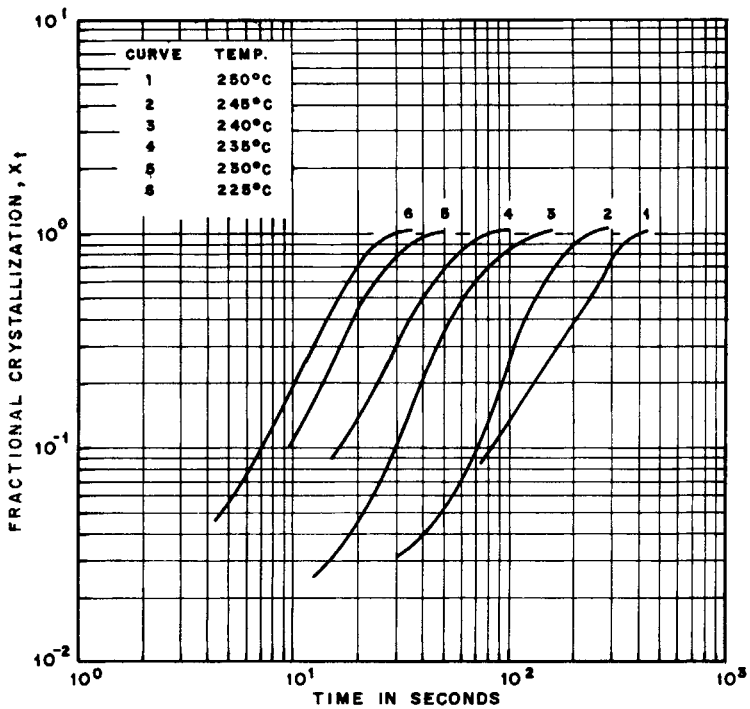


Fig. 6. Crystallization isotherms of Ryton V-1 (cooling mode). Temperature (°C): (1) 250; (2) 245; (3) 240; (4) 235; (5) 230; (6) 225.

TABLE II
Crystallization Parameters for PPS

Observation number	Crystallization temperature T_c (°C)	Crystallization time (s)				Avrami exponent		Rate constant (s ⁻ⁿ)		Heat of crystallization (cal/g)	
		R-4		V-1		R-4	V-1	R-4	V-1	R-4	V-1
		t_c	$t_{1/2}$	t_c	$t_{1/2}$	n	n	K	K	ΔH^a	ΔH
1	250	340	170	440	240	2.64	2.04	8.69×10^{-7}	9.66×10^{-6}	9.34	11.89
2	245	200	100	300	140	2.88	2.43	1.20×10^{-6}	4.2×10^{-6}	—	—
3	240	120	48	150	60	2.25	2.16	1.15×10^{-4}	1.0×10^{-4}	9.66	10.77
4	235	75	34	106	40	2.33	2.06	1.85×10^{-4}	3.47×10^{-4}	7.66	11.25
5	230	60	26	—	—	2.56	—	1.67×10^{-4}	—	7.59	11.80
6	220	38	17	50	22	2.53	2.48	5.34×10^{-4}	3.2×10^{-4}	7.53	—
7	215	31	14	36	17	2.64	2.19	6.53×10^{-4}	1.36×10^{-4}	7.81	10.91
8	112	120	42	—	—	—	—	—	—	6.29	—
9	115	51	19	—	—	—	—	—	—	7.18	—
10	117	42	16	—	—	—	—	—	—	2.37	—
11	118	29	12	—	—	—	—	—	—	1.83	—

^a The values of ΔH_c have been corrected for 40% fiber glass content.

the rate of crystallization. Thus the crystallization data collected using this sample in heating mode would not be as accurate as the data collected by using the cooling mode in DSC.

In the heating mode, the partially amorphous sample was heated to the desired crystallization temperature by heating at 10°C/min, and the crystallization isotherms were obtained at 112°C, 115°C, 117°C and 118°C by following the point-by-point analysis of the isothermal peak.

In order to find out the maximum extent of crystallization attainable, PPS samples, grades V-1 and R-4, were annealed at 204°C for 2.5 h in the DSC. Results of the thermal characterization of the annealed samples are given in Table I.

RESULTS AND DISCUSSION

The crystallization isotherms for the glass-fiber-reinforced and unfilled grades of PPS are shown in Figures 4–6. The crystallization time t_c and the crystallization half-time $t_{1/2}$ were obtained from the S-shaped curves. The crystallization half-time is defined as the time at which the extent of crystallization is 50% complete. The total crystallization time was determined from the base width of the isothermal crystallization peak. These data are summarized in Table II.

