

Keywords: polyphenylene sulfide, non-isothermal kinetics, crystallization kinetics, Avrami, Malkin, polymer crystallization

TA395

## ABSTRACT

The dependence of process melting temperature of polyphenylene sulfide (PPS) on crystallization temperature and kinetics was demonstrated by a simple DSC experiment in which the sample was held at isothermally at several temperatures above the equilibrium melting temperature for five minutes to destroy any crystals or other structure that may aid in nucleation. Cooling the samples at 10 °C / min showed the crystallization temperatures asymptotically converge at a crystallization temperature that corresponds to an isothermal hold temperature of 350 °C or approximately 50 °C above the equilibrium melting temperature. A non-isothermal kinetic study on PPS resin held at the lowest, highest and an intermediate isothermal temperature show a correlation in crystallization activation energy confirming that 'seed' crystals or other structure aid in nucleation. The kinetic parameters were calculated from rate data obtained from non-isothermal or dynamic DSC experiments using the Avrami and Malkin macro kinetic models and Friedman's isoconversional approach using data taken directly from the DSC experiment.

## INTRODUCTION

Polyphenylene Sulfide (PPS) is an engineering thermoplastic typically used in applications demanding high modulus, good chemical resistance, heat resistance, and UV stability.

Several authors have demonstrated the effect of processing melt and mold temperatures on the properties of plastics. [17, 19, 20] One of the important properties of semi-crystalline polymers is crystallinity which is correlated with physical properties such as flexural and tensile modulus, tensile strength, abrasion resistance, and toughness.

It is known that many semi-crystalline polymers retain a 'structural memory' at temperatures above the melting temperature and that complete eradication of this retained structure and other thermal history is needed to obtain accurate intrinsic crystallization information. Muller and Arnal demonstrated that crystal structure above the apparent melting transition seeded nucleation and was the basis on their work on polymer fractionation by DSC [21].

The first part of this work demonstrates the dependence of the crystallization temperature on the isothermal hold temperature, the second part demonstrates that this dependence can be quantified in a non-isothermal crystallization kinetics experiment.

## The Isothermal Kinetics Experiment

Crystallization of semi-crystalline polymers can be described as the sequence of two processes: primary and secondary crystallization. Primary crystallization consists of two mechanisms: primary nucleation and secondary nucleation or crystal growth. Secondary crystallization occurs in melted areas in the interstitial zones formed during the primary crystallization process [1].

The isothermal crystallization experiment involves heating the sample to above the equilibrium melting temperature and cooling to a temperature where the sample crystallizes. Several crystallization temperatures are chosen, and the resultant heat of crystallization is measured. The fraction crystallized as a function of time  $[X(t)]$  is used to determine kinetic parameters of the crystallization process using one of many macro kinetic models. The most frequently used model to describe primary crystallization is the Avrami equation. Many other models have been proposed and used. For this work, we will focus on the Avrami equation and an alternative macro kinetic equation proposed by Malkin[2] et. al., but we will use a non-isothermal experiment which will be described further in the section below.

## Basic Definitions

If the crystallinity occurring during cooling at a time  $t$  and the maximum crystallinity possible at infinite time can be expressed as  $\chi_t$  and  $\chi_\infty$  respectively, then the fraction crystallized at any time  $X(t)$  can be written as:

$$X(t) = \left( \frac{\chi_t}{\chi_\infty} \right) \quad (1)$$

For the DSC experiment, this is the fractional area of the crystallization exotherm normalized to the entire exotherm area:

$$X(t) = \frac{\int_0^t (dH_C / dt) dt}{\int_0^\infty (dH_C / dt) dt} = \frac{\int_0^t (dH_C / dt) dt}{\Delta H_C} \quad (2)$$

Where  $dH_C/dt$  is the heat flow measured by the DSC and  $\Delta H_C$  is the total heat of crystallization.

The Avrami equation is

$$X(t) = 1 - \exp(-k_a t^{n_a}) \quad (3)$$

where

$X(t)$  = fraction crystallized as a function of time

$k_a$  = Avrami Rate Constant (function of nucleation and crystal growth rate)

$n_a$  = Avrami Exponent (function of growth geometry)

$t$  = time (seconds or minutes)

The Avrami equation can be linearized:

$$\log(-\ln(1 - X(t))) = \log k_a + n_a \log t \quad (4)$$

A plot of the  $\log(-\ln(1 - X(t)))$  versus  $\log t$  is linear (typically  $0.2 \leq X(t) \leq 0.8$ ) and yields the Avrami parameters  $k_a$  (antilog of intercept) and  $n_a$  (slope).

