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Crystallization kinetics of homopolymers: bulk crystallization

9.1 Introduction

In discussing the crystalline state of polymers the concern up to now has been primarily with equilibrium concepts and expectations. Although the fusion of polymers is well established to be a problem in phase equilibrium, stringent experimental procedures must be employed to approach the necessary conditions. It is concluded from equilibrium theory that for homopolymers of regular structure high levels of crystallinity should be attained.(1) However, this conclusion is contrary to usual experience. Since the crystalline phase only develops at a reasonable rate at temperatures well below the equilibrium melting temperature, the state that is actually observed in a real system is a nonequilibrium one. The constitution and properties of the state that is achieved are the result of the competition between the kinetic factors involved in the transformation and the requirements for thermodynamic equilibrium. In a formal sense one is dealing with a metastable state. This generalization is not unique to polymer crystallization. It also holds for a vast majority of substances that undergo a liquid to crystal transformation. For polymers, however, kinetic control is the dominant factor. For example, the crystallization from the melt of an *n*-alkane of about one hundred carbon atoms occurs extremely rapidly at a temperature just infinitessimally below its equilibrium melting temperature. On the other hand, a comparable crystallization rate in a low molecular weight linear polyethylene fraction of the same molecular weight is only achieved at undercoolings of about 25 °C. Polymer crystallization only occurs at a reasonable rate at temperatures well below the equilibrium melting temperature. The reasons for this behavior will emerge from the discussion of crystallization kinetics that ensues.

Kinetic studies, by their nature, represent a general type of experimental observation. Therefore, caution must be exercised in deducing specific molecular mechanisms from kinetic data. Very often several different mechanisms can explain the same experimental results. Despite this restraint it is possible, with care,

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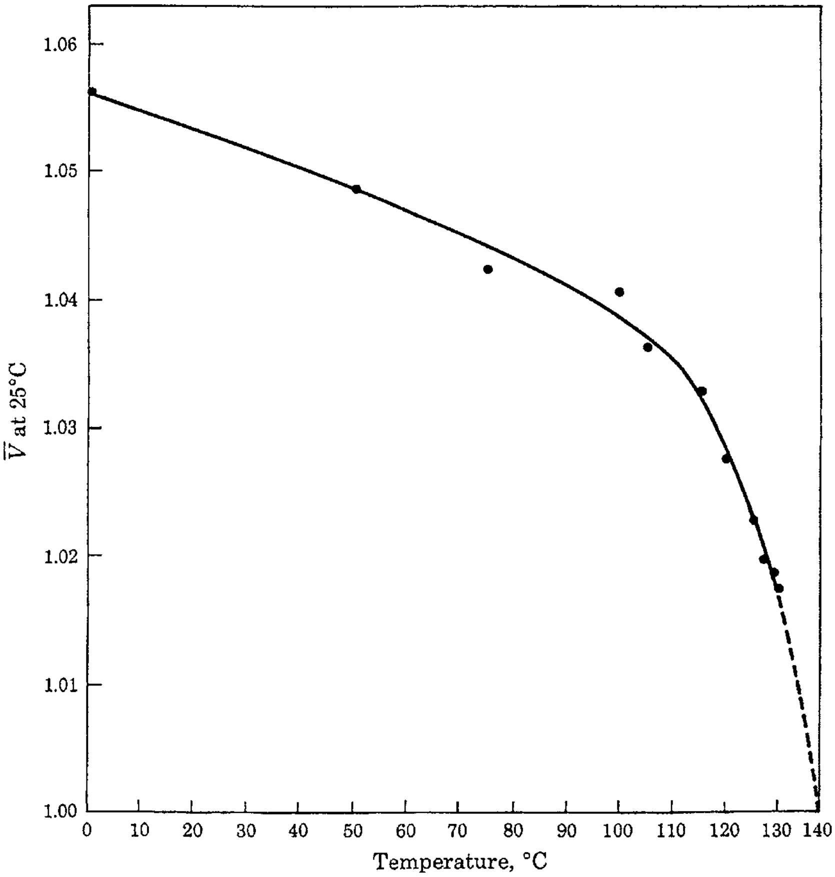

Fig. 9.1 Plot of specific volume at 25 °C for an unfractionated linear polyethylene (Marlex50) against the crystallization temperature. Time of crystallization is adjusted so that the crystallization is essentially complete at the specified temperature.(2)

to deduce some of the salient features that are important to the understanding of the crystallization process in polymers. Although the general results that are obtained are important, any specific deductions that are made are not necessarily unique. The possibility of different interpretations always needs to be recognized.

