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Review

Crystallization kinetics of homopolymers: overall crystallization: a review

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This paper is dedicated to the memory of Professor John D. Ferry, a fine gentlemen, an outstanding scholar who has made major and seminal contributions to polymer science

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Abstract

This paper is a brief review of the overall crystallization kinetics of synthetic homopolymers. The basic experimental results are presented and compared with theory that is currently available. It is found, surprisingly, that the more sophisticated theories do no better in explaining experimental results than does the free-growth approximation. This is contrary to what is observed for the crystallization of low molecular weight substances. The reason can be attributed to entanglements and other topological defects that are present in the pure melt and are relegated to the non-crystalline regions as crystallization progresses. This results in a more protracted crystallization than is predicted and is yet to be included in theory.

Keywords: Overall crystallization; Crystallinity level; Entanglements; Topological defects; Free growth; Impingement

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Contents

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1. Introduction

Long chain molecules of sufficient structural regularity can crystallize under suitable condition. Crystalline polymers display three-dimensional order similar to that of crystalline low molecular weight substances and follow all the dictates of a first-order phase transition [1]. Major changes in both microscopic and macroscopic are observed upon the transformation from the liquid, or conformationally disordered state, to the crystalline. However, rarely if ever is the development of crystallinity complete in polymers. The extent of the transformation can vary from 10% to 90% depending on the polymer, the molecular weight and crystallization temperature [2]. In effect, therefore, one is always studying and dealing with a non-equilibrium or metastable state. For example, the normal alkane, $C_{94}H_{190}$, can only be supercooled a fraction of a degree. On the other hand, even a low molecular weight fraction of linear polyethylene has to be

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cooled 15° to 20° below its melting temperature in order for crystallization to proceed at a reasonable rate. The fact that crystallization has to be carried out well-removed from the melting temperature leads to the non-equilibrium state. The reason for this is the high interfacial free energy involved in the nucleation process.

All properties of a crystalline polymer, be it thermodynamic, spectroscopic, physical or mechanical ones, depend on the details of the structure and morphology that evolve from the melt. Thus, understanding crystallization mechanisms is a key to understanding properties. Studies of crystallization kinetics can lead to an understanding of mechanism. There are several experimental methods that can be used to study different aspects of the kinetics. Overall crystallization kinetics can be studied by density, enthalpy of fusion and spectroscopic methods among others. Spherulite growth rates can be investigated using either optical microscopy or small-angle light scattering. In a few favorable cases, the growth of specific crystallographic faces can be measured. All of the major methods for studying crystallization kinetics complement one another [2].

In the present paper, status and understanding of the overall crystallization kinetics of homopolymers from the pure melt will be reviewed. Typical experimental data will be presented. A comparison will be made between experiment and the available theory. Important problems that are still in need of resolution will be emphasized. Although John Ferry did not work directly in the area of crystalline polymers, the shortcoming of theory can be directly related to problems concerned with the structure of the residual melt and of the non-crystalline polymer. This is any area where he has made substantial contributions.

2. Theoretical background

Based on experimental studies cf. seq., it is clear that polymer crystallization involves nucleation and growth processes. Therefore, the theories that have been developed depend on these concepts as developed for monomeric systems and adopted to polymers. One starts with what is known as the "free growth" theory developed by Gõler and Sachs. Details of the development of this theory can be found in Refs. [2,3]. In this case, once initiated a given center grows unimpeded by the initiation and growth of other centers. We let N' be the steady-state nucleation rate per unit of untransformed mass. If $w(t,\tau)$ is the mass of a given center at time t, that was initiated at time $\tau(\tau \leq t)$ then:

$$1-\lambda(t)=\int_0^t w(t,\tau)N'(\tau)\lambda(\tau)\mathrm{d}\tau \tag{1}$$

Here, $\lambda(\tau)$ is the fraction untransformed at time τ. Alternatively Eq. (1) can be written as:

$$1-\lambda(t)=\frac{\rho_c}{\rho_1}\int_0^t v(t,\tau)N(\tau)\lambda(\tau)\mathrm{d}t \tag{2}$$

where $N(\tau)$ is the nucleation frequency per untransformed volume, $v(t,\tau)$ is the volume of a growing center and ρ_c and ρ_1 are the densities of the crystalline and liquid phases, respectively. In order to solve the integral equation given by Eq. (2) it is necessary to specify the details of the nucleation and growth rate. We take as a simple example the case where the nucleation rate $N(\tau)$ is a constant equal to N and the growth rate, G, is linear and isotropic in three dimension. Under these conditions, the solution of the integral equation (Eq. (2)) is given by:

$$1(t)=1-\cosh k_3t\ \cos k_3t \tag{3}$$

where $(k_3{=}(3/2Nf_3G_3)^{1/4}$ and f_3 is the shape factor.