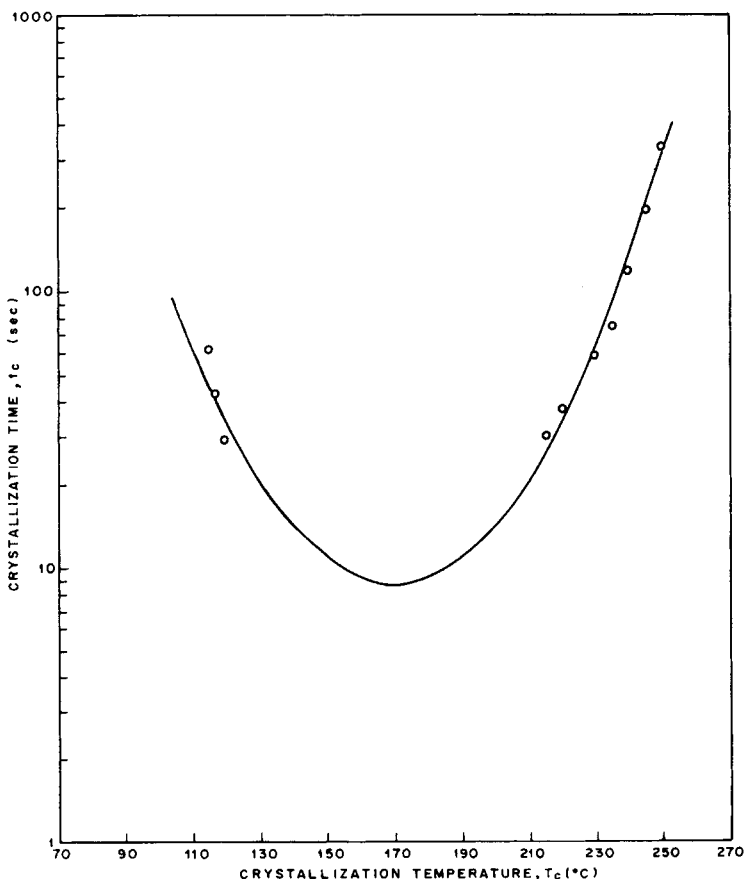


Fig. 7. Variation of crystallization time t_c (s) with crystallization temperature T_c (°C).

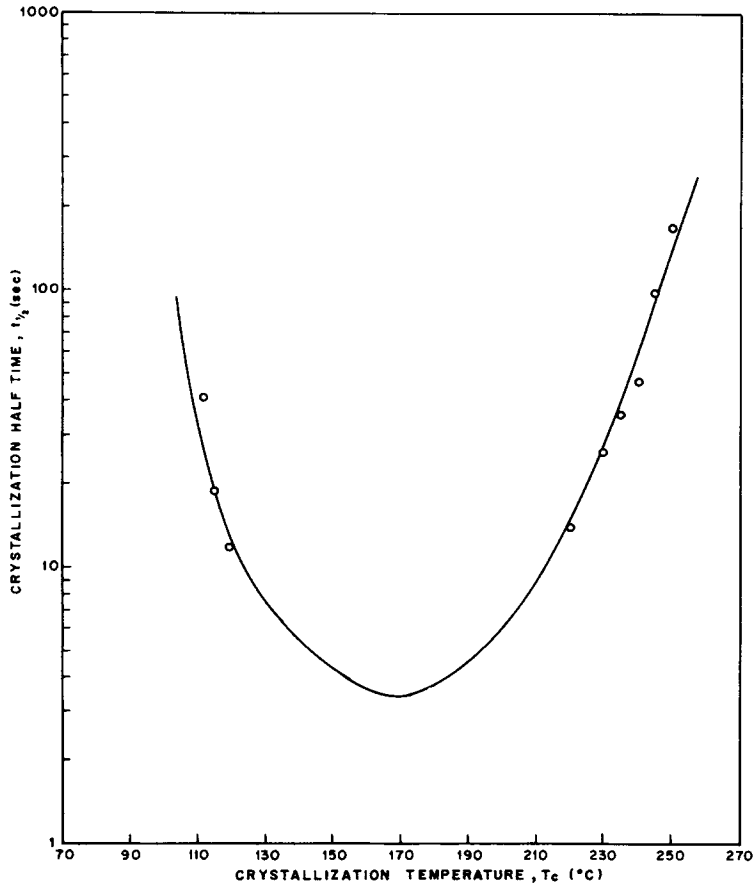


Fig. 8. Variation of crystallization half-time $t_{1/2}$ (s) with crystallization temperature T_c (°C).

The crystallization time values, t_c and $t_{1/2}$, were curve-fitted using a polynomial equation form; the equations are given below:

$$\log_{10} t_c = 7.66 - 7.934 \times 10^{-2} T_c + 2.343 \times 10^{-4} T_c^2 \quad (2)$$

$$\log_{10} t_{1/2} = 7.954 - 8.719 \times 10^{-2} T_c + 2.562 \times 10^{-4} T_c^2 \quad (3)$$

The multiple correlation coefficient for eq. (2) is 0.971 and it is 0.9179 for eq. (3). The curves along with the experimental data points are shown in Figures 7 and 8.