### Calculations With The Avrami Equation

Crystallization half time ( $t_{1/2}$ ) (min) can be expressed as:

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

Sometimes it is more convenient to express a crystallization rate ( $\tau$ ) ( $\text{min}^{-1}$ ) which is simply the reciprocal half-time:

$$\tau = \frac{1}{t_{1/2}} \quad (6)$$

### The Malkin Equation

Malkin et al. [1, 2] proposed a different macro kinetic model based on the principal that the overall crystallization rate is a summation of the variation in crystallinity due to the emergence of primary nuclei and the rate of variation in crystallinity due to the emergence of primary nuclei and the rate of variation in crystallinity due to crystal growth. [1]

$$X(t) = 1 - \frac{C_0 + 1}{C_0 + \exp(C_1 t)} \quad (7)$$

Where

$X(t)$  is the degree of conversion

$C_0$  is proportional to the ratio of linear growth rate to the nucleation rate or specifically  $C_0 \propto G/I$  (in Lauritzen and Hoffman terms)

$C_1$  is directly related to the overall crystallization rate or  $C_1 = aI + bG$  where  $a$  and  $b$  are constants.

The Avrami constants  $n$  and  $k$  can be estimated from the Malkin equation:

$$C_0 = 4n - 4 \quad (8)$$

$$C_1 = \ln(4n - 2) \left( \frac{k}{\ln(2)} \right)^{1/n} \quad (9)$$

### Crystallization Activation Energy

It is desirable to obtain the crystallization activation energy to be able to quantify the differences between samples. This can be done by using obtained rate data in the Arrhenius equation:

$$\psi_{T_c} = \psi_0 \exp(-\Delta E / RT) \quad (10)$$

Where

$\Delta E$  = Crystallization Activation Energy (kJ/mol)

$R$  = Gas Constant

$T$  = Crystallization Temperature (K)

$\Psi_{T_c} = k, k^{1/n}, C_1, \tau$  or  $[dX/df]_{X(t)}$  [5, 6]

$k$  = Avrami Rate Constant ( $\text{min}^{-1}$ )

$C_1$  = Malkin Rate Constant ( $\text{min}^{-1}$ )

$n$  = Avrami Exponent

$\tau$  = Reciprocal half-time ( $\text{min}^{-1}$ )

$[dX/df]_{X(t)}$  = instantaneous crystallization rate (Friedman isoconversional method)

The differential method is the isoconversional one described by Friedman [7, 8] and has the advantage of following the change in activation energy as a function of conversion.

### The Non-Isothermal Kinetics Experiment

Many authors have proposed macro kinetic models for determining crystallization kinetics under non-isothermal conditions including Ozawa, Liu, and Jeziorny and often these models modify the Avrami equation for the non-isothermal experiment. Others have used the Avrami equation to model non-isothermal crystallization [3,4]. The non-isothermal crystallization experiment involves heating the sample to above the equilibrium melting temperature and cooling at several heating rates. The crystallization temperatures at some degree of conversion (typically  $X(t) = 0.5$ ) are obtained from the DSC data.

For non-isothermal data, Equation 11 describes the fraction converted as a function of temperature:

$$X(T) = \frac{\int_{T_0}^T \left( \frac{dH_c}{dT} \right) dT}{\Delta H_c} \quad (11)$$

where:

$X(T)$  is weight fraction crystallized at temperature  $T$ .

$\Delta H_c$  = Overall heat of crystallization - area under the crystallization curve of the DSC experiment.

$dH_c$  = enthalpy of crystallization released during infinitesimal temperature range  $dT$ .

$T_0$  = the temperature at crystallization onset taken from the DSC curve.

$T$  = temperatures during crystallization process

Transforming the data from the temperature domain to the time domain is done by using Equation 12.

$$t = \frac{T_0 - T}{\beta} \quad (12)$$

where

$t$  = time in minutes or seconds

$T_0$  = temperature at crystallization onset

$T$  = Temperature during crystallization

$\beta$  = cooling rate ( $^{\circ}\text{C} / \text{min}$ )

## EXPERIMENTAL

### Instrument and Sample Preparation

The DSC experiment was performed using a TA Instruments Discovery DSC 2500 using nitrogen gas as the purge. Samples of 2 mg nominal mass were encapsulated using Tzero<sup>®</sup> aluminum pans. A fresh sample was prepared for each of the runs. The poly(1,4-phenylene sulfide) (PPS) sample used in this study was obtained Sigma Aldrich<sup>®</sup> (catalogue # 182354-100G) and has a number average molecular weight of ~ 10,000 and is in powder form.