There are many examples that demonstrate that polymer properties depend on the crystallization conditions, and thus the crystallization kinetics. This generalization can be illustrated by examining some simple properties. In Fig. 9.1 the specific volume at 25 °C of an unfractionated linear polyethylene is plotted against the crystallization temperature.(2) In this example the crystallization was conducted isothermally from the pure melt. The times of crystallization were adjusted so that no significant crystallization occurred on cooling, prior to the specific volume

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measurement. For crystallizations carried out at relatively low temperatures, the specific volumes varied from 1.06 to 1.04 $\text{cm}^3\ \text{g}^{-1}$. These values are in the range usually reported for this polymer. However, as the crystallization temperature is raised a sharp decrease in the specific volume occurs. This quantity is now sensitive to small changes in the crystallization temperature. The lower values are indicative of the high levels of crystallinity that are achieved as the crystallization is conducted at temperatures closer to the melting temperature. The extrapolation of the plot in Fig. 9.1, as indicated by the dashed curve, portends the distinct possibility that at still higher crystallization temperatures even lower specific volumes would be observed. For crystallization conducted at the melting temperature, a specific volume of about 1.00 $\text{cm}^3\ \text{g}^{-1}$ is predicted. This value is very close to the density of the completely crystalline polymer as deduced by Bunn from the x-ray determination of the unit cell of polyethylene.(3) It implies the formation of a nearly perfect macroscopic single crystal under these crystallization conditions. Experimental confirmation of the extrapolated curve would involve crystallization for such intolerably long periods of time as to be impractical to carry out. As a general rule the transformation in polymers is rarely, if ever, complete. For a pure homopolymer of regular structure the fraction transformed can vary from about 0.90 to as low as 0.30, depending on molecular weight, molecular weight distribution and crystallization temperature.[1]

A wide range in densities can thus be obtained at 25 °C for the same crystalline homopolymer. The values depended directly on the crystallization temperature. Other thermodynamic, physical, and mechanical properties are also sensitive to the manner in which the crystallization is conducted. Another example of the importance of crystallization conditions in governing properties is illustrated in Fig. 9.2.(4) Here the crystallite thickness of a molecular weight fraction of linear polyethylene ($M_\text{w} = 1.89 \times 10^5$, $M_\text{n} = 1.79 \times 10^5$) is plotted as a function of the crystallization temperature. There is a dramatic increase in these values at about 125 °C. A profound effect is observed in the maximum crystallite thickness.

A striking example of the importance of crystallization kinetics and mechanisms on properties is seen in the influence of molecular weight. It was found in Chapter 2 (Volume 1) that above a very modest chain length the equilibrium melting temperature and equilibrium level of crystallinity only increase slightly with a further increase in chain length. Yet, because of kinetic factors the crystallinity level that can actually be obtained depends very strongly on molecular weight. This dependence is reflected in the major influence of molecular weight on all of the microscopic and macroscopic properties of crystalline polymers. In general, the morphology of polymers, as well as other key structural variables, can be expected to be governed by the

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[1] A detailed discussion of the level of crystallinity that can be attained will be given in Volume 3. The role of molecular constitution and crystallization conditions will be examined in detail at that point.

