THE CRYSTALLIZATION OF FLEXIBLE POLYMER MOLECULES

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Received December 9, 1955

CONTENTS

I. INTRODUCTION

According to modern concepts a polymer molecule is composed of a large number of units which are linked together by covalent bonds. Because of the freedom of rotation of the chain atoms about single bonds a polymer molecule can assume a large number of configurations. The concept of the random-chain-like nature of polymer molecules has been very successful in explaining and interpreting the thermodynamic and hydrodynamic behavior of these molecules in solution as well in the interpretation of some of the bulk physical properties. Under appropriate conditions a spontaneous ordering of portions of the chain units is possible for those polymers that possess a reasonably regular chain structure. This spontaneous ordering is popularly termed crystallization, and its occurrence vastly alters the thermodynamic, physical, and mechanical properties of the polymeric system as compared to the liquid state, which is the state of the random configurations. For example, at room temperature natural rubber possesses its characteristic extensibility and recoverability. However, on cooling to a suitable temperature crystallization ensues and the polymer becomes hard and relatively inelastic. Most synthetic fibers are highly crystalline and consequently are hard and rigid and have high strength. However, when crystallinity disappears the physical properties of these polymers resemble very closely those of a viscous liquid. These two examples are typical of the changes that crystallization can cause in the properties of polymers.

Because of the inherent difficulty of envisaging and quantitatively describing the ordering of molecules composed of thousands of units joined together, the understanding of this phenomenon has not developed as rapidly as have some other aspects of polymer chemistry and physics. However, during the last decade, owing primarily to the pioneering work of Flory (46, 48, 52), a statistical thermodynamic treatment of crystallization in polymers has been developed and has resulted in a better understanding of these phenomena.

The main purpose of this review is to consider the fundamental principles which govern the crystallization behavior of polymeric systems and to compare the experimental results with theoretical deductions. By an approach of this sort it is hoped that those areas that appear to be reasonably well understood will become delineated, at the same time that attention is drawn to those areas that are not completely understood or where there are significant gaps in our theoretical or experimental knowledge. With this objective in mind this review will not contain a compilation of all the experimental results in the field nor include an exhaustive bibliography, though efforts have been made to be as comprehensive as possible consistent with the primary goal. Discussions of the morphology of the crystalline polymers and details of the crystalline structure, which comprise the first section of the paper, are intentionally brief, because these aspects of the problem have been extensively reviewed recently (23). This portion of the paper is intended to serve only as an introduction to and background for the main body of the paper, which deals with the general problem of the thermodynamics and kinetics of crystallization and a discussion of these problems in terms of molecular and chemical structure.

II. Structure of Crystalline Polymers

A. MORPHOLOGY

The most direct evidence for the occurrence of long-range order in polymers is provided by x-ray diffraction investigations. The diffraction patterns display both the relatively sharp features typical of diffraction by a crystalline array and also the more diffuse characteristics observed in the diffraction by liquids. The crystalline features of the diffraction pattern indicate that not only do portions of different molecules lie parallel to one another but also that the lateral arrangements are such that full three-dimensional order is achieved. Reflections are observed from a sufficient number of planes to indicate that the substituents of the different chains have a preferred alignment. The three-dimensional order possessed by regions in the polymer is thus structurally very similar to that of crystals composed of simpler molecules. The diffuse, liquid-like scattering that is observed indicates that the ordering does not extend throughout the complete sample. The incompleteness of the ordering process as indicated by the x-ray diffraction studies is supported by other physical measurements.

The diffracted x-ray beam of the crystalline regions at large Bragg angles is usually broader than observed from macroscopically perfect crystals. The breadth of the diffraction line can be caused by the smallness of the crystallite size, but other factors can contribute as well, crystal distortion and imperfection being very possible causes in the case of polymers. If it is assumed that the broadening of the diffraction line is caused only by the crystallite size, then an estimate can be made of the size of the crystalline regions from the x-ray patterns. Such estimates have been made in a variety of polymers (20, 26, 64, 70, 105) and the crystallite size has been found to be of the order of tens to hundreds of Ångström units. Since this general size range is found in many different polymers, even after careful annealing, it can be taken to be a reasonable estimate. This estimate is also confirmed by an analysis of the intensities of the diffracted x-rays at small Bragg angles, where the complications caused by crystallite imperfections are absent. Low-angle x-ray diffraction patterns for a variety of polymers (3, 43, 73, 112, 163) indicate structural regularities over a distance of several hundred Ångström units.

The size of the crystallites in polymers is much smaller than the extended length of a typical polymer molecule, which usually is of the order of several thousand Ångström units. Thus only portions of the molecules participate in a given crystallite, the remaining portion of a molecule being either in the amorphous regions or in other crystallites. Therefore a partially ordered polymeric system may best be termed semicrystalline. The x-ray diffraction patterns of polymers crystallized by cooling further indicate that the crystallites are randomly arranged relative to one another. The structure of a semicrystalline polymer can then be schematically illustrated as shown in figure 1. The crystal-

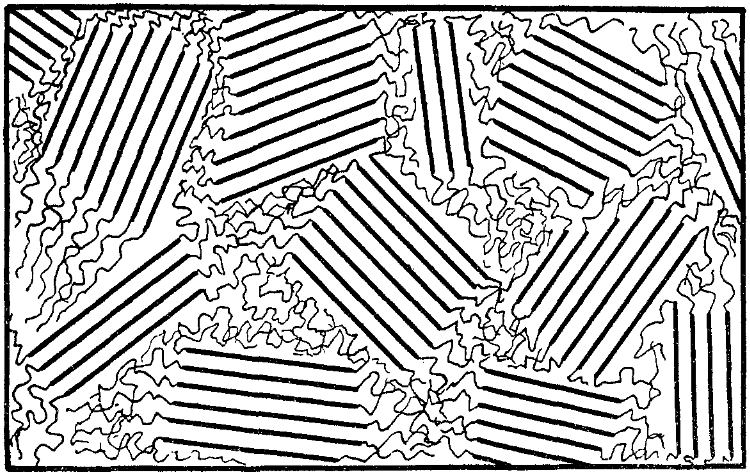


FIG. 1. Schematic representation of morphology of a semicrystalline polymer (Flory (50a)).

lites are indicated by a parallel array of portions of polymer chains; these ordered regions are randomly arranged relative to one another and are connected by the portions of the chains passing through amorphous or disordered regions.