Similar equations can be derived for two and three-dimensional growth and other types of nucleation [2,3]. There is, however, a fundamental problem with these equations and the assumptions upon which they are based. Eq. (3), and those for other types of growth and nucleation, do not provide a natural termination to the crystallization process, since real solutions exist for $1-\lambda(t)>1$. Therefore, their use must be restricted to $1-\lambda(t)=1$.

For the initial portion of the transformation the rate equation can be expanded in series in terms of k_3t. When the first two terms of the expansion are retained Eq. (3) becomes:

$$1-\lambda(t)\cong(k_3t)^4/4 \tag{4}$$

for three-dimensional growth. The corresponding expression for two- and one-dimensional growth become:

$$1-\lambda(t)\cong(k_2t)^3/6 \tag{5}$$

and

$$1-\lambda(t)\cong(k_1t)^2/2 \tag{6}$$

respectively.

The Gőler–Sachs formulation has the obvious shortcoming in that no mechanism has been introduced to terminate the transformation. This problem is of serious concern not only for the crystallization of polymers, but for low molecular weight substances as well. Some mechanism for terminations needs to be introduced into the analysis. One factor that needs to be taken into account is the mutual interference of growing crystallites that originate from different nuclei. When two crystallites impinge upon one another, a common interface develops and growth will cease along the interface. This is a natural mechanism that will cause crystal growth to cease. The initial treatment of this effect as crystallization kinetics was given by Johnson and Mehl [4], Avrami [5–7] Evans [8] among others. The results of these investigators were essentially the same. We shall discuss the Avrami approach in some detail, since it has been the one most widely applied to polymers.

The result of Avrami's analysis is given by:

$$1 - N(t) = 1 - \exp - \frac{\rho_c}{\rho_l} \int_0^t v(t,\tau) N(\tau) \mathrm{d}\tau \qquad (7)$$

Eq. (7) is the general, or basic Avrami relation. Only an integral needs to be evaluated by specifying the nucleation and growth laws that are operative. There are obviously many different possibilities that can be considered, resulting in a wide variety of expressions. These should be considered to be derived Avrami equations. Selecting the same conditions used previously in analyzing the free-growth expression, constant nucleation rate and constant linear growth, one obtains:

$$1 - \lambda(t) = 1 - \exp(-kt^n) \qquad (8)$$

Although Eq. (8) is commonly termed the Avrami equation it is actually only a derived expression that is based on a specific set of assumptions. The exponent n is usually termed the Avrami exponent. It is not unique, and represents the nucleation and growth processes. For a constant nucleation rate, n=4 for three-dimensional linear growth. It is equal to 3 for two-dimensional growth and 2 from one-dimensional growth for the same nucleation process. When fitted to the early stages of the transformation, it has been shown that the exponent n does in fact represent the morphology that is evolving [2]. Eq. (8) reduces to:

$$1 - \lambda(t) = kt^n \qquad (9)$$

for small times. Eq. (9) has the same form as Eqs. (4), (5) and (6), deduced from the free-growth expression. Eq. (8) can also be written as:

$$\ln(1 - \lambda(t)) = k + n \ln t \qquad (10)$$

It is tempting to use Eq. (10) to analyze experimental data. However, caution must be exercised in using this equation since it is extremely sensitive toward the end of the transformation to small experimental errors. Interpretive errors can easily be made. It is preferable to actually fit the experimental results to one of the derived Avrami expressions.

The Avrami procedure has to be modified in order to account for the incomplete transformation in polymers. An arbitrary normalization procedure was introduced that followed the Avrami framework [9]. It was found that:

$$\frac{1 - \lambda(t)}{1 - \lambda(\infty)} = 1 - \exp\left(1 \frac{-1}{1 - \lambda\infty} kt^n\right) \qquad (11)$$

where $1-\lambda(\infty)$ represents the final level of crystallinity that is attained. The normalization procedure that has been proposed to adapt the Avrami equation to polymer is a formal one. The unique structural feature of polymers, in particular the connectivity of chain units and the structure of the melt, has not been explicitly taken into account.