### Crystallization Experiment

Nine (9) samples were prepared as described in the previous section representing 5  $^{\circ}\text{C}$  increments from 310  $^{\circ}\text{C}$  to 350  $^{\circ}\text{C}$ . Samples were held at the isothermal hold temperature for 5 minutes to allow for as much melting to occur as possible. The initial temperature was chosen arbitrarily at 10  $^{\circ}\text{C}$  above the equilibrium melting temperature of 300  $^{\circ}\text{C}$  for PPS [9]. The samples were cooled at 10  $^{\circ}\text{C} / \text{min}$  to 23  $^{\circ}\text{C}$  and subsequently reheated to 325  $^{\circ}\text{C}$ . Crystallization temperature ( $T_c$ ), heat of crystallization ( $\Delta H_c$ ), melting temperature ( $T_m$ ), and heat of fusion ( $\Delta H_f$ ) data was obtained for each run.

### Non-Isothermal Kinetics

Three (3) samples were chosen for the non-isothermal kinetics study and prepared in the same manner as in the crystallization experiment. The samples were heated to the isothermal hold temperature and held for 5 minutes. The isothermal temperatures chosen were 310, 320, and 350  $^{\circ}\text{C}$ . DSC data using cooling rates of 20, 10, 5, and 2  $^{\circ}\text{C} / \text{min}$  were obtained. Again, fresh sample was used for each of the isothermal / dynamic cooling runs. Analysis of the data was performed using Table Curve<sup>®</sup> Software from Systat. Data was fit using the Avrami and Malkin models with  $t_0$  taken at  $X(t)$  from 0 to 0.8. The linear form (Eq. 4) of the Avrami model was fit using Excel with limits of  $X(t)$  from 0.2 to 0.8.

## RESULTS AND DISCUSSION

### Comparison of Crystallization and Melting Curves at Different Isothermal Temperatures

Overlays of the crystallization exotherms at a cooling rate of 10  $^{\circ}\text{C} / \text{min}$  are shown in Figure 1, the crystallization peak temperature as a function of isothermal temperature is plotted in Figure 2. Crystallization temperature and heat of crystallization data is summarized in Table 1. The crystallization peak temperatures show a strong dependence on the

isothermal hold temperature and asymptotically converge at approximately 214  $^{\circ}\text{C}$  corresponding to an isothermal hold temperature of 350  $^{\circ}\text{C}$ , which is approximately 50  $^{\circ}\text{C}$  above the equilibrium melt temperature for PPS.

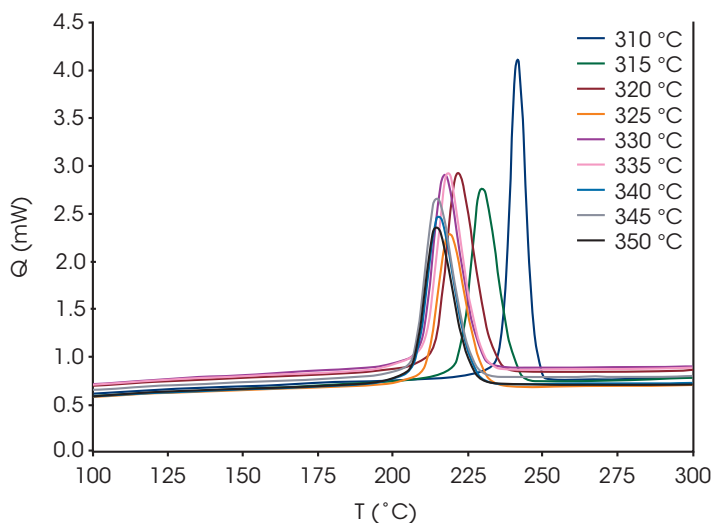


Figure 1. Polyphenylene Sulfide Crystallization Exotherms; Cooling Rate is 10  $^{\circ}\text{C} / \text{min}$