The arrangements of the atoms in the ordered regions of a polymer can be obtained by detailed study of the x-ray diffraction patterns of highly oriented crystalline specimens by the same method used in determining the structure of simpler crystalline compounds. Despite the fact that single crystals are usually not available to polymer crystallographers, many of the characteristics of the unit cells such as the crystal system, dimensions, and the positions of the atoms have been evolved for a wide variety of polymers (21, 23a, 60). Normal bond distances, angles, and other elements of structure appear to be the general rule. The role of the chemical repeating unit in these systems is analogous to the part played by molecules in crystals of low-molecular-weight organic compounds. It is not uncommon to find more than one chain passing through the unit cell; the unit cells are usually composed of from one to eight chain units. The realization that a unit cell need not contain a complete molecule was important in the development of the concept that a polymer consists of a succession of chain units joined by covalent bonds (50a).

Since the crystallites are much smaller than the wavelengths of visible light, specimens of semicrystalline polymers should be transparent and their presence should not be detectable by the techniques of optical microscopy. On the contrary, bulk samples and fibers of semicrystalline polymers are usually opaque and microscopic observations indicate a large organized structure. Thus there must be an aggregation of crystallites large enough to scatter light and to be seen microscopically. These organized structures have been termed spherulites and can be considered to be partly oriented, aggregated crystallites and their attached amorphous regions. Spherulitic structure has been observed in such a wide variety of the crystallizable polymers that it appears to be a characteristic mode of crystallization (23b, 146). Spherulite formation is not, however, a unique property of chain molecules; this type of crystal formation has been observed in a wide variety of the simpler inorganic and organic crystalline compounds (120).

When viewed between crossed polarizers in the polarizing microscopes, the most common type of spherulites observed in polymeric systems has well-defined spherical boundaries, and though the size is variable, a typical structure might have a diameter of about 0.1 mm. These structures appear illuminated except for a characteristic dark Maltese cross. The arms of this black cross are parallel to the vibration directions of the polarizer and analyzer, respectively, since the crystallites are in their extinction position. This type of spherulite has been interpreted (23b) as being produced by an aggregation of crystallites radiating outwards from a common point, with the crystallographic axis of each of the crystallites pointing outwards. By comparing the magnitude and sign of the birefringence of these structures with drawn fibers of the same material it has been concluded that the long axes of the molecules are arranged perpendicular to the radii of the spherulites (23b, 26). However, the magnitude of the birefringence is low when compared to the birefringence of drawn fibers and indicates that the perpendicular orientation of the chains is rather imperfect. A similar conclusion has been reached from studies of the orientation of the unit cells within the spherulite, using microbeam x-ray techniques (92).

Recent renewed interest (88, 89, 91, 146, 147) in the nature of spherulites has indicated that not all spherulites in polymers are of the Maltese-cross type just described. Though a given polymer may display this type of spherulite under certain crystallization conditions, when the crystallization conditions change the spherulite structure can be modified. For example, Keller (88, 89, 91) has observed in polyethylene terephthalate that at relatively low temperatures of crystallization, in the range of about 100–180°C., usual types of spherulites displaying the Maltese cross occur. When the polymer is crystallized at higher temperatures, the black cross appears as zigzag lines with the angular extension of the zigzag increasing with the temperature of the crystallization. At 239°C. the ends of the zigzags meet and the spherulites consist of concentric black circles with an apparent black cross at an angle of 45° to the direction of vibration. Above this temperature of crystallization the resulting patterns are too irregular to be defined. Similar types of spherulites have been observed in polyethylene and some polyamides at higher temperatures, although the zigzag distortions are not as marked (88, 89, 91). The various types of spherulites that appear in gutta percha under different crystallization conditions have also been described (147). Though all these polymers display the Maltese cross or normal type of spherulites at crystallization temperatures well below the melting temperature, at temperatures closer to the melting point various specific types of spherulites develop.

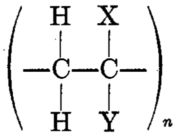
The spherulites observed in polymeric systems find their counterpart in most cases in the spherulites observed in simpler compounds (120). Observation of the spherulitic structures under the electron microscope (23b, 131) indicates the occurrence of rod-shaped and sheaf-shaped bundles as well as spherical aggregates. According to Morse and Donnay (119) the former structures are precursors to the growth of the truly spherical aggregates. The more nearly perfect spherical structures seen in the optical microscope are probably due to inferior resolution wherein the details of the structure are lost.

Two major problems arise in connection with the formation of spherulites in polymeric systems. The first problem involves the question as to why it is the usual mode in which crystallinity develops in polymeric systems. The second problem concerns itself with the elucidation of the molecular mechanism that is involved in the development of the radiating growth pattern. Neither of these problems has as yet been resolved completely. It has been suggested (91, 120) that a necessary condition for the formation of spherulites is that crystal growth must occur in a medium of high viscosity. It has also been postulated that a necessary requirement is that the magnitude of the crystal growth rate in two mutually perpendicular directions must differ appreciably. Both of these requirements appear to be fulfilled by polymeric systems. From the observed spherulitic structure it is obvious that in relation to the initiating point or center of a spherulite the crystallites that are formed must be non-parallel. A variety of suggestions have been put forth (16, 23b, 84, 88, 90, 93, 116, 129, 146, 147) as to the manner in which this non-parallelism is obtained and the way in which the radiating growth develops. None of the mechanisms postulated has as yet received independent verification or widespread acceptance. It is clear, however, that a foreign heterogeneity is not a necessary requirement for the initiation of a spherulite. Since the normal mode of polymer crystallization is in the form of spherulites, it is extremely important that mechanisms of their formation be elucidated.