It is of interest at this point to compare the isotherm that are predicted by the derived Avrami (Eq. (8)) and the free-growth of Gőler–Sachs. A comparison is given in Fig. 1 for the case of n=4 [10]. In this case, the isotherms are virtually identical to about 30% of the transformation. The difference between the two remains small up to about 70% of the transformation and is well within experimental error. At the higher levels of the transformation there is a significant difference in the two isotherms. The Avrami isotherm becomes more protracted reflecting the influence of the termination process. In contrast, when n=1 agreement is only found for the first 10% of the transformation. In

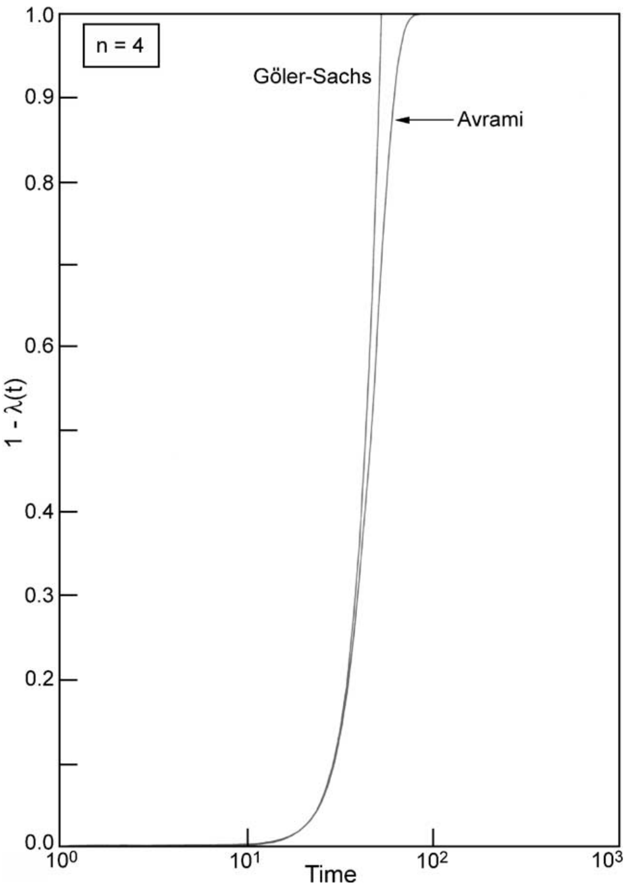

Fig. 1. Comparison of theoretical isotherms for Gőler–Sachs and derived Avrami for exponent n=4 [10].

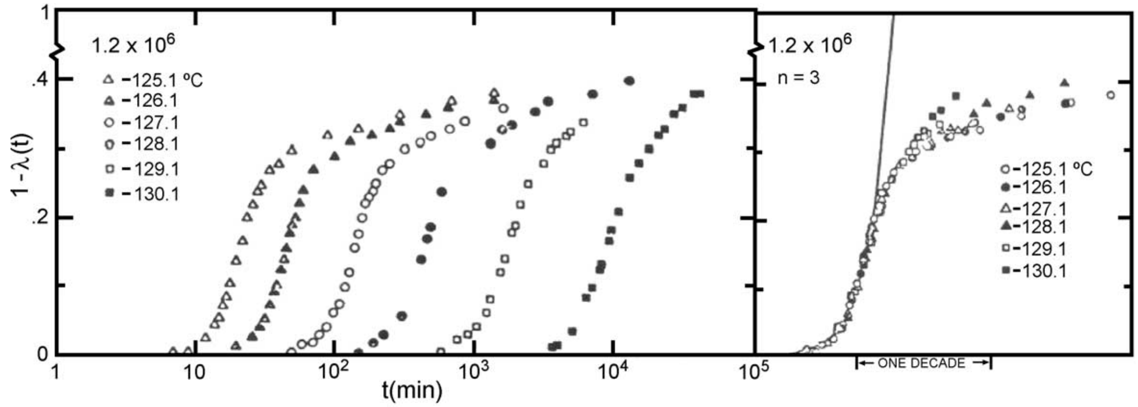

Fig. 2. (Left) Plot of degree of crystallinity, $1-\lambda(t)$, against log t at indicated temperatures for a molecular weight fraction of linear polyethylene, $M_w=1.2\times10^6$. (Right) Superposed isotherms. Solid line derived Avrami expression with $n=3$ [3].

summary, the two theories give essentially the same results at low levels of crystallinity. As the transformation progresses, however, differences are predicted depending on the value of the exponent n. One is now in the position to analyze experimental results in terms of the background that has been developed.