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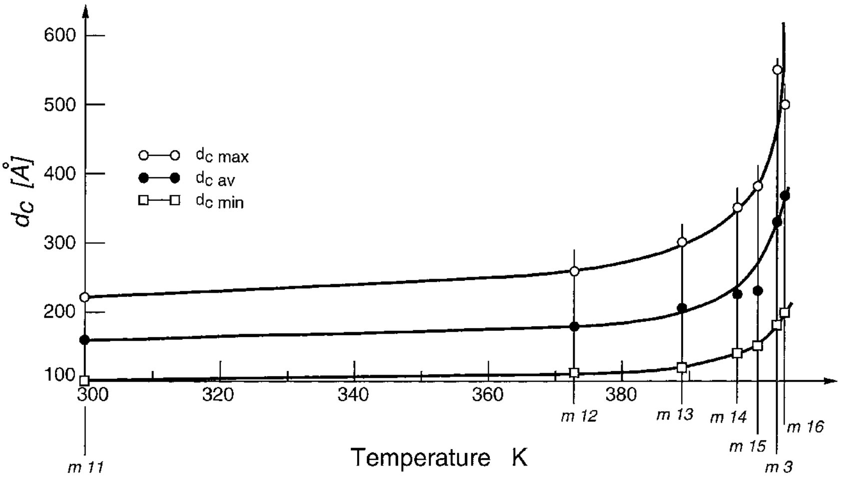

Fig. 9.2 Plot of crystallite thickness as a function of crystallization or quenching temperature for a molecular weight fraction of linear polyethylene, $M_w = 1.89 \times 10^5$, $M_n = 1.79 \times 10^5$.(4)

crystallization conditions. This behavior will be discussed in more detail in chapters concerned with morphology, structure and properties (Volume 3). A complete understanding of properties and behavior of crystalline polymeric systems requires knowledge and information of the mechanisms involved in the transformation, in addition to the equilibrium characterization. In principle, this information can be deduced from crystallization kinetic experiments.

There are several different kinds of experimental methods that are commonly used to observe the time development of crystallinity in polymers. One method is concerned with assessing the isothermal rate at which the total amount of crystallinity develops from the supercooled liquid. This procedure involves measuring the overall rate of crystallization. In carrying out these experiments it is necessary to follow a change in a property that is sensitive to crystallinity. Measurements of the changes in density or specific volume are commonly used for this method. However, other techniques have also been successfully used. These include wide- and small-angle x-ray scattering, vibrational spectroscopy, nuclear magnetic resonance, depolarized light microscopy and differential scanning calorimetry. Each method has a characteristic and different sensitivity to crystallinity.

In another widely used method, the isothermal rate of formation and subsequent growth of spherulites are studied by either polarized light microscopy or small-angle light scattering. Spherulites are spherical aggregations of individual crystallites that develop into supermolecular structures that are easily visible in the light microscope. Although spherulite structures are widely observed they are not, however, a universal mode of polymer crystallization. In particular, spherulites are not

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observed at the extremes of either high or low molecular weights and their formation is sensitive to polydispersity.(5–7) Thus, kinetic studies that are restricted to spherulite growth rates do not encompass the complete range of molecular weights. In favorable situations, particularly when the crystallization takes place from dilute solution, the growth rate of specific crystal faces can be followed using electron microscopy.(8a,b, 9)