B. STRUCTURAL CHARACTERISTICS GOVERNING CRYSTALLIZATION

It would appear almost axiomatic that the major requirement for the crystallization of a chain molecule is that it possess structural regularity (24). In the main, for a polymer to be capable of crystallizing, its chemical and stereochemical structure should be regular and geometric isomerism should be absent. Thus the typical crystalline polymers are homopolymers obtained by the methods of condensation polymerization as the polyesters or polyamides, or the addition-type polymers in which the substituents on a given chain atom are identical. This is an idealized criterion for the crystallizability of polymers, since a certain amount of chain irregularity can be tolerated. It is well known that many copolymers crystallize as do branched polymers and cross-linked systems. On the other hand, not all polymers that possess the requirement of chain regularity have been successfully crystallized simply by cooling. The most notable example of a polymer in this latter category is polyisobutylene, which can be easily crystallized by stretching but has not as yet been crystallized by cooling. For this polymer it is clear that kinetic factors play an important role in the development of crystallinity. Polyesters derived from diethylene glycol have not been crystallized, while other aliphatic polyesters do crystallize rather easily. Similarly, though polyethylene terephthalate crystallizes very easily at appropriate temperatures, polyethylene phthalate and polyethylene isophthalate have not as yet been prepared in the crystalline state (24).

The typical non-crystalline homopolymers are the vinyl polymers of the type



$$\left(\begin{array}{c} \mathrm{H}\quad\mathrm{X} \\ |\quad\;| \\ -\mathrm{C}-\mathrm{C}- \\ |\quad\;| \\ \mathrm{H}\quad\mathrm{Y} \end{array}\right)_n$$

in which two different substituents are attached to alternate chain atoms. This class of polymers, of which ordinary polymerized polystyrene, polymethyl methacrylate, and polyvinyl acetate are examples, presumably do not crystallize because the alternate chain carbon atoms are asymmetric and the polymers are in reality copolymers consisting of equal number of units in the *d* and *l* configurations randomly dispersed along the chain. However, polyvinyl chloride, polyacrylonitrile, polyvinyl alcohol, and polychlorotrifluoroethylene are partially crystalline despite the possibility of the occurrence of stereochemical irregularities. According to Bunn (22), although the hydroxyl groups are randomly placed on the alternate carbon atoms of polyvinyl alcohol, the spacings in the crystal are sufficiently large to tolerate this irregularity. Thus the occurrence of stereochemical irregularities does not in itself prevent the occurrence of crystallization, and no generalization appears at present capable of predicting the chemical structures that will or will not crystallize.

Recently, in a notable accomplishment Natta and coworkers (122, 123) have, by means of special polymerization conditions, prepared crystalline polymers from several olefins such as propylene, styrene, and α-butylene. Preliminary x-ray analysis of these polymers indicates that all the asymmetric carbon atoms have the same configuration along a major portion of the chain. The directive influence during the polymerization is presumed to be caused by the nature of the catalyst. Previously, by carefully controlled low-temperature cationic polymerization, Schildknecht (145) was able to prepare crystalline polyvinyl isobutyl ether, while ordinary polymerization methods yield an amorphous polymer.

Polymers prepared from the 1,3-dienes are subject to both stereochemical and geometric isomerism (47). Thus synthetic polyisoprene, polychloroprene, and polybutadiene can contain units that are in the *trans* 1,4 or *cis* 1,4 configuration as well as pendant vinyl groups which may be in either the *d* or the *l* configuration. The proportion of the various configurations that are present depends on the polymerization conditions. For the usual emulsion polymerization, the polymerization temperature is the most easily controlled variable in this respect. The percentage of the units in the *trans* 1,4 configuration can be varied in the case of polybutadiene from about 80 per cent at a polymerization temperature of −20°C. to about 40 per cent at 100°C. Despite the various chain irregularities that can exist in this type of polymer, it can be crystallized when a sufficient concentration of units in the *trans* 1,4 configuration is present. The minimum concentration for crystallization of polybutadiene is usually about 55 to 60 per cent, so that diene polymers prepared at sufficiently low temperatures satisfy this requirement while polymers prepared at the higher temperatures are non-crystalline (169).

III. Thermodynamics of Crystallization

A. THE FUSION OF HOMOPOLYMERS

Since the morphology of a semicrystalline polymer is complex and has as yet not been completely elucidated, it can be questioned whether it is possible to develop a systematic understanding of this type of polymer. It is then extremely important to decide whether the ordered regions can be considered as a true crystalline phase and to understand the thermodynamic nature of the transformation to the disordered state. The changes that occur in the x-ray diffraction pattern and in the thermodynamic and physical properties upon disordering strongly suggest that this transformation is very similar to the crystal–liquid transformation in low-molecular-weight materials. For the ordered regions in polymers to be considered as a true crystalline phase, the existence of an equilibrium melting temperature is required, even though single crystals are not observed nor complete crystallinity generally achieved. This temperature would represent the melting of a perfect, macroscopic crystal. Since polymers are not completely crystalline, the degree to which this temperature is approached is best judged by the sharpness and reproducibility of the melting temperature when the fusion process is conducted under conditions conducive to the formation of the most perfectly ordered regions. If it can be deduced from experiment that an equilibrium melting temperature does exist, then the transformation must be describable by the thermodynamic laws of phase equilibria.

Before assessing the experimental evidence as to the existence of an equilibrium melting temperature, it will be advantageous to consider the various methods used in determining the melting temperatures of polymeric systems. The conventional capillary-tube method is highly inadequate for these systems, because it does not distinguish flow or softening from true melting. For example, if a conventionally polymerized, non-crystalline polystyrene is heated in a capillary tube, there would be a tendency on the part of the observer to report a melting temperature in the vicinity of 100°C. This temperature is in actuality the glass transformation temperature and the softening and flow which occur can by cursory observation be erroneously identified with melting. Alternatively, it has been reported (17) that melting does not occur in polymethylene after heating to rather high temperatures in a capillary tube. The fusion process for this polymer is actually well defined (100), but because of its extremely high viscosity, the lack of flow in the capillary can easily be confused with the absence of melting. A method must be used that directly measures the changes in the amount of crystallinity and is a sensitive detector of small amounts of crystallinity. This suggests measurements of the density or specific volume, of the specific heat, of the changes in intensity and ultimate disappearance of the x-ray diffraction pattern, or of an infrared absorption band as possible techniques. Though methods that depend on the softening of a polymer or changes in its flow properties may in some cases give indications of the melting range, they are, in general, very unreliable. Unfortunately, many of the melting points reported have been determined by these methods and thus a great deal of uncertainty exists as to their actual values.