3. Experimental results

Fig. 2 gives a set of crystallizing isotherms for a molecular weight fraction, $M_w=1.2\times10^6$, of linear polyethylene [3]. (Here, $1-\lambda(t)$ is plotted against $\ln t$.) Such a set of isotherms is typical of homopolymers. The equilibrium melting temperature for linear polyethylene is 145.5 °C. Thus, in this case the crystallization is carried out at undercoolings in the range 15–20°. Some important characteristics of the crystallization process are illustrated in this figure. There is an apparent induction period before crystallinity is detected. This time period is primarily a measure of the sensitivity of the method that is being used to detect crystallinity. In this time frame transient nucleation followed by steady-state nucleation is taking place. The induction period is followed by an autocatalytic process resulting in a sigmoidal shape isotherm. An isotherm of this type is characteristic of nucleation and growth processes. It is found in all types of substances. In particular, it is an inherent property of homopolymer crystallization. The transformation is concluded by a long tail portion that represents the development of extremely small amounts of crystallinity over many decades of time [3].

The fact that the sigmoidal shape isotherms are characteristic of nucleation and growth processes is a very important conclusion. Although there are many problems involving the crystallization of polymers that are still in need of resolution, the importance of nucleation and growth cannot be ignored, neglected, or relegated to minor importance.

Another important and typical feature found in these isotherms is the marked negative temperature coefficient of the crystallization rate. In the example illustrated, the time scale varies by about three orders of magnitude for only a 5° change in the crystallization temperature. Such drastic change in rate with temperature is typical of nucleation in the vicinity of the equilibrium melting temperature. Typically, as illustrated in the right hand side of the figure, the isotherm can be superposed one upon the other merely by shifting them along the horizontal axis. This procedure indicates that there is a reduced time–temperature variable, as is found in all homopolymers.[1]

When the crystallization of many polymers is conducted over a wide temperature range, a maximum in the rate results. This behavior was first shown by Wood and Bekkedahl [11] in their classical study of the crystallization kinetics of natural rubber. Such maxima have since been found in a variety of polymers. The maximum results from the competition between the nucleation rate and the transport term in the expression for the rate of crystallization. The transport term becomes small and then nonexistent as the glass temperature is approached. On the other hand, the nucleation rate becomes very rapid at low temperatures with a marked decrease in sensitivity to crystallization temperature.

The curve drawn in the right hand figure represents the best fit of the derived Avrami equation with $n=3$. The experimental results adhere to this expression for about half of the transformation. As crystallinity proceeds beyond this point the crystallization becomes more protracted. Eventually, the crystallization becomes very slow. This isotherm is rather flat in this "tail" portion of the isotherm. For this polymer the final level of crystallinity that is attained is about 0.4 and deviations are found at crystallinity levels of about 0.2. Such deviations from Avrami are found in other fractions of linear polyethylene, and other homopolymers as well, from about half to two-thirds of complete transformation. A crucial matter is to ascertain the reason for the deviations.

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[1] This superposition is not found in the random type copolymer because of the changing melt composition as crystallization proceeds isothermally [2].

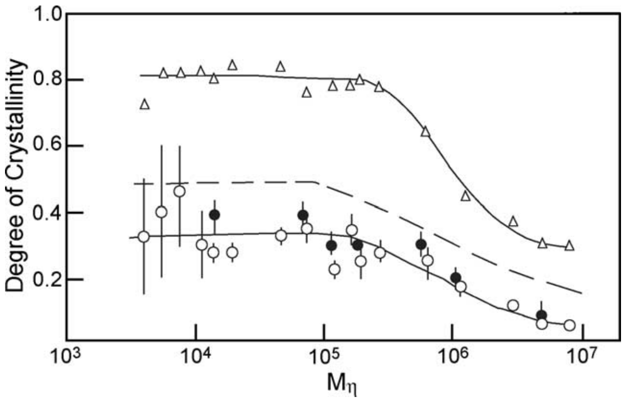

Fig. 3. Plot of crystallinity level as a function of molecular weight for linear polyethylene fractions. Pseudo equilibrium level of crystallinity that is attained △; crystallinity level at which deviation occurs from theory: Gőler–Sachs ●; Avrami O. Dashed curve represents ratio of crystallinity level at which deviation occurs to that actually attained [2].