The rate of crystallization of PPS was found to be maximum at about 170°C. The crystallization time is less than 10 s over a temperature range of 155–190°C. It implies that the molding conditions should be so specified that the polymer spends at least 10–15 s over this temperature range during cooling, before demolding, in order to ensure dimensional stability of the molded part.

At a given temperature, the crystallization half-time for the glass-fiber-reinforced grade is shorter than that of the unfilled grade. This accelerating influence of the reinforcing fibers is related to the faster heterogeneous nucleation occurring in the filled polymer vs. homogeneous nucleation in

the unfilled grade. The effect is therefore more pronounced at high temperatures of crystallization approaching the melting point. These results are consistent with earlier investigations on crystallization of filled polymers.¹⁰⁻¹⁵

Referring to Table II the heats of crystallization of the PPS samples crystallized at 240°C and 250°C are comparable to the respective heats of fusion of the annealed samples (Table I) for both the filled and the unfilled grades. This indicates that better crystal perfection and higher levels of crystallinity are achieved at low degrees of super cooling due to the slower crystal growth rate. It is also pertinent to note here that the heat of fusion of the annealed sample is higher for the unfilled grade (12.3 cal/g) than for the glass-reinforced grade (9.6 cal/g). This may be attributed to the effect of molecular weight on crystallizing ability of the polymer. The unfilled grade of PPS, V-1, used mainly for coating, is a lower molecular weight polymer as compared to the polymer used in preparing the glass-reinforced grade, R-4, used for injection molding. Thus, due to the higher chain mobility of the polymer in the unfilled PPS grade, a higher degree of crystallinity is achieved.

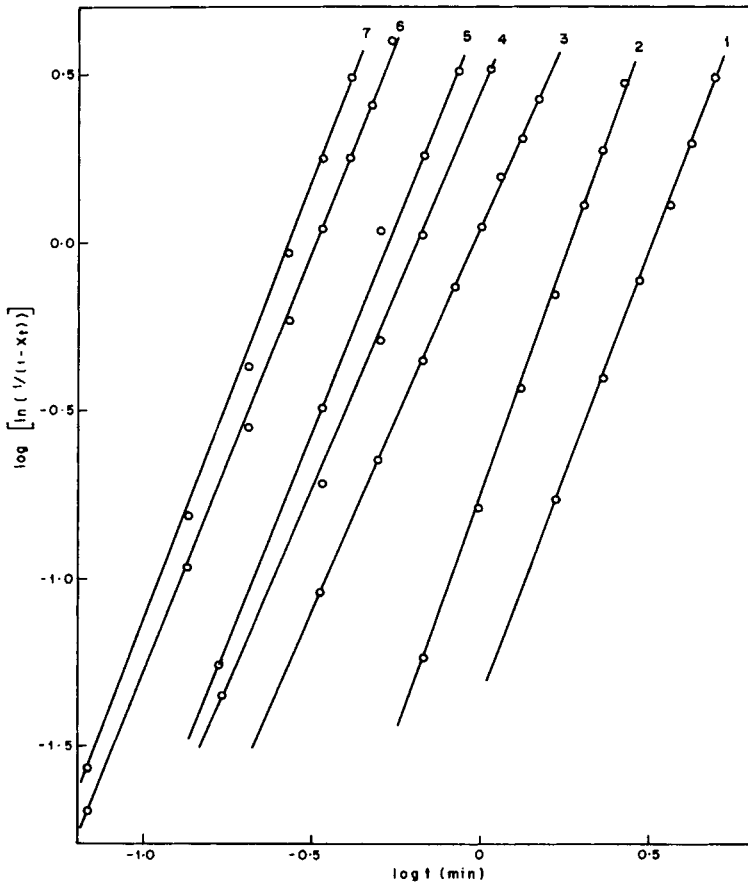


Fig. 9. Avrami plots for Ryton R-4. Temperature (°C): (1) 250; (2) 245; (3) 240; (4) 235; (5) 230; (6) 220; (7) 215.