In order to decide how closely an equilibrium melting temperature can be approached in polymeric systems, it is of prime importance to conduct the crystallization and subsequent fusion under conditions conducive to the formation of the most perfectly ordered regions. If subsequent to crystallization, at temperatures where the crystallization proceeds relatively rapidly, the polymer sample is heated at rates of 1° per 10 min. to 1° per several hours, the melting temperatures that are observed depend in all instances on the temperature of the crystallization and the heating rate employed. This behavior was first observed by Carothers and Arvin (29) in their pioneering study of the physical properties of polyesters, studied in detail by Wood and Bekkedahl (171) for natural rubber, and has more recently been observed in studies of the melting behavior of polyesters (41), polyamides (56), and polychloroprene (114). This apparent lack of an equilibrium melting temperature in polymeric systems has led to the opinion that the fusion process cannot be described by a thermodynamic analysis. However, x-ray diffraction investigations give rather poor and diffuse reflections under the crystallization conditions just described (7, 26, 61). When the polymers are annealed, the diffraction patterns indicate a much higher degree of order and larger crystallite size.

Following the ideas suggested by these observations, it is found that for a wide variety of polymers, if the heating following the crystallization is carried out extremely slowly, particularly in the region just below the melting temperature, the melting points observed are independent of the crystallization conditions and of any previous thermal history (41, 56, 99, 100, 139). The melting temperatures obtained in this manner are reproducible and are invariably found to be significantly higher than those obtained employing fast heating rates. In these experiments care must be taken to insure that the crystallites are randomly oriented relative to one another, for if they are not an abnormally high melting temperature may be observed (140). The observation that on slow heating reproducible melting temperatures are obtained is the first indication that an equilibrium melting temperature may exist. The dependence of the melting temperature on crystallization temperature when rapid heating rates are employed has not as yet received quantitative explanation, but these observations themselves are not of thermodynamic significance.

The fusion process for three typical homopolymers is illustrated in figure 2,

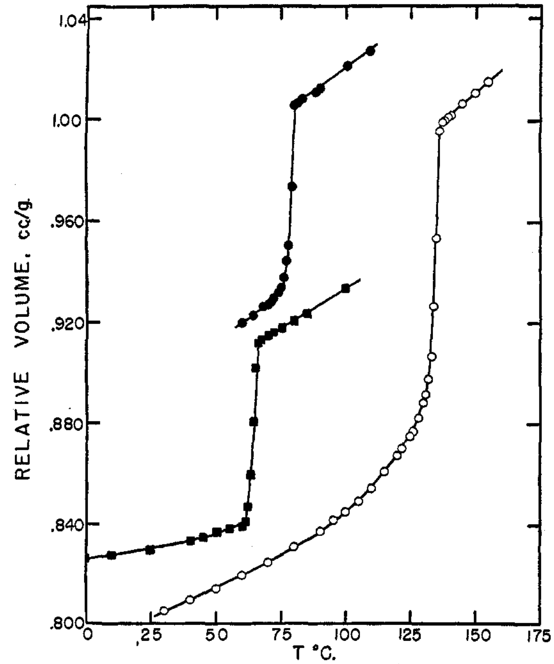


FIG. 2. Plot of relative volume vs. temperature: ○, polymethylene (100); ■, polyethylene oxide (97); ●, polydecamethylene adipate (99).

where the relative volumes, obtained using slow heating rates, are plotted against temperature. It can be seen that the melting is surprisingly sharp, as approximately 80 per cent of the melting occurs in an interval of 3° to 4°. The fact that the temperature at which the last traces of crystallinity disappears is well defined is significant in that it indicates an abrupt termination to the fusion. This temperature represents the disappearance of the most perfectly ordered regions that can be obtained in a realistic time interval and has been identified, subject to a small uncertainty, with the melting temperature of the hypothetical macroscopic perfect crystal (50b). The validity of this conclusion is further confirmed by consideration of the experimental results on the temperature coefficient of the crystallization rate, where it becomes almost mandatory to assume the existence of an equilibrium melting temperature.

Though the melting is relatively sharp, it does occur over an interval of several degrees and hence does not display the characteristics of a classical first-order transition, which requires the melting to be infinitely sharp. One obvious reason for the slight broadening of the melting range in polymers is that even with the use of slow heating rates some imperfectly formed crystallites persist which will be unstable at temperatures slightly below the equilibrium melting temperature. The requirement that all of the crystalline regions be perfectly ordered appears to be too stringent to be realized experimentally (50b). On the other hand, Flory's (48) statistical theory of fusion in polymers (discussed below) indicates that even under equilibrium conditions the melting process should extend over a small temperature interval. This transition might then best be called a diffuse first-order transition in the terminology of Mayer and Streeter (51, 108). However, as Rutgers (143) has shown, transitions of this type can still be treated by the laws of phase equilibria appropriate to a first-order transition. Because of the slightly diffuse nature of the transition, even for a homopolymer, a plot of $\mathrm{d}V/\mathrm{d}T$ against T will yield a curve resembling a typical lambda-type curve (similar results would be obtained in the plot of specific heat against temperature). This has led in some instances (121) to the description of the melting transition in polymers as a second-order transition in the Ehrenfest sense. A transition of this type, however, will not obey the thermodynamic laws applicable to a first-order transition.

The available experimental evidence strongly supports the concept that polymers possess an equilibrium melting temperature and that the disordering process which occurs is closely related to a classical first-order transition temperature. Thus, the fusion process should be describable by statistical and thermodynamic methods, and the dependence of the melting temperature on other components or various external parameters should be predictable.

B. STATISTICAL THERMODYNAMIC THEORY

Early attempts at a statistical thermodynamic description of the crystallization in unoriented polymers were made by Frith and Tuckett (59) and Richards (134), using the lattice treatment (45, 80) of polymer configurations. These investigations did not, however, take into account the fact that the ends of crystallites are attached to amorphous segments nor the fact that chain ends (being structural irregularities) should be excluded from the crystal lattice. Flory (48), also relying on the lattice treatment but taking cognizance of these facts, has developed a quantitative description of the unoriented semicrystalline polymer and of its fusion which has proven to be of great utility in the understanding of the crystallization behavior of polymers.