9.2 General experimental observations

The isothermal rate at which the total amount of crystallinity develops in homopolymers follows a universal pattern that was first observed by Bekkedahl in his classic study of natural rubber.(10) Some typical isotherms that represent the course of crystallization in polymers are illustrated in Figs. 9.3 and 9.4 for natural rubber (10) and linear polyethylene (11) respectively. Changes with time of the specific volume were used to follow the crystallization in both of these examples. For polyethylene, the relative extent of the transformation is plotted against the time; for natural rubber the percentage decrease in specific volume is given. When the polymer sample is quickly transferred from a temperature above the melting temperature to the predetermined crystallization temperature, there is a well-defined time interval during which no crystallinity is observed. This time has often been termed the induction or incubation period. It was pointed out many years ago that this time interval must depend on the detector used to monitor the development of crystallinity.(12) Different experimental techniques vary in their sensitivity to detect crystallinity.(13) Within a given technique, the sensitivity will also depend on the particular instrument used. A quantitative investigation of these differences, involving several different methods, has been reported.(13) Imai, Kaji and collaborators (14,15) have shown, using small-angle x-ray scattering produced by synchrotron radiation, that density fluctuations occur within the so-called induction period. Subsequently, higher level fluctuations have also been observed.(13,16) An understanding of the molecular and structural basis for these fluctuations is evolving. It has been suggested that nucleation and growth processes take place during this induction period.(13,16,17) Serious consideration also needs to be given to transient (non-steady-state) nucleation that precedes the attainment of the steady state.(17a,b) The non-steady-state nucleation, with its associated embryonic nuclei, will occur within the induction time scale. Rheological and light scattering studies have shown that a network structure develops at the very early stages of crystallinity development.(17c,d) Presumably, the network structure is formed within the induction period by very small crystallites. A variety of possible structures can develop within the induction period and some have been observed.(17e) However, the induction time itself is a measure of the sensitivity of the detector being used. Spreading out of the time scale,

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by studies at low undercoolings, will enable a definitive analysis of the structures involved.

After the onset of observable crystallization, the process proceeds at an accelerating rate that is autocatalytic in character. Finally, a pseudo-equilibrium level of crystallinity is approached. A small, but finite, amount of crystallinity develops at very slow rates over many decades of time in this region. This flat portion of the isotherm is often referred to as the "tail". There are thus several regions in an isotherm where the rate of change of crystallinity with time is clearly different. However, the crystallization process is a continuous one. No sudden changes, or discontinuities, are discernible in the isotherms. The sigmoidal shaped isotherms, which are illustrated in Figs. 9.3 and 9.4, are characteristic of the overall crystallization of all homopolymers. Such isotherms are prima facie evidence of nucleation and growth processes.

When the change in the property being studied is plotted against the logarithm of time, as illustrated in Fig. 9.5 for a molecular weight fraction of linear polyethylene, important additional information can be obtained.(18) The major features of the crystallization isotherms are still maintained. However, in this plot the isotherms all have the same shape. With the exception of the tail portion in some cases, the isotherms can be superposed upon one another by merely shifting the curves along the horizontal axis. This implies that there is a reduced temperature–time variable. Consequently, from a purely experimental point of view a single isotherm, based on the reduced variable involving time and temperature, can be constructed. This isotherm is representative of the crystallization of a given polymer. The implications of this observation will be discussed subsequently.

An important feature of Figs. 9.3, 9.4 and 9.5 is the strong negative temperature coefficient displayed by the crystallization process. This phenomenon is observed in all polymer crystallization conducted in the vicinity of the melting temperature. For the example shown in Fig. 9.5 the rate decreases by more than four orders of magnitude over only a seven degree temperature interval. A temperature coefficient of this type and magnitude is quite different from a chemical process. It is a very strong indication of nucleation controlled crystallization. We shall find, in detailed discussion later in this chapter, that nucleation plays a central role in polymer crystallization.

When the crystallization is conducted over the complete accessible temperature range, i.e. from below the melting temperature to above the glass temperature, a more complex temperature dependence evolves. A typical example is given in Fig. 9.6 for natural rubber.(19) Here the time taken for half of the crystallization to develop is plotted as a function of the crystallization temperature. Many other homopolymers behave in a similar manner. This type of temperature dependence is not restricted to long chain polymers. It is also observed during the crystallization

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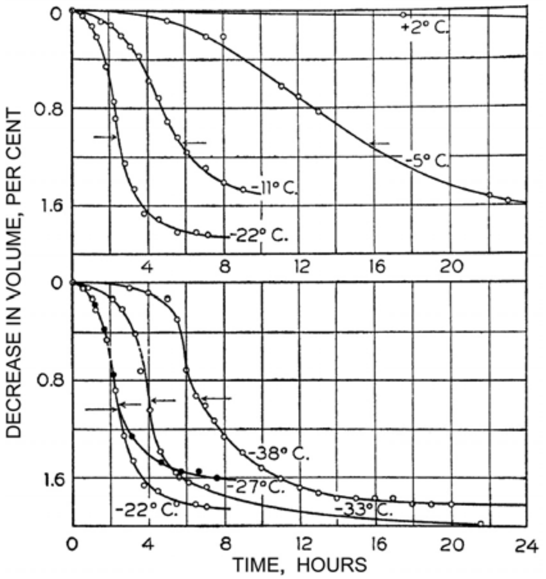