As a point of reference, it is illustrative to compare the deviation from theory between the free growth expression and the derived Avrami. The result of such a comparison is given in Fig. 3 for molecular weight fractions of linear polyethylene [2]. The crystallinity levels are plotted against molecular weight for different situations in this figure. The influence of molecular weight on the crystallinity level that is attained at an isothermal crystallization temperature is quite profound. This crystallinity level remains constant until $M \approx 10^5$. A precipitous drop then occurs with a further increase in chain length. Of particular interest in terms of crystallization kinetics is that the deviation from either the Avrami or free-growth expressions follow a similar pattern. Most important and striking is the fact that both theories give the same result. Thus, as far as agreement between theory and experiment is concerned the free growth approximation does just as well as Avrami or similar expressions. The crystallization kinetics of poly(ethylene oxide) follow a similar pattern [12]. Studies with single molecular weight samples of many other polymers lead to a similar conclusion [2]. It becomes clear from these experimental results that other factors, beside the Avrami termination mechanism, must be involved in polymer crystallization.

The strong influence of molecular weight on the crystallization kinetics yields a clue as to why the free growth concept is adequate at the early sages of the crystallization and that deviations occur from the Avrami theory as the transformation progresses. The initial melt, prior to the onset of crystallization, contains topological defects such as entangled chains, loops and knots. These structures cannot participate in the crystallization and are relegated to the non-crystalline regions as the transformation progresses. The concentrations of such units are molecular weight dependent. Moreover, there will also be a region around these defects that are also non-crystallizeable. Thus, as crystallinity progresses the concentration of potentially transformable units will decease relative to the number of non-crystalline ones. Therefore neither the nucleation nor growth rate will be constant with the extent of the transformation. Consequently, the level of crystallinity that can be attained will decrease with molecular weight.

The crystallization kinetics of poly(dimethyl siloxane) (M_n=740,000) from the melt is a good example of the influence of chain entanglements. For this case, the derived Avrami equation with n=3 accounts for 95% of the transformation [13]. This is quite an unusual result for the crystallization of a homopolymer from the pure melt. However, it can be explained by the fact that the molecular weight between entanglements for poly(dimethyl siloxane) is 12,000 as compared with 830 for linear polyethylene [14].

When linear polyethylene is crystallized at high temperature under elevated pressure, a crystallinity level of about 0.90–0.95 is achieved. Upon fusion, the entanglement concentration in the pure melt will be low or non-existent. There is a time interval, of about 30 min in the melt, before the conventional entangled melt is regenerated. Galeski et al. [15] took advantage of this fact to study the crystallization kinetics in this time interval. They found a significant enhancement on the crystallization rate relative to that of the conventional melt of the same polymer.

Studies of polymers that were originally freeze-dried from dilute solution demonstrate quite vividly the role of chain entanglements in retarding the crystallization rate. Samples prepared in this manner contain a minimal concentration of entanglements sine they were prepared from dilute solution. It was found that the freeze-dried samples crystallized much faster than the untreated polymer. An example of this enhancement is illustrated in Fig. 4 for