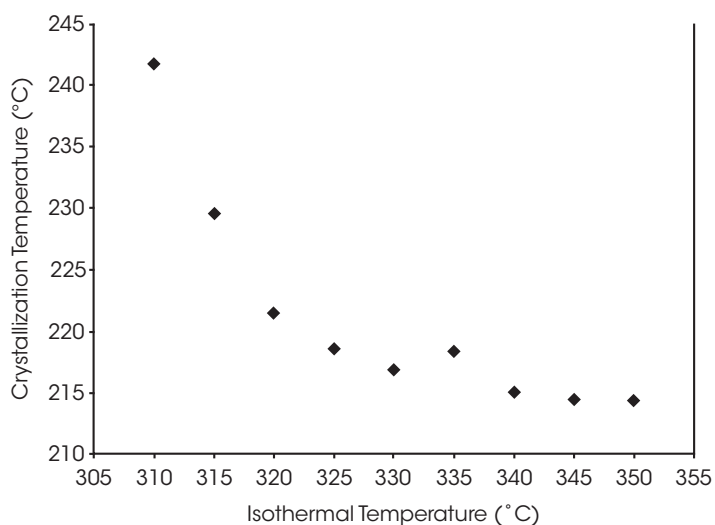


Figure 2. Crystallization Temperature as Function of Isothermal Hold Temperature for Polyphenylene Sulfide

Table 1. Crystallization Temperature as Function of Isothermal Hold Temperature and Heat of Crystallization Data for Polyphenylene Sulfide at Varying Isothermal Temperatures; Cooling at 10  $^{\circ}\text{C} / \text{min}$ .

Isothermal T ( $^{\circ}\text{C}$ )	$T_c$ ( $^{\circ}\text{C}$ )	$\Delta H_c$ (J/g)
310	241.7	58.77
315	229.6	55.9
320	221.5	55.71
325	218.6	53.78
330	216.9	54.11
335	218.4	54.07
340	215.1	52.15
345	214.5	53.96
350	214.4	54.29

As expected, the melting transitions appear to overlay (Figure 3) except for the isothermal at 310 °C which shows a slight melting depression and a slightly higher heat of fusion (Table 2).

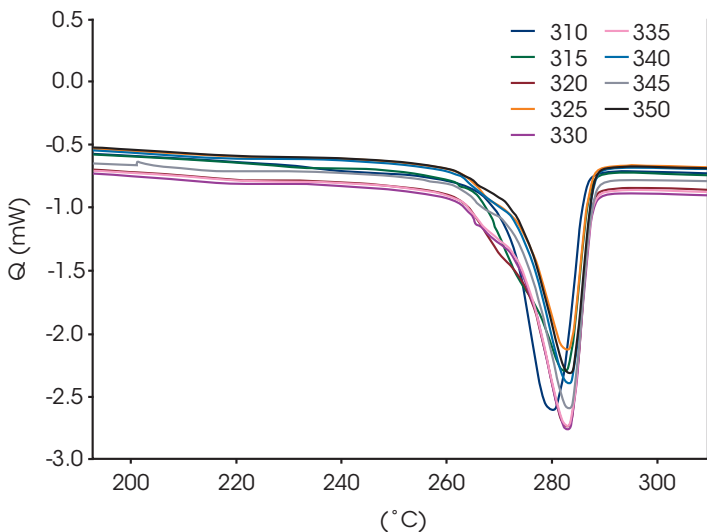


Figure 3. Melting Transitions after Isothermal Hold for PPS

Table 2. Melting and Heat of Fusion Data for PPS as Function of Isothermal Hold Temperature

Isothermal T (°C)	T <sub>M</sub> (°C)	ΔH <sub>f</sub> (J/g)
310	280.0	58.78
315	282.5	54.47
320	282.8	55.21
325	282.9	52.35
330	283.0	54.53
335	282.8	54.63
340	283.2	52.64
345	283.3	54.32
350	283.3	52.67

### Non-Isothermal Crystallization Kinetics

Figure 4 shows an overlay of the cooling curves for the three isothermal hold temperatures and Table 3 summarizes the non-isothermal crystallization kinetics data obtained using Avrami and Malkin macro kinetic models.