Fig. 9.3 Crystallization of natural rubber at various temperatures as measured by the decrease in specific volume. Temperature of crystallization is indicated for each isotherm. (From Bekkedahl (10))

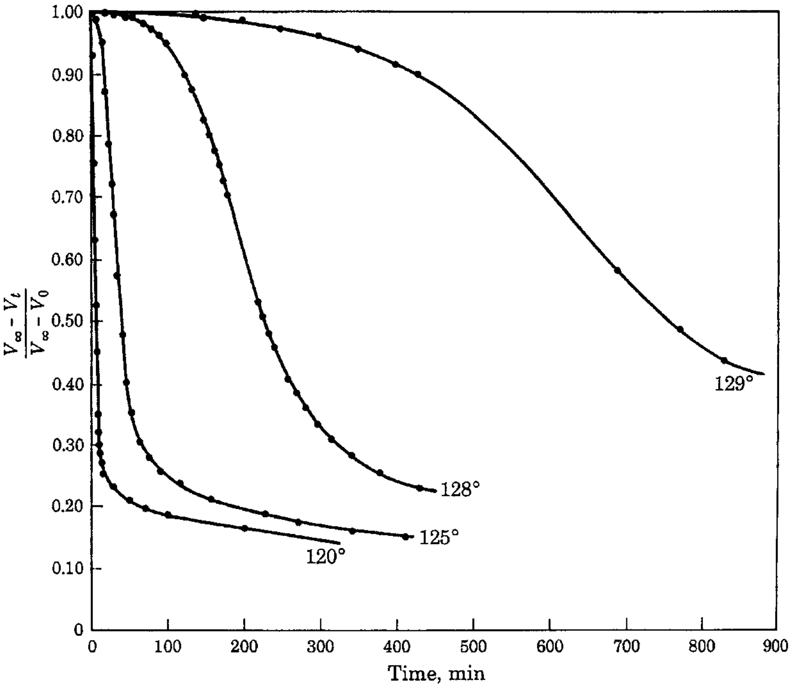

Fig. 9.4 Plot of quantity $(V_\infty - V_t)/(V_\infty - V_0)$ against the time for the crystallization from the melt of an unfractionated linear polyethylene. Temperature of crystallization is indicated for each isotherm.(11)

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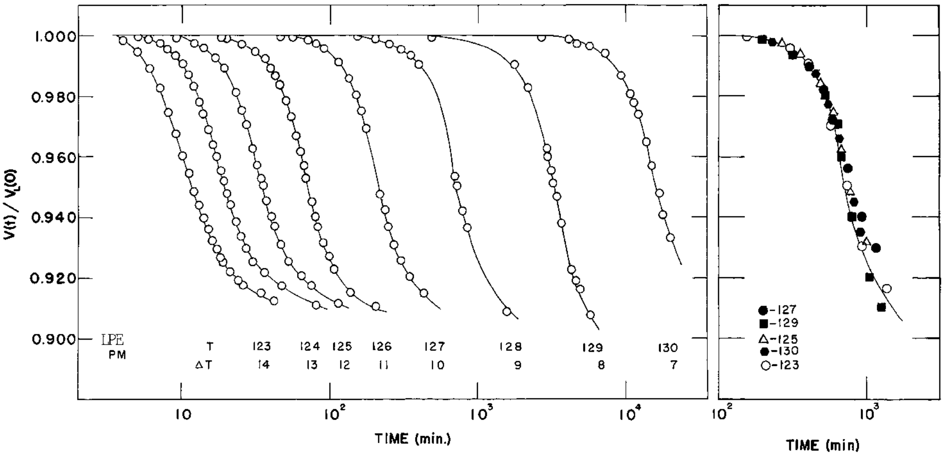

