

# Modified Avrami Expression for Polymer Crystallization Kinetics

FERNANDO C. PÉREZ-CÁRDENAS, L. FELIPE DEL CASTILLO, and RICARDO VERA-GRAZIANO\*

Departamento de Polímeros, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, Coyoacán 04510, México D.F.

## SYNOPSIS

The Avrami equation has been widely used to describe polymer crystallization kinetics. However, the equation accurately fits experimental data only during the early stages of the crystallization process, and is unsuccessful in describing the entire process because it does not take into account secondary crystallization. Here we present a modified Avrami expression that describes polymer crystallization kinetics that takes into account both primary and secondary processes. The expression uses a new parameter introduced to indicate the fraction of material that has completed crystallization when the primary crystallization process has terminated. The theoretical results are in good agreement with experimental data.

## INTRODUCTION

It has been well established that there are two main processes during bulk polymer crystallization.<sup>1,2</sup> One called primary crystallization, PC, is characterized by the predominance of nucleation and a relatively fast growth of lamellar crystals. The other is called secondary crystallization, SC, which consists of both the crystallization of chains and chain segments between the crystalline structures already formed, and the crystallization of the amorphous intercrystalline areas.

Crystallization kinetics studies usually consider that the SC starts after the PC process has been completed. Here, we propose a different approach, where the SC starts before the PC is completed. The resulting model leads to a modified Avrami equation that better fits the experimental data.

## FORMULAE

The following model was established to obtain the Avrami equation. We suppose that the temperature

of a crystallizable polymer is raised to a value above its melting temperature,  $T_m$ . After equilibrium is reached, the time is set to zero, i.e.,  $t = 0$ . The polymer temperature,  $T$ , is then reduced at a slow rate to a value between  $T_m$  and the glass transition temperature,  $T_g$ , ( $T_g < T < T_m$ ). The weight fraction of crystallized polymer,  $x(t)$ , increases from zero,  $x(0) = 0$ , to a temperature-dependent value  $x(\infty)$ , generally after a very long time.

Considering first an ideal case in which only PC takes place, the following differential equation for crystallization kinetics is obtained:

$$\frac{dX(t)}{dt} = k_a n_a [1 - X(t)] t^{n_a - 1}, \quad (1)$$

where

$$X(t) = \frac{x(t)}{x(\infty)} \quad (2)$$

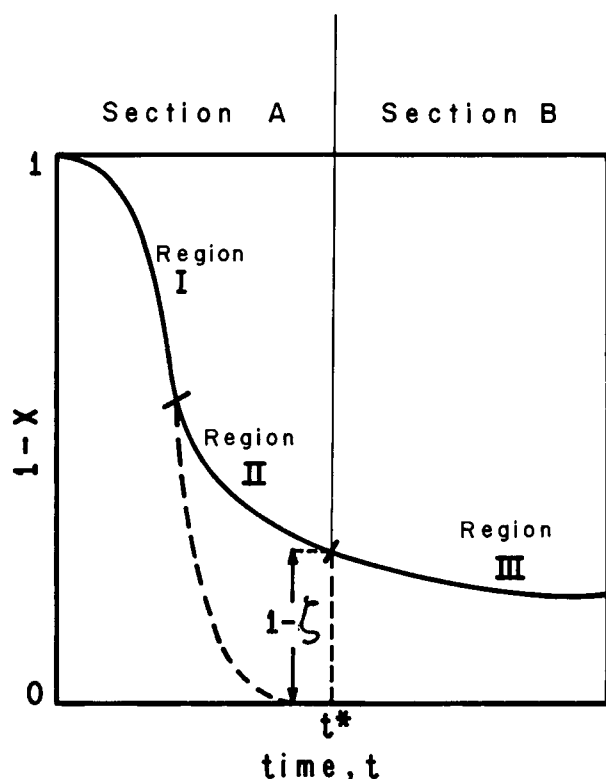
and  $k_a$  and  $n_a$  are the Avrami parameters that depend upon temperature as well as on nucleation and growth kinetics.<sup>3,4</sup> Since the Avrami parameters are assumed to be constant during the PC process, the following basic assumptions are involved: The nucleation is homogeneous and its time rate is constant. Together with that, the change of volume does

\* To whom correspondence should be addressed.

not appreciably affect the crystallization growth rate. The Avrami parameters are also independent of the presence of SC and the nature of the crystallization, e.g., the presence of the two phases of crystallization. Solving eq. (1) and rearranging terms, the following well-known Avrami expression is obtained.