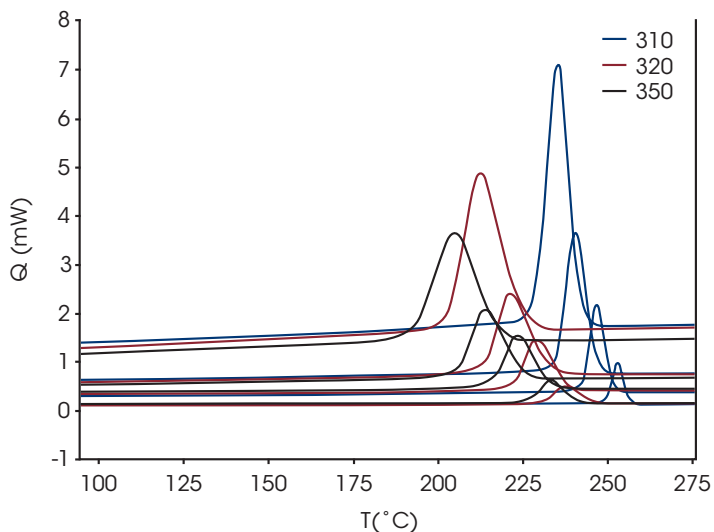


Figure 4. Overlay of Cooling Curves at Cooling Rates of 20, 10, 5, and 2 °C/min (Non-Isothermal Crystallization)

Crystallization half times (Figure 5) decrease with lower isothermal temperatures. The largest differences in the half-times appear to occur at the lower cooling rates and appear to move toward convergence at the higher cooling rates.

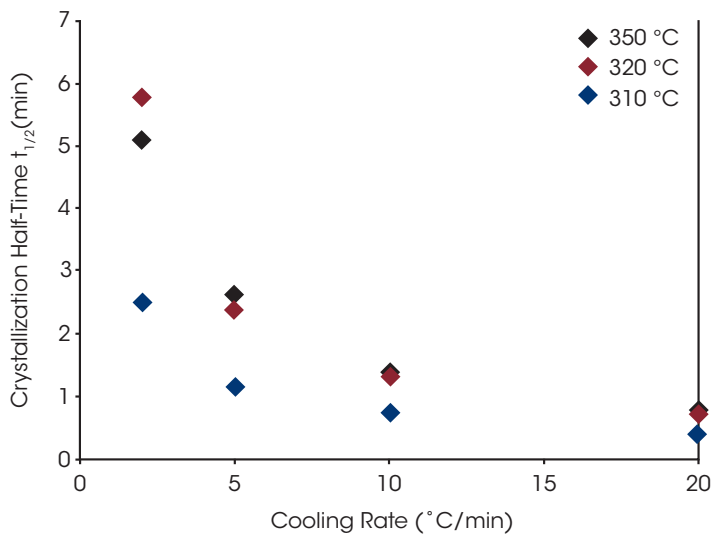


Figure 5. Crystallization Half Time as Function of Heating Rate

The Malkin rate constant  $C1$  which represents the overall crystallization rate shows a marked increase at the isothermal temperature of 310 °C contrasted with the higher isothermal temperatures (Figure 6).

The Malkin constant  $C0$  which is proportional to the ratio of secondary to primary nucleation shows a slight decrease at the lower isothermal temperature (Figure 7).

The Avrami geometric constant 'n' (Table 3) remains relatively consistent between 2.5 and 3, while the normalized Avrami rate constant ( $k^{1/n}$ ) is significantly higher at the 310 °C isothermal temperature (Figures 8 and 9).