Flory (48) considered the general case of N homogeneous polymer molecules, each comprised of x identical repeating units mixed with n_1 molecules of a low-molecular-weight diluent. The composition of the mixture is characterized by the volume fraction of polymer, v_2. Since, in general, the diluent will be structurally different from the polymer repeating unit, it is assumed that neither the diluent nor the chain ends can participate in the crystallization. The entropy of the unoriented semicrystalline polymer is assumed to arise solely from the number of configurations that are available to the polymer molecule. Contributions from the random orientation of the crystallites or their further subdivision into small crystallites are neglected. In considering the configuration of polymer chains, where the size and the flexibility of the repeating unit become important, it is necessary to distinguish between the configurational segment and the structural repeating unit. The configurational segment is chosen in the conventional manner so that the hypothetical chain comprised of these completely flexible segments of appropriate length has the same contour length and mean square end-to-end distance as the real chain.

If x' represents the number of such configurational segments per molecule and z represents the number of segments per structural repeating unit, then x' equals zx. The configurational properties of the semicrystalline polymer are conveniently described by using a lattice having a coordination number Z, and the size of the cells is chosen to accommodate one segment. Thus, if z_s is equal to the ratio of the molar volume of the solvent to the volume of a segment, n_1', which is equal to $z_s n$, is the number of lattice cells occupied by solvent molecules. Definite regions in the lattice are reserved for occupancy by the crystallites. There are assumed to be ν crystallites, each having an average length of ζ' segments (or ζ repeating units) and having a cross section of σ chains. The total number of crystalline sequences m is equal to $\nu\sigma$; $m\zeta$ is the total number of chain units participating in the crystallization. The major problem to be solved is the calculation on this lattice of the configurational entropy of the semicrystalline polymer.

For purposes of the calculation it is convenient to join the polymer and diluent molecules together in random fashion to form a single linear chain. This corresponds to an entropy change

$$S_1 = k\{-n_1 \ln [n_1/(n_1 + N)] - N \ln [N/(n_1 + N)]\} \tag{1}$$

This single chain is then introduced into the lattice, one segment at a time, observing the conditions set forth by the reserved regions. For each segment whose location relative to its predecessor is not restricted there will be a contribution to the entropy of $k \ln [(Z - 1)/e]$. All segments except those beyond the first in a crystalline sequence are unrestricted in this respect, so that the configurational entropy of the chain on the lattice is

$$S_2 = k[n_1' + x'N - (\zeta - 1)m] \ln [(Z - 1)/e] \tag{2}$$

In this arrangement of the chain, chain ends and diluent have been allowed to enter the lattice cells reserved for crystallites, and a given arrangement is acceptable only if these cells are occupied by polymer segments. The probability of fulfilling the latter condition has been calculated (48) for small degrees of crystallinity and leads to an entropy contribution of

$$S_3 = km\{\ln [x'N/(n_1' + x'N)z + \ln [(x - \zeta + 1)/x]\} \tag{3}$$

Finally, the severing of the linkages between molecules leads to an entropy contribution

$$S_4 = -k\{(n_1 + N) \ln [(Z - 1)/e] + (n_1 + N) \ln [(n_1 + N)/(n' + x'N - \zeta'm)] \tag{4}$$

The configurational entropy S_c of the semicrystalline polymer–diluent mixture is the sum of the above four entropy contributions. We wish to subtract from this sum the entropy S_l of the completely disordered mixture and thus find that

$$\begin{aligned} \Delta S_f = \zeta m \Delta S_u - k\{(n_1 + N) \ln [(n_1' + x'N - \zeta m)/(n_1' + x'N)] \\ + m \ln [Dx'N/(n_1' + x'n)] + m \ln [(x - \zeta + 1)/x] \end{aligned} \tag{5-1}$$

or, in terms of molar quantities,

$$\begin{aligned} \Delta S_f/xN = (1 - \lambda)\Delta S_u - R[(V_u/V_1)(1 - v_2)/v_2 + 1/x] \\ \ln [1 - v_2(1 - \lambda) - R[(1 - \lambda)/\zeta] \{\ln v_2 D + \ln [(x - \zeta + 1)/x]\} \end{aligned} \tag{5-2}$$

where λ, the fractional amount of polymer which is amorphous, is equal to $(xN - \zeta m)/xN$; $(Z - 1)/ze$ has been defined as D and $kz \ln [(Z - 1)/e]$ as ΔS_u. V_u and V_1 are the molar volumes of the repeating unit and diluent, respectively. In equations 5-1 and 5-2 ΔS_u represents the entropy of fusion per structural unit. In calculating ΔS_f the assumption was made that sharp boundaries exist between the crystalline and the amorphous regions. It was recognized that this situation is a physically untenable one and that some degree of order must persist at least some distance beyond the crystallite ends. This effect can be partially accounted for by redefining the parameter D to include the free-energy change due to the crystallite ends. Because of the various simplifications that are introduced in the calculation, D is most conveniently treated as an arbitrary parameter. The term v_2D has an important role in specifying the equilibrium crystallite length and in determining the rate at which stable nuclei are formed from the liquid. Equations 5-1 and 5-2 represent both a melting and a dilution process, so that even in the absence of diluent ΔS_f depends on the degree of crystallinity and the crystallite size and hence is not an inherent property of the polymer. On the other hand ΔS_u, the entropy of fusion per structural unit, is characteristic of a given polymer.

The enthalpy change accompanying the fusion also consists of two parts, the contribution arising from the melting of the crystallites and that caused by the mixing of the previously crystalline segments with the amorphous mixture. The former contribution can be written as $\zeta m \Delta H_u$, ΔH_u being the heat of fusion per structural unit. The effect of the lower energy expected at the crystallite ends is incorporated in the parameter D. The heat of mixing can be expressed in the van Laar form as is customary in polymer solution theory (50c). The free-energy change accompanying the fusion, i.e., the melting of the crystallites and the dilution of the newly melted segments, can be expressed as

$$\Delta F_f/xN = (1 - \lambda)(\Delta H_u - T\Delta S_u) + RT\{[(V_u/V_1)(1 - v_2)/v_2 + 1/x] \ln[1 - v_2(1 - \lambda)] + [(1 - \lambda)/\zeta] \ln v_2 D + \ln(x - \zeta + 1)/x + \chi_1(1 - v_2)^2(1 - \lambda)/(1 - v_2 + v_2\lambda) \quad (6)$$