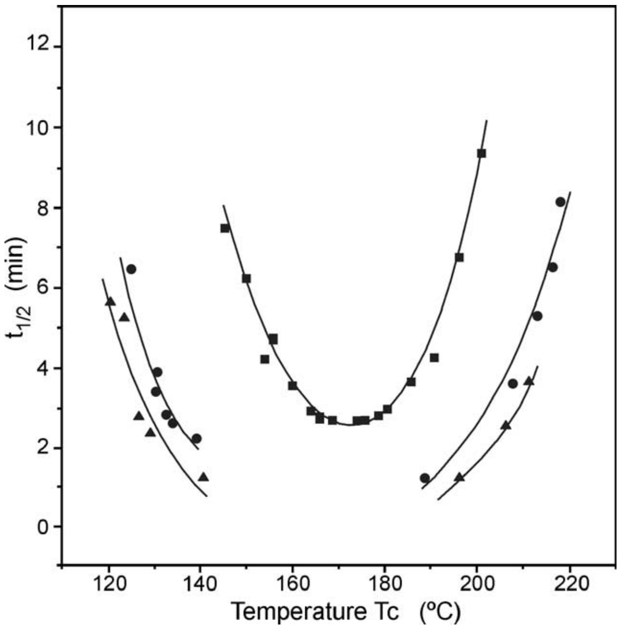

Fig. 4. Plot of half-time, $t_{1/2}$, of the crystallization of isotactic poly(styrene) as a function of the crystallization temperature, ■ bulk polymer; ● 1×10^{-1} wt.% freeze dried solution, ▲ 1×10^{-2} wt.% freeze dried solution [16].

the crystallization of a freeze-dried sample of isotactic poly(styrene) [16]. Isotatic poly(styrene) shows a maximum in the rate (minimum in the half time). The half-times for crystallization are reduced 8–10 fold as a consequence of the freeze drying and minimizing the role of entanglements. This is a substantial enhancement of the crystallization rate. The freeze-drying of dilute solution of isotactic poly9propylenes leads to similar results [17].

It has been argued, based on calculations, that entanglements in the melt present no impediment to a growing crystal front so that they play a negligible role in the crystallization process [18,19]. Theory has shown that chain entanglements influence many physical and structural properties [20,21]. The evidence cited above indicates a strong influence of entanglements on the crystallization rate. Further evidence for the importance of entanglements is found when the role of molecular weight is examined in more detail.

Fig. 5 gives a set of isotherms, that are superposed to 127 °C, for the crystallization of the indicated molecular weight fraction of linear polyethylene. Here, the absolute level of crystallinity is plotted against log time. The solid curve represents the derived Avrami expression for n=3. The crystallinity level at which deviations occur from the Avrami theory decreases as the molecular weight increases.

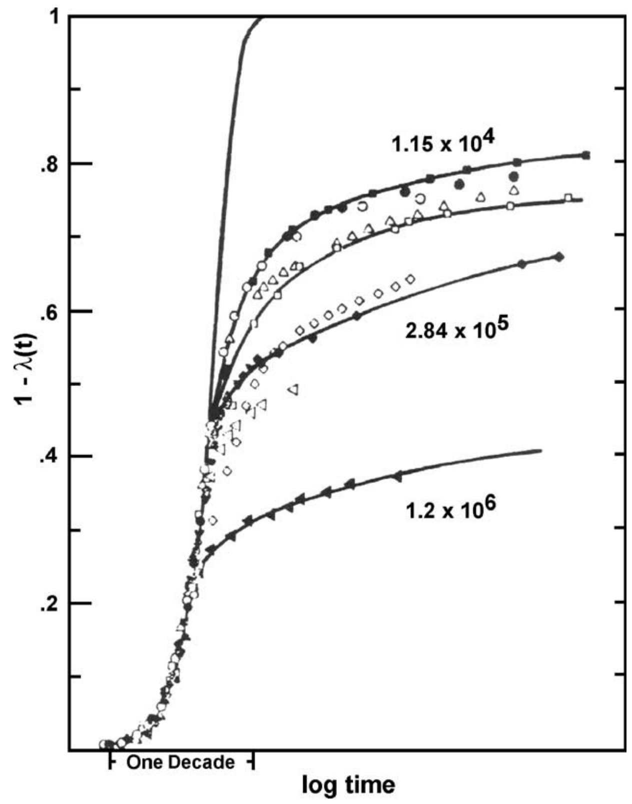

Fig. 5. Plot of degree of crystallinity, $1-\lambda(t)$, against log time for indicated molecular weight fractions of linear polyethylene. Isotherms for each molecular weight superposed to 127 °C. Theoretical curve derived Avrami, n=3 [3].