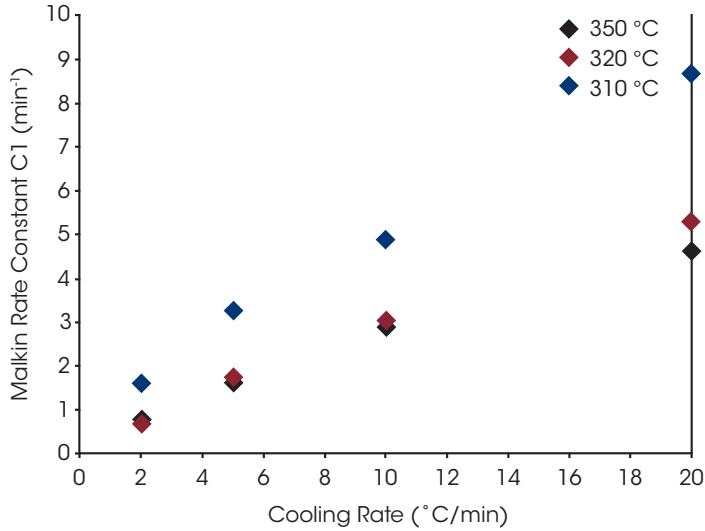


Figure 6. Malkin Rate Constant  $C1$  as Function of Cooling Rate

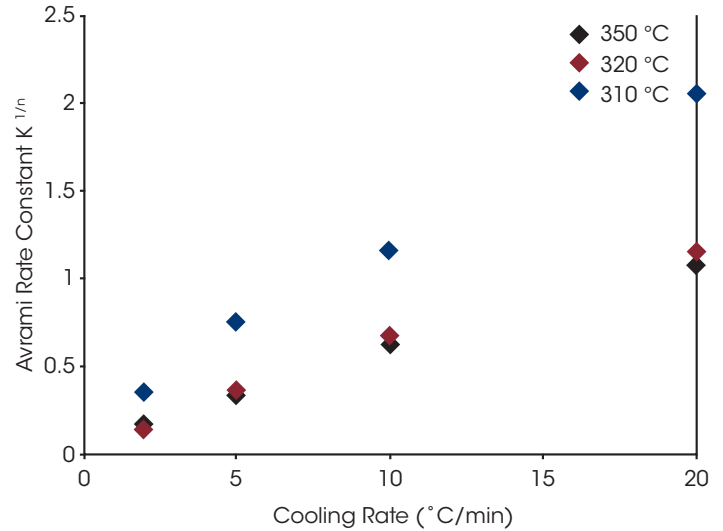


Figure 8. Avrami Rate Constant as Function of Cooling Rate

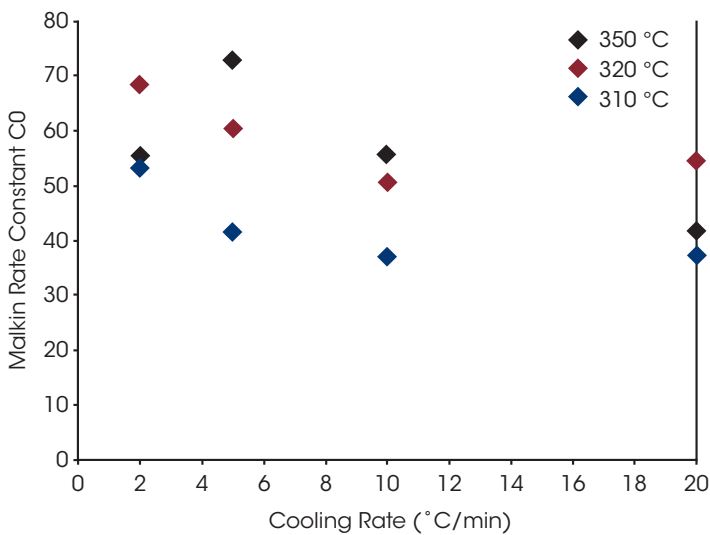


Figure 7. Malkin Constant  $C0$  as Function of Cooling Rate

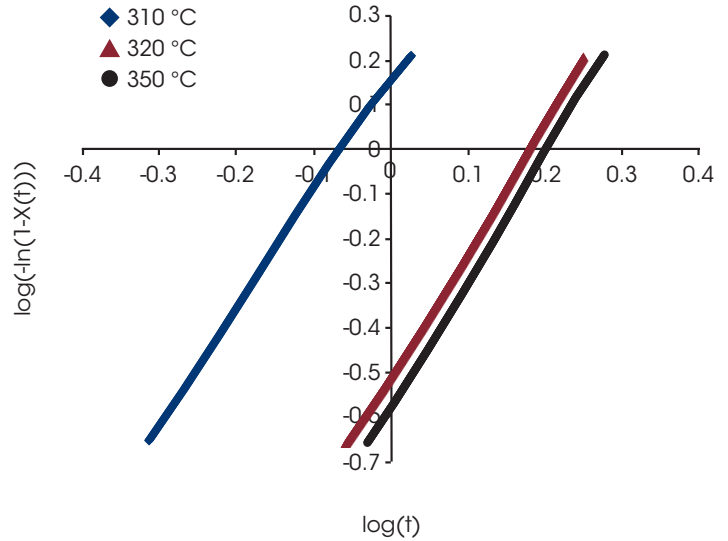


Figure 9. Avrami Fit of PPS Samples

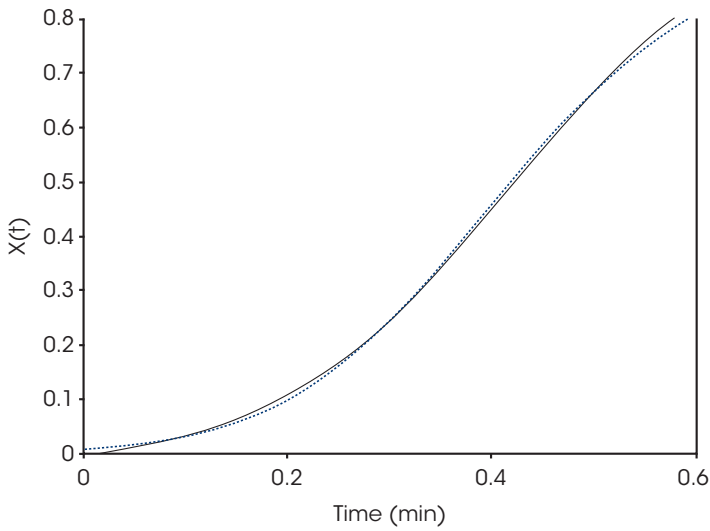


Figure 10. Example Malkin Fit for PPS; Cooling rate =20 °C / min, Isothermal

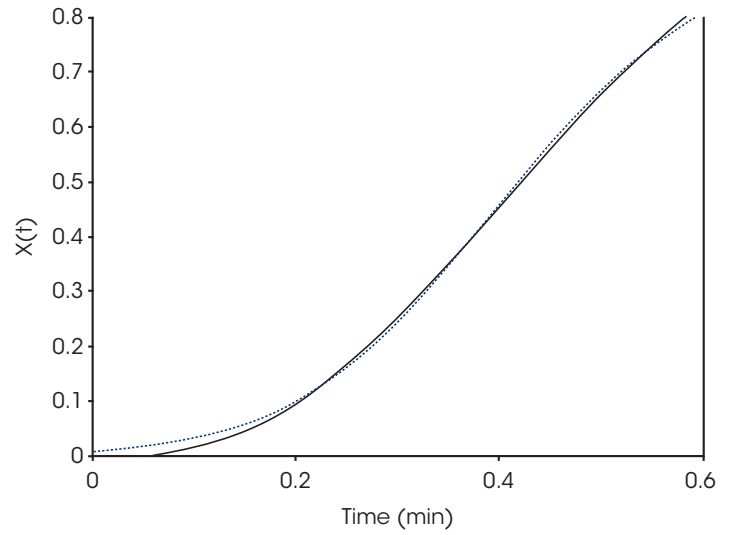


Figure 11. Example Avrami Fit for PPS; Cooling rate =20 °C / min, Isothermal hold at 310 °C

Table 3. Crystallization Kinetics Data for Polyphenylene Sulfide

Isothermal Temperature °C	310				320				350			
	20	10	5	2	20	10	5	2	20	10	5	2
Cooling Rate °C/min	20	10	5	2	20	10	5	2	20	10	5	2
Avrami Linear Fit												
T <sub>c</sub> (°C)	235.37	240.74	246.87	252.91	212.59	221.31	228.67	237.57	204.61	213.67	222.93	233.53
ΔH <sub>c</sub> (J/g)	57.10	59.03	58.86	61.99	53.33	54.57	55.36	58.68	51.56	53.83	55.70	56.42
T @ X(t) = 0.5	235.10	240.55	246.85	253.00	213.15	222.05	229.50	237.70	204.60	214.35	223.60	233.45