The most stable semicrystalline state characterized by the equilibrium values of $\lambda = \lambda_e$ and $\zeta = \zeta_e$ is achieved when ΔF_f assumes its maximum value. The equilibrium crystallite length is then defined by the expression

$$-\ln v_2 D = \zeta_e/(x - \zeta_e + 1) + \ln[(x - \zeta_e + 1)/x] \quad (7)$$

and the equilibrium degree of crystallinity λ_e by

$$1/T - 1/T_m^0 = R/\Delta H_u\{[(V_u/V_1)(1 - v_2) + v_2/x]/[1 - v_2(1 - \lambda_e) + 1/(x - \zeta_e + 1) - \chi_1[(1 - v_2)/(1 - v_2(1 - \lambda_e))]^2 \quad (8)$$

which the absence of diluent reduces to

$$1/T - 1/T_m^0 = R/\Delta H_u[1/x\lambda_e + 1/(x - \zeta_e + 1)] \quad (9)$$

where $T_m^0 = \Delta H_u/\Delta S_u$ is the equilibrium melting temperature of pure polymer of infinite chain length. The fact that in equation 7 the equilibrium crystallite length appears to be independent of the degree of crystallinity is a consequence of the approximation used in calculating ΔS_f. Values of ζ_e that have physical significance, i.e., greater than unity and less than x, will occur only for values of $v_2 D$ less than unity.

Equation 9 indicates that even for a pure polymer crystallinity will disappear over a finite temperature range owing to the effect of the end groups. This is in accord with experimental observations illustrated in figure 2, where about 80 per cent of the crystallinity disappears over a temperature interval of three to four degrees. In this respect the fusion process in polymers differs from that of low-molecular-weight materials where the crystalline phase has no forewarning of the impending transformation. The melting range in polymeric systems will depend on the value of $v_2 D$ and will be expected to broaden as the diluent concentration increases, as has been observed in numerous polymer–diluent mixtures (41, 56, 97, 99). Despite the fact that the melting of a semicrystalline polymer will occur over a range of temperatures, as λ approaches unity $(\partial\lambda/\partial T) \neq 0$. Thus the final traces of crystallinity should disappear at a well-defined temperature, which is conveniently termed the melting temperature T_m, since above this temperature $(\partial\lambda/\partial T) = 0$. This temperature is characteristic of a given polymer and is analogous to the melting point of a low-molecular-weight crystalline compound. Hence at $\lambda = 1$, where $T = T_m$, we find that

$$1/T_m - 1/T_m^0 = R/\Delta H_u\{(V_u/V_1)(1 - v_2) + (1/x)[v_2 + x/(x - \zeta_e + 1)] - \chi_1(1 - v_2)^2\} \quad (10)$$

which in the absence of diluent reduces to

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(1 + b)/x \quad (11)$$

where

$$b = [1 - (\zeta_e - 1)/x]^{-1}$$

Equation 11 expresses the effect of chain length on the melting temperature for homogeneous polymers and indicates that except for polymers of extremely low molecular weight T_m should be independent of M. It has also been found (48) that for heterogeneous polymers having the most probable molecular-weight distribution

$$1/T_m - 1/T_m^0 = (2R/\Delta H_u)\bar{x}_n \quad (12)$$

where $\bar{x}_n$ is the number average degree of polymerization.

For large x equation 10 reduces to

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_u/V_1)[(1 - v_2) - \chi_1(1 - v_2)^2] \quad (13)$$

and indicates that the melting-point depression caused by a given amount of diluent will depend on the heat of fusion per structural unit, the ratio of the molar volume of the structural unit to that of the diluent, and the nature of the thermodynamic interactions between polymer and diluent. Thus, a good solvent will cause a greater depression than a poor one, a diluent of smaller size molecules will cause a greater depression than a diluent having larger molecules, and the melting point of a polymer having a lower heat of fusion per repeating unit will be depressed more than one having a larger heat of fusion for the same amount and type of diluent. The close similarity between equation 13 and the classical expression for the depression of the melting point of low-molecular-weight binary systems suggests the possibility of its derivation by the application of the thermodynamics of phase equilibria (53).

According to the thermodynamic theories of polymer solutions (45, 80), the chemical potential of a chain unit in a high-molecular-weight polymer can be expressed as

$$\mu_u - \mu_u^0 = RT(V_u/V_1)(v_1 - \chi_1 v_1^2) \quad (14)$$

where μ_u^0 is the chemical potential of the pure liquid polymer. The difference between the chemical potential of the crystalline unit in the polymer μ_u^c and that of the pure liquid polymer can be written as

$$\mu_u^c - \mu_u^0 = -\Delta F_u = -(\Delta H_u - T\Delta S_u) \quad (15)$$

Since

$$\Delta H_u/\Delta S_u = T_m^0$$

equation 15 becomes

$$\mu_u^c - \mu_u^0 = \Delta H_u(1 - T/T_m^0) \tag{16}$$

At the melting point T_m of the polymer–diluent mixture,

$$\mu_u^c - \mu_u^0 = \mu_u - \mu_u^0$$

so that

$$1/T_m - 1/T_m^0 = (RV_u/V_1\Delta H_u)(v_1 - \chi_1 v_1^2) \tag{13}$$

which is identical with the equation derived from statistical considerations. A substantiation of equation 13 by experiment would be clear indication that at the melting temperature the standard thermodynamic relationships of first-order transitions are applicable to polymeric systems.