Fig. 9.5 Plot of $V(t)/V_L(0)$ against log time for an unfractionated very high molecular weight linear polyethylene at indicated crystallization temperatures. Insert at right demonstrates a common superposed isotherm.(18)

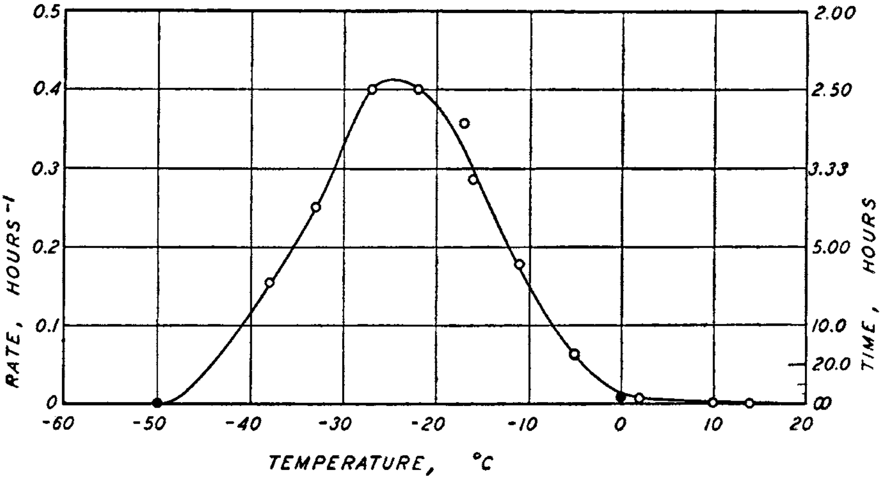

Fig. 9.6 Plot of the crystallization rate of natural rubber over an extended temperature range. The rate plotted is the reciprocal of the time requested for one-half the total volume change. (From Wood and Bekkedahl (19))

of monomeric substances.(20,21) At temperatures in the vicinity of T_m^0 the crystallization rate is very slow, so that for any reasonable time of measurement the appearance of crystallinity will not be detected. As the temperature is lowered, the rate progressively increases and eventually passes through a maximum. At crystallization temperatures below the maximum, the overall rate of crystallization is retarded once again. This interval coincides with the temperature range where the

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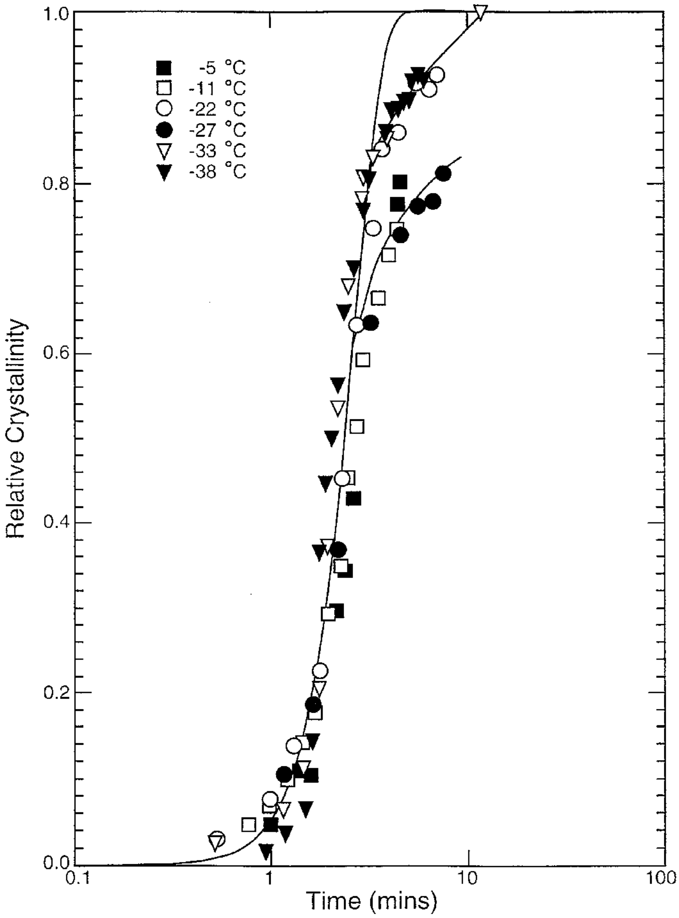