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

To describe our modification, the typical polymer crystallization process is first divided into three regions as illustrated in Figure 1. The first region contains the start of PC, which proceeds at an accelerated rate, while SC is negligible. Here, eq. (3) well fits the experimental curve (solid line in region I of Fig. 1). In region II, the crystallization rate begins to slow down as the material available for crystallization is consumed. Within this region, SC becomes significant and PC and SC develop simultaneously. This combined process continues at a rather slow rate until PC is completed, and a pseudoequilibrium level of crystallinity is achieved.<sup>1,2</sup> During



**Figure 1** Comparison between a typical experimental isotherm for a crystallization process (solid line) and the Avrami equation (broken line). The three regions I, II, and III correspond to PC, PC and SC, and SC, respectively. Section A comprises regions I and II. Section B comprises only region III.

this combined process, eq. (3) predicts a much higher rate of crystallization (broken line in Fig. 1) than that seen experimentally. Finally, in region III the process continues at a very slow rate, due exclusively to SC.

For our purpose, the complete crystallization process is divided into two sections: (A) The first comprises region I (PC) and II (PC and SC); (B) the second comprises only region III (SC) (see Fig. 1).

We now describe how inclusion of SC into the first section A leads to a modified Avrami equation that fits quite well the experimental data.

By taking into account PC and SC,  $X(t)$  can be expressed as the sum of two terms:

$$X(t) = X_p(t) + X_s(t), \quad (4)$$

where  $X_p$  and  $X_s$  are the weight fractions of polymer crystallized by PC and SC, respectively. Let  $\zeta$  be the weight fraction of the polymer that has crystallized by PC and SC at the moment that PC terminates (end of region II), so that  $[1 - \zeta]$  represents the fraction that corresponds to the process where only SC is present (region III). Under these assumptions, PC will be governed by:

$$\begin{aligned} \frac{dX_p(t)}{dt} &= kn[1 - X(t) - (1 - \zeta)]t^{n-1}H[\zeta - X(t)] \\ &= kn[\zeta - X(t)]t^{n-1}H[\zeta - X(t)], \end{aligned} \quad (5)$$

where  $k$  and  $n$  depend on the temperature, on nucleation, and on growth nature; and  $H[\zeta - X(t)]$  is the Heaviside step function defined as:

$$\begin{aligned} H[\zeta - X(t)] &= 1, & X(t) &\leq \zeta; \\ H[-X(t)] &= 0, & X(t) &> \zeta. \end{aligned}$$

Here it has also been assumed that the processes responsible for SC obey a differential equation similar to eq. (1), of the form:

$$\frac{dX_s(t)}{dt} = k'n'[1 - X(t)]t^{n'-1}, \quad (6)$$

where  $k'$  and  $n'$  are also temperature-dependent parameters. Equation (6) implies that SC takes place during all the crystallization process.

By using eqs. (4)–(6), one can obtain:

$$\begin{aligned} \frac{dX(t)}{dt} &= kn[\zeta - X(t)]t^{n-1}H[\zeta - X(t)] \\ &\quad + k'n'[1 - S(t)]t^{n'-1}, \end{aligned} \quad (7)$$

which takes into account both PC and SC.

As a result of

$$\frac{d(1-X)}{dt} = -\frac{dX}{dt} \quad (8)$$

eq. (7) becomes:

$$\frac{d(1-X)}{dt} + (knt^{n-1} + k'n't'^{n'-1})(1-X) = kn(1-\zeta)t^{n-1}. \quad (9)$$

The solution of eq. (9) is divided into two parts,<sup>5</sup> according to the limits of the Heaviside step function:

$$1-X(t) = \exp(-kt^n - k't'^n) [kn(1-\zeta) \times \int_0^t \exp(k\tau^n + k'\tau'^n) \tau^{n-1} d\tau + 1] \quad (10a)$$

and

$$1-X(t) = (1-\zeta)\exp(k't'^n)\exp(-k't'^n). \quad (10b)$$

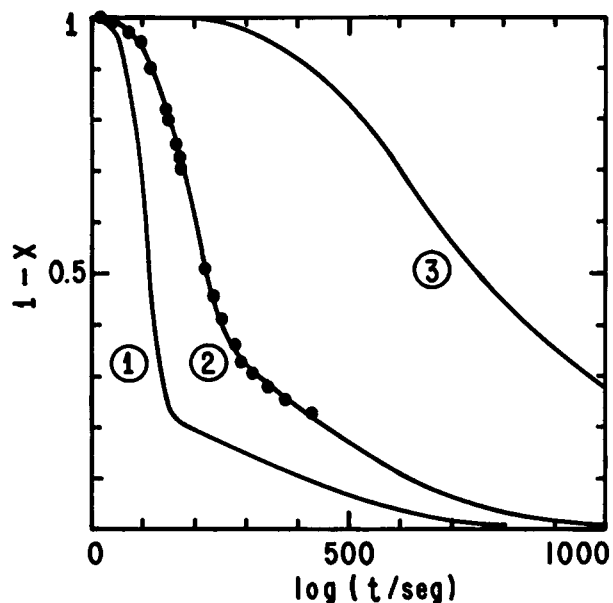
Equation (10a) is valid only for  $X(t) \leq \zeta$ , and eq. (10b) for  $X(t) > \zeta$ , where  $t^*$  satisfies  $\zeta = X(t^*)$ .