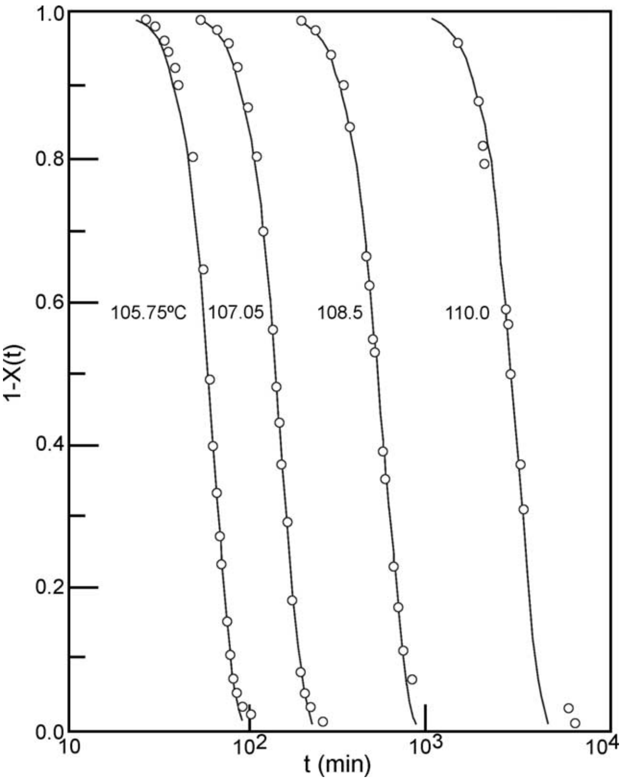

Fig. 6. Plot of the relative extent of transformation, $\lambda(t)$ against log time for a molecular weight fraction of linear polyethylene, $M=3\times10^5$, in crystallizing from n-hexadecane solution at a concentration of 0.555 g/100 ml. Temperature of crystallization indicated for each isotherm. Solid curves derived Avrami equation with n=4. From Ref. [23].

For example, the deviations occur at a crystallinity level of about 0.20 for $M=1.2\times10^6$ and monotonically increases to about 0.55 for $M=1.15\times10^4$. There is a direct correlation between the deviation level and the final level of crystallinity that is attained. The same factor that restricts the use of the Avrami theory limits the final crystallinity level. Similar results have been found in poly(ethylene oxide) [2] and poly(tetra-p-silphenylene siloxane [22]. This type behavior appears to be general for homopolymers crystallized from the pure melt.

Another way by minimizing the presence of chairs entanglements is to crystallize from dilute solution. A set of isotherm for a molecular weight fraction of linear polyethylene crystallizing from a dilute n-hexadecane solution is given in Fig. 6 [23]. These are typical isotherms for crystallization from dilute solution. The theoretical derived Avrami equation, for n=4, is given by the solid curves in the figure. Inspection of this figure clearly indicates extraordinarily good adherence between the experimental data and the Avrami formulation over the complete extent of the transformation. Only trivially small deviations are observed at the very end of the transformation. These results are in marked contrast to the crystallization from the pure melt of a similar faction. Thus, when entanglements and other topological defects are absent, the Avrami theory is followed exactly. This is contrary to what is observed in bulk crystallization.

4. Discussion and conclusion

The analysis of the experimental results described above indicates that for bulk crystallized homopolymers there is no significant gain is using the Avrami formulation over the free-growth approximation. The impingement concept, the key portion of the Avrami theory, has substantially improved the fitting of the crystallization of metals and other monomeric systems. However, with rare exception, it has not done so for polymers. One can conclude that the retardation and cessation of crystal growth in polymers is not due, in the main to the impingement of growing centers. This is true even when the incomplete transformation is taken into account. Therefore one must seek other reasons that are unique to polymers, for the cause for the retardation in rate expected from the Avrami theory.

The realization early on that the derived Avrami equation does not account for the isotherms over the complete transformation has led to many proposed modifications [24–34]. The proposals are primarily concerned with either the modification of the impingement process, on the introduction of several different nucleation and growth processes that occur in either series or parallel, or the arbitrary variation of the nucleation and growth rate as the transformation progresses. Major improvements between theory and experiment have not been achieved by these proposals. The rate of entanglement, and other topological defects, have not as been explicitly taken into account in a quantitative manor. Incorporating the role of entanglements into the theory of overall crystallization of homopolymers has not as yet been accomplished. An important part of resolving this problem is understanding the detailed structure of molten polymers in general and the amorphous portion of crystalline ones in particular. John Ferry, with his background and scientific contributions, would have been in a strong position to make major contributions to the resolution of the problem, now that the nature of the problem has been clarified.

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