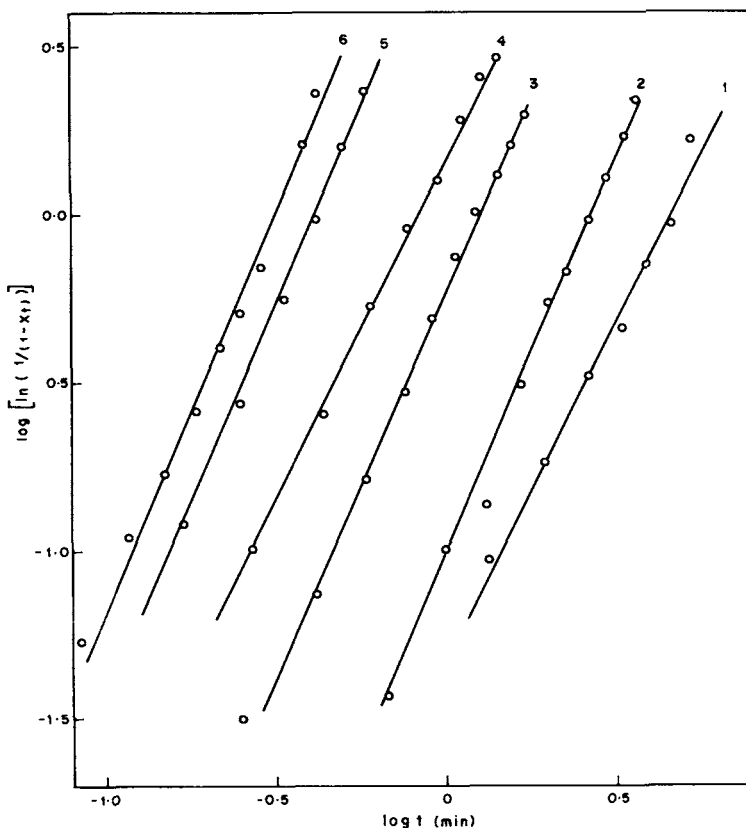


Fig. 10. Avrami plots for Ryton V-1. Temperature (°C): (1) 250; (2) 245; (3) 240; (4) 235; (5) 220; (6) 215.

The crystallization-time dependence was analyzed graphically by means of the Avrami¹⁶ equation:

$$(1 - X_t) = \exp(-Kt^n) \quad (4)$$

where X_t = weight fraction of the crystallized material at time t , K = rate constant, n = Avrami exponent. The rate constant K includes the combined rate effects of nucleation and crystal growth. The crystallization kinetic parameters, K and n , are dependent on the molecular weight and structure of the polymer, the molecular weight distribution, degree of tacticity, presence of impurities, etc.

The plots of $\log [\ln 1/(1 - X_t)]$ vs. $\log t$ for the glass-fiber-reinforced and unfilled grades of PPS are shown in Figures 9 and 10, respectively. The values of n were determined from these plots. The rate constants K were calculated by using the equation

$$K = \frac{\ln 2}{(t_{1/2})^n} \quad (5)$$

The values of the Avrami exponent n do not vary significantly with temperature. The average value of n is 2.55 for the glass-filled grade (R-4) and 2.23 for the unfilled grade. The nonintegral values of n cannot be explained in terms of the physical assumptions made in arriving at the Avrami equation. Fractional values of n may be expected mathematically, if certain constraints are imposed such as diffusion controlled growth, as illustrated by Mandelkern.¹⁷ The observed deviations could also be attributed to factors such as time-dependent nucleation, variant growth rate constants, combination of homogeneous, and heterogeneous nucleation. However, in general, it is difficult to elucidate the growth geometry and type of nucleation solely from the value of the exponent n .

Since the values of Avrami exponent n for both filled and unfilled grades of PPS lie between 2 and 3, the following mechanisms of nucleation and growth may be speculated on the basis of Mandelkern's analysis.¹⁷

For the unfilled grade of PPS, the crystallization may involve homogeneous nucleation either with one directional growth or two directional diffusion controlled growth ($n = 2$).

For glass-fiber-filled PPS, the value of the Avrami exponent ($2 < n < 3$) suggests heterogeneous nucleation with two directional diffusion controlled growth.

Considering the effect of fillers on growth geometry two directional diffusion controlled growth with homogeneous and heterogeneous nucleation seem to be the probable mechanism of crystallization in unfilled and filled PPS.

In the case of the glass-fiber-reinforced grade, heterogeneous nucleation will occur on the surface of the glass fibers occupying about 28% of the volume (40% weight). Homogeneous nucleation may also take place simultaneously in the polymer melt not in the vicinity of the fiber surface. Such nonuniform nucleation density could lead to different crystallization kinetics and mechanism for different regions of the sample, and the experimental kinetic results may represent a combined effect.

CONCLUSIONS

The maximum rate of crystallization of PPS is observed at about 170°C. The glass fibers have an accelerating influence on crystallization which leads to a 15–25% reduction in crystallization time. This effect is more pronounced at high temperatures near the melting point. From the crystallization data, it is recommended that the molding parameters should be so specified that the polymer spends 10–15 s over the temperature range of 155–190°C. during cooling, before demolding, in order to ensure stable morphology of the molded part.

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