Equations (10a) and (10b) describe the complete crystallization process. But now, instead of having the two Avrami parameter  $k_a$  and  $n_a$ , there are five parameters with sound physical meaning:  $k$  and  $n$  depend on the temperature, nature of nucleation, and the fast growth; the SC parameters  $k'$  and  $n'$  depend on the conditions under which the slow crystallization of remaining amorphous regions takes place; and a fifth parameter,  $\zeta$ , indicates the weight fraction of material crystallized up to the moment PC ends.

As can be seen, eq. (10a) resembles the one obtained by Hillier<sup>6</sup> to describe PC, a work explaining crystallization kinetics of spherulitic polymers, although his parameters are somewhat different.

## FITNESS WITH EXPERIMENTAL DATA

In Figure 2, three curves obtained from eqs. (10a) and (10b) are presented, together with points representing experimental data (from Ref. 7) that correspond to isothermal crystallization from the melt of a linear polyethylene at 128°C. The experimental data are accurately predicted with a theoretical curve



**Figure 2** Solid lines represent theoretical isotherms from eqs. (10a) and (10b). Points represent experimental data from Ref. 7.

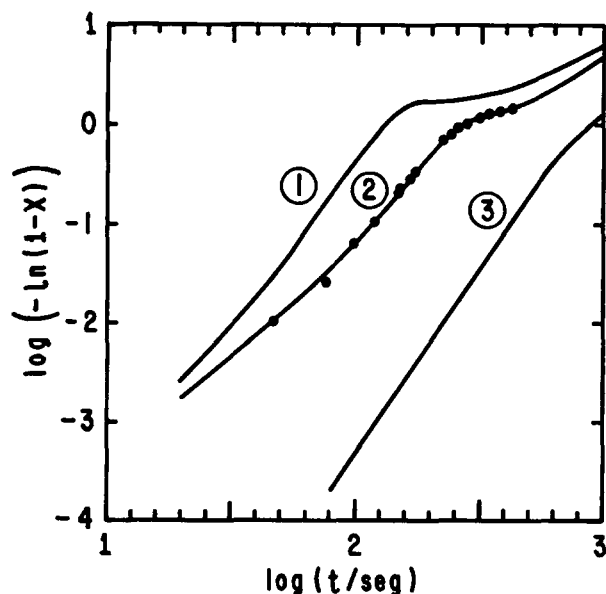
whose parameter values are:  $n = 4$ ,  $k = 3.7 \times 10^{-10}$ ,  $n' = 2$ ,  $k' = 4 \times 10^{-6}$ , and  $\zeta = 0.68$ .

When  $\log[-1n(1-X)]$  is plotted as a function of  $\log(t)$ , the Avrami equation is represented by a single straight line, whereas, eqs. (10a) and (10b) are generally shown by curves that can be approximated by two Avrami-type equations. This is demonstrated in Figure 3, where the same theoretical curve and experimental data are presented. The experimental curve shows two linear sections that can be described by two Avrami-type equations. This behavior has also been reported by Grebowics et al.<sup>8</sup> in a paper related to Condis crystal formation. Some experimental data from Ref. 9 adjust to this type of kinetics.

## CONCLUSION

By taking into account SC in the initial stages of crystallization, a modified Avrami-type set of eqs. (10a) and (10b) are obtained, which are similar to the two Avrami-type behaviors reported by Grebowics for bulk polymer crystallization.

The new parameter  $\zeta$  is introduced to indicate the weight fraction of material crystallized up to the moment PC ends and serves to indicate the point at which the two Avrami-type equations reported by Grebowics intersect. It should be noted that in our formulation  $\zeta = 1$  results in the normal simple Avrami equation.



Parameter Values

Curve	$n$	$k$	$n'$	$k'$	$\zeta$
1	4	$5 \times 10^{-8}$	2	$5 \times 10^{-6}$	0.8
2	4	$3.7 \times 10^{-10}$	2	$4 \times 10^{-6}$	0.68
3	4	$3 \times 10^{-12}$	3.5	$3 \times 10^{-6}$	0.58

Figure 3 The same curves as in Figure 2, but in logarithmic form.

Although our eqs. (10) involves five parameters instead of four, as in the case of the two Avrami

equation description, all our parameters have sound physical meanings related to PC and SC. The fifth parameter,  $\zeta$ , is necessary to obtain a complete description of the crystallization process.

The authors are grateful to Lucia Vera-Graciano for her support during the translation of the manuscript from Spanish into English.

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Received June 28, 1990

Accepted December 12, 1990