Recognizing that $\chi_1 = BV_1/RT$, where B represents the interaction energy of the polymer–solvent system, equation 13 can be rewritten as

$$(1/T_m - 1/T_m^0)/v_1 = (RV_u/V_1\Delta H_u)(1 - BV_1v_1/RT_m) \tag{17}$$

Thus, according to equation 17 a plot of the quantity $(1/T_m - 1/T_m^0)/v_1$ against v_1/T_m for a given polymer–diluent system should yield a straight line. The intercept should equal $(RV_u/V_1\Delta H_u)$ and the interaction energy parameter B can be computed from the slope of the resulting straight line. A typical plot of this type is given in figure 3, where the polymer is natural rubber and the three different diluents employed are indicated (139). The straight lines obtained are characteristic of those obtained for a wide variety of polymer–diluent mixtures (10, 18, 56, 87, 98, 99, 102, 139), and lend strong support to the validity of equation 13. It should be recalled that ΔH_u is an inherent property of the polymer repeating unit and is independent of the nature of the diluent. In table 1 some typical results obtained for ΔH_u for several different polymer–diluent mixtures are given. These results show quite strongly that ΔH_u is indeed independent of the nature of the diluent employed and is an inherent property of the polymer chain. The above observations substantiate to a large extent the validity of applying thermodynamic principles applicable to first-order transitions to polymeric systems and support the view that the disordering process in these systems is closely related to the conventional melting of crystals of low-molecular-weight materials. ΔH_u is the heat required to melt one mole of repeating units and should be sharply contrasted with the heat of fusion, ΔH_u^*, obtained calorimetrically when a semicrystalline polymer is melted. ΔH_u^* will be less than ΔH_u (at best the two quantities can be equal) and will depend on the state of the semicrystalline polymer.

The dependence of the melting temperature on molecular weight has also been deduced from the statistical theory. For a heterogeneous polymer having the most probable molecular-weight distribution this dependence is given by

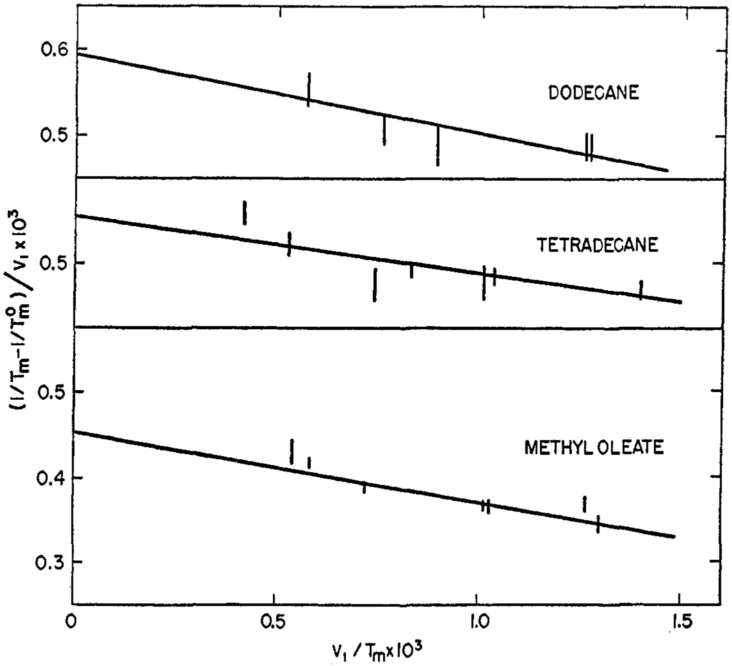


Fig. 3. Plot of $(1/T_m - 1/T_m^0)/v_1$ vs. v_1/T_m for natural rubber mixed with the indicated diluents (139).

TABLE 1

Some typical results for the heat of fusion as determined by the diluent method

Polymer	Diluent	ΔH_u
		cal. per mole of repeating unit
Natural rubber (139)	Tetradecane	1040
	Methyl oleate	980
	Dodecane	1100
Cellulose tributyrate (98)	Tributyrin	2800
	Benzophenone	2900
	Hydroquinone monomethyl ether	2800
	Dimethyl phthalate	2800
	Ethyl benzoate	3200
	Ethyl laurate	3100
Polychlorotrifluoroethylene (18)	Toluene	1220
	Mesitylene	1100
	o-Chlorobenzotrifluoride	1260
	Cyclohexane*	1330

* Melting-point data scattered so that ΔH_u is only approximate.

equation 12, while for molecular-weight fractions it is given by equation 11. For either of these cases, the values of ΔH_u usually observed indicate that the limiting values of the melting temperature should be reached for degrees of polymerization of about 100. This conclusion has been verified by the studies of Ueberreiter, Kanig, and Brenner (159) for fractions of polyethylene succinate and of Evans, Mighton, and Flory (41) on samples of polydecamethylene adipate, the latter prepared in such a manner as to possess the most probable molecular-weight distribution. The latter investigators found that equation 12 was valid for values of $\bar{x}_n$ as low as several repeating units. The melting temperature observed will be caused by the disappearance of crystallites formed from the larger molecules but the melting temperature itself will depend on $\bar{x}_n$. For polydecamethylene adipate the values of ΔH_u as deduced from equation 12 are in very good agreement with those deduced from the melting-point depression of diluents (equation 13). These studies (41) have also substantiated the assumption that the terminal units of a polymer chain do not participate in the crystallization. Recently (100) the asymptotic relation between T_m and molecular weight in linear polymers was illustrated for the case of polymethylene, where the observed T_m (136–137°C.) is very close to the convergence temperature predicted for a normal paraffin of high molecular weight (63).

C. THE FUSION OF COPOLYMERS

Copolymers consisting of sequences of different chemical repeating units are capable of crystallizing as long as a sufficient concentration of one of the units, the homopolymer of which crystallizes, is present. Thus in a copolymer composed of A and B units with the A units capable of undergoing crystallization, the B units act as a foreign ingredient and will depress the melting point from that of the homopolymer and will also alter the course of the fusion process. A statistical thermodynamic analysis of the fusion of copolymers has also been given by Flory (48, 52) and will be briefly summarized.

Let ζ be the number of A units of a chain which traverses a given crystallite from one end to another. Further growth of this crystallite is restricted along the direction of the chain by the occurrence of B units, while growth in the transverse direction will depend on the availability of the crystallizing units in sequences of sufficient length, as well as on the decrease in free energy that will occur during the crystallization. The probability that an A unit, which is being added to a specified site on the lateral surface of the crystallite, is suitably situated within a sequence of at least ζ units is given by P_ζ.