Fig. 9.7 Demonstration of superposition over extended temperature range for natural rubber. Plot of relative crystallinity against log time for crystallization at indicated temperatures. (Data from Fig. 9.3 and Bekkedahl (10))

glass temperature of the supercooled polymeric liquid is approached. For some polymers the crystallization rate becomes so rapid at temperatures below T_m^0 that it is extremely difficult to detect the temperature at which the rate is a maximum. As is illustrated in Fig. 9.7, the superposition of isotherms is also maintained for crystallization over this extended temperature range. The isotherms of other polymers that show a rate maximum can also be superposed over the complete range of crystallization temperatures.

Studies of the rates of spherulite formation and growth in thin films have provided important information about the crystallization kinetics of polymers. In the vicinity of the melting temperature, the rate at which spherulites are formed depends very strongly on the crystallization temperature and increases very rapidly

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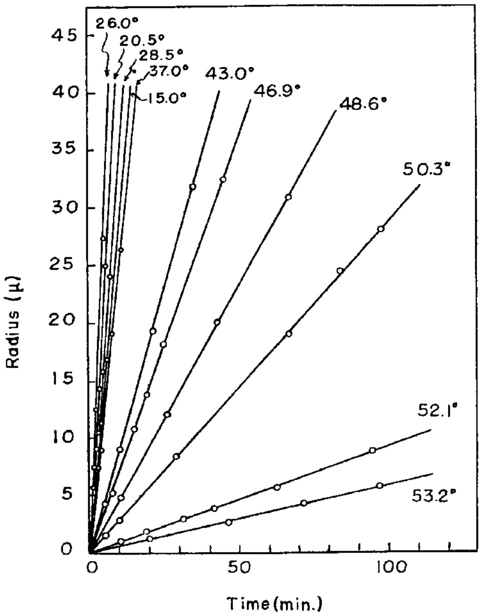

Fig. 9.8 Plot of spherulite growth rates against time for poly(ethylene adipate), $M = 9900$, at indicated crystallization temperatures. (From Takayanagi (23))

as the temperature is lowered. For example, for poly(decamethylene adipate) the rate at which spherulitic centers are generated deceases by a factor of 10^5 as the crystallization temperature is raised from 67 to 72 °C.(22) These results clearly indicate that the birth of spherulites is also governed by a nucleation process.

An impressive body of experimental evidence, involving many polymers, demonstrates that at a fixed temperature the radius of a growing spherulite of a pure homopolymer increases linearly with time. These observations are consistent with the autocatalytic nature of the isotherms illustrated in Figs. 9.3, 9.4 and 9.5. The linear growth rate is also sensitive to temperature as illustrated in Fig. 9.8 for poly(ethylene adipate).(23) The growth rates are clearly defined by the slopes of the straight lines. A marked negative temperature coefficient is again observed. Thus, both the birth of spherulites and their growth are nucleation controlled processs. As the level of crystallinity increases, problems of resolution caused by the overlapping of spherulites make counting and measuring their sizes difficult. Consequently, although a potent quantitative tool, this technique is restricted to relatively low levels of crystallinity and a restricted molecular weight range.

As the crystallization temperature is lowered the growth rate increases until a maximum is observed. With a further decrease in the temperature, the rate of growth diminishes. The temperature variation of the spherulitic growth rate is thus qualitatively similar to the temperature coefficient of the overall rate of

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