n	2.61	2.62	2.70	2.84	2.95	2.89	2.99	3.09	2.73	2.92	3.09	2.92
k (min <sup>-1</sup> )	6.60	1.48	0.47	0.05	1.54	0.31	0.05	0.00	1.23	0.26	0.03	0.01
t <sub>1/2</sub> (min)	0.42	0.75	1.16	2.50	0.76	1.32	2.39	5.79	0.81	1.40	2.64	5.12
τ (min <sup>-1</sup> )	2.37	1.34	0.86	0.40	1.31	0.76	0.42	0.17	1.24	0.71	0.38	0.20
Malkin Fit												
C0	37.30	37.05	41.48	53.36	54.61	50.66	60.46	68.20	41.68	55.58	72.74	55.40
C1 (min <sup>-1</sup> )	8.68	4.89	3.25	1.61	5.29	3.00	1.73	0.74	4.66	2.90	1.64	0.79
n	2.68	2.68	2.75	2.92	2.94	2.89	3.01	3.09	2.76	2.95	3.13	2.95
k (min <sup>-1</sup> )	6.98	1.50	0.46	0.05	1.53	0.31	0.05	0.00	1.24	0.26	0.03	0.01
t <sub>1/2</sub> (min)	0.42	0.75	1.16	2.50	0.76	1.32	2.39	5.78	0.81	1.40	2.64	5.12
τ (min <sup>-1</sup> )	2.36	1.33	0.86	0.40	1.31	0.76	0.42	0.17	1.23	0.71	0.38	0.20
Avrami Fit												
n	2.56	2.55	2.62	2.78	2.80	2.75	2.87	2.95	2.63	2.81	2.99	2.81
k (min <sup>-1</sup> )	6.34	1.46	0.48	0.05	1.49	0.33	0.06	0.00	1.22	0.27	0.04	0.01
t <sub>1/2</sub> (min)	0.42	0.75	1.15	2.49	0.76	1.31	2.38	5.77	0.81	1.40	2.63	5.10
τ (min <sup>-1</sup> )	2.38	1.34	0.87	0.40	1.31	0.76	0.42	0.17	1.24	0.72	0.38	0.20

## Crystallization Activation Energy

Crystallization activation energy calculated by the Avrami and Malkin models is summarized in Table 4. Activation energy calculated by Friedman's isoconversional method is summarized in Table 5 and plotted in Figure 12. The crystallization energy directly correlates with the isothermal temperature confirming that retained crystalline or other structure aids in nucleation. By implication properties correlated with crystallization will be affected by processing temperatures.

Table 4. Crystallization Activation Energy Calculated from Avrami and Malkin Macro Kinetic Models

Isothermal Temperature °C	310	320	350
	$\Delta E$ kJ mol <sup>-1</sup>	$\Delta E$ kJ mol <sup>-1</sup>	$\Delta E$ kJ mol <sup>-1</sup>
Malkin [ $\psi = \ln(C1)$ ]	-202.4	-164.1	-123.5
Avrami [ $\psi = 1/n \ln(k)$ ]	-212.2	-168.5	-128.7
Avrami Linear [ $\psi = 1/n \ln(k)$ ]	-212.3	-140.9	-120.8
Average R <sup>2</sup>	0.994	0.992	0.996

Table 5. Crystallization Activation Energy as Function of Conversion (Friedman Method)

Isothermal Temperature °C	310	320	350
X(t)	$\Delta E$ kJ mol <sup>-1</sup>	$\Delta E$ kJ mol <sup>-1</sup>	$\Delta E$ kJ mol <sup>-1</sup>
0.025	-279.4	-217.4	-175.8
0.05	-257.3	-202.2	-158.2
0.1	-241.7	-190.7	-148.1
0.2	-230.2	-176.3	-139.5
0.3	-217.9	-169.3	-132.2
0.4	-211.6	-168.2	-127.4
0.5	-201.2	-166.0	-122.4
0.6	-190.9	-163.7	-118.7
0.7	-185.3	-162.0	-116.0
0.8	-196.6	-157.4	-117.8
0.9	-227.6	-171.4	-94.8
Average R <sup>2</sup>	0.989	0.992	0.995

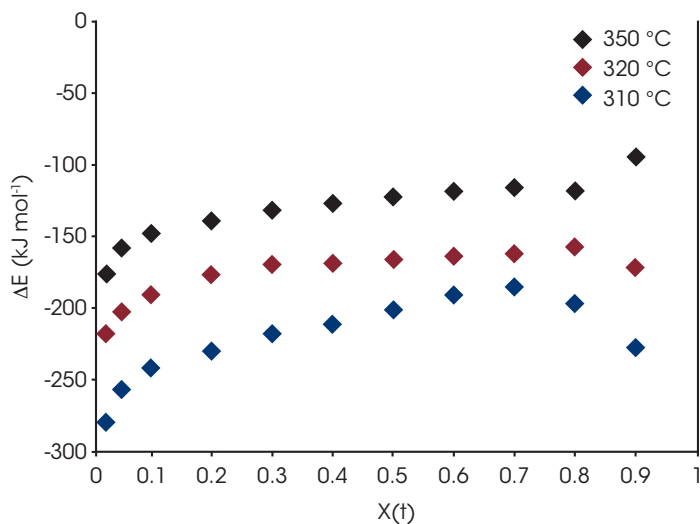


Figure 12. Crystallization Activation Energy as Function of Conversion

## CONCLUSION

A non-isothermal crystallization kinetics DSC experiment demonstrates the influence of retained structure on the crystallization properties of a semi crystalline polymer held at various temperatures isothermally above the melting temperature. This is an important consideration when evaluating potential molding and processing conditions for semi crystalline plastics and especially important if other factors such as chemical nucleators or fillers may be included in the formulation.

For more information or to place an order, go to <http://www.tainstruments.com/> to locate your local sales office information.

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