Under equilibrium conditions

$$P_\zeta^e = \exp\left(-\Delta F_\zeta/RT\right) \tag{18}$$

where

$$\Delta F_\zeta = \zeta\Delta F_u - 2\sigma_e \tag{19}$$

and

$$\Delta F_u = \Delta H_u(1 - T/T_m^0) \tag{15}$$

ΔF_u is the free energy of fusion per mole of A units, so that T_m^0 is the equilibrium melting temperature of the homopolymer composed of A units. The surface free energy per repeating unit at the ends of the crystallite is represented by σ_e and the crystallite has been assumed to be sufficiently large so that the lateral surface free energy can be neglected. Equation 18 can be conveniently rewritten as

$$P_\zeta^e = (1/D)e^{-\zeta\Theta} \tag{20}$$

where

$$\Theta = (\Delta H_u/R)(1/T - 1/T_m^0) \tag{21}$$

and

$$D = \exp\,(-2\sigma_e/RT) \tag{22}$$

It can be shown (52) that if crystallites of length ζ, $\zeta + 1$, and $\zeta + 2$ are present and if equilibrium conditions prevail, the residual concentration of sequences of length ζ in the amorphous regions of the copolymer is given by

$$w_\zeta^e = \zeta D^{-1}(1 - e^{-\Theta})^2 e^{-\zeta\Theta} \tag{23}$$

For a random copolymer prior to the development of crystallinity the concentration of sequences of length ζ is given by

$$w_\zeta^0 = \zeta(X_A/p)(1 - p)^2 p^\zeta \tag{24}$$

where X_A is the mole fraction of A units (it being assumed that the A and B units have the same volume, otherwise volume fractions should be used) and p is the probability that in the copolymer an A unit is succeeded by another A unit, independent of the number of A units preceding the given one. For a random copolymer $p = X_A$, while for an ordered copolymer $p \geq X_A$ and $p < X_A$ for an alternating copolymer.

From equations 23 and 24 it can be seen that at a critical crystallite length ζ_{cr}, the initial concentration and the equilibrium concentration of sequences in the amorphous regions are equal. Thus

$$\zeta_{cr} = -\{\ln\,(DX_A/p) + 2\ln[(1 - p)/(1 - e^{-\Theta})]\}/[\Theta + \ln p] \tag{25}$$

For values of ζ less than ζ_{cr}, w^e is less than w_ζ^0, while for ζ greater than ζ_{cr}, w_ζ^0 is greater than w_ζ^e.

At equilibrium, crystallites of size equal to or greater than ζ_{cr} may exist, but those smaller cannot.

Prior to crystallization

$$P_\zeta^0 = X_A p^{\zeta-1} \tag{26}$$

and the necessary and sufficient condition for crystallization to occur is that $p_\zeta^0 > p_\zeta^e$ for one or more values of ζ. Thus for crystallization to be possible

$$(X_A/p)p^\zeta > (1/D)e^{-\Theta\zeta} \tag{27}$$

and since for the cases usually occurring $(X_A/p) < 1/D$, the requirement of equation 27 becomes

$$\Theta > -\ln p = \Theta_m \tag{28}$$

The highest temperature at which crystallinity can occur is the melting temperature T_m, which is defined by

$$1/T_m - 1/T_m^0 = -(R/\Delta H_u) \ln p \tag{29}$$

When there is a large tendency for alternation of the units or if σ_e is small, X_A/p may be greater than $1/D$. The inequality $\Theta > \Theta_n$ will not hold and equation 29 will not be fulfilled. However, in this case the inequality expressed by equation 27 could be satisfied by crystallites of smaller length and crystallization is still possible.

For the usual case equation 29 should be appropriate and it is deduced from it that the melting-point depression will depend not only on ΔH_u and the copolymer composition but also on the nature of the copolymerization kinetics. Thus if the two types of units occur in random sequences, $p = X_A$ and

$$1/T_m - 1/T_m^0 = -(R/\Delta H_u) \ln X_A \tag{29-1}$$

However, if the units alternate to a greater extent than that which occurs in a random distribution, $p < X_A$ and the melting-point depression will be greater than for the random case. Similarly, if the crystallizing units occur in long sequences as in a blocked polymer, then $p > X_A$ and the depression of the melting point will not be as large as in the random case. In developing equation 29 cognizance was not taken of the fact that, subsequent to melting, the A units which participated in the crystallization can interact thermodynamically with the previously amorphous A and B units. Consideration of this effect (48) leads to a slight modification of equations 29 and 29-1 but does not significantly alter them.

From the standpoint of theory the melting of a copolymer will occur at a well-defined temperature. Before considering the melting of copolymers and the validity of equations 29 and 29-1 in terms of experimental results, it is advisable to consider the theoretical predictions as to the manner in which crystallinity disappears in a semicrystalline copolymer. A satisfactory approximation for the fraction of the units crystalline can be obtained by summing up all the sequences of A units participating in the crystallization. Thus for the fraction crystalline

$$\begin{aligned} w_c &= \sum_{\zeta_{cr}}^{\infty} (w_\zeta^0 - w_\zeta^e) \\ &= (X_A/p)(1-p)^2 p^{\zeta_{cr}}\{p(1-p)^{-2} - e^{-\Theta}(1-e^{-\Theta})^{-2} \\ &\qquad + \zeta_{cr}[(1-p^{-1}) - (1-e^{-\Theta})^{-1}]\} \end{aligned} \tag{30}$$

Plots of equation 30 for a random copolymer (52) indicate that crystallinity disappears over a wide temperature range and that a small but finite amount of crystallinity, undetectable by the usual experimental methods, will persist for an appreciable interval below T_m. The breadth of the temperature interval in which this small amount of crystallinity persists will increase as X_A decreases. Thus equation 30 indicates a sigmoidal-shaped melting curve as contrasted to the relatively sharp melting of homopolymers. This is a consequence of the broad distribution of sequence lengths present in copolymers. Although the last traces of crystallinity will disappear at a sharply defined temperature, $w_c = 0$ at $\Theta = \Theta_m$, the detection of this temperature by the usual experimental methods will be extremely difficult if not impossible.

The rather broad melting range characteristic of copolymers has been exemplified many times in studies of the fusion of polyethylene. This polymer is highly branched and since the branched units do not participate in the crystallization, it can, for crystallization purposes, be considered as a copolymer. Heat capacity measurements (35, 130) and specific volume–temperature measurements (82, 100) give broad melting ranges; approximately half the crystallinity disappears over about a forty-degree temperature interval. This behavior can be contrasted rather sharply with that of the linear analog polymethylene (see figure 2), wherein all the melting occurs over a rather narrow temperature interval. In figure 4 the volume–temperature plots for three different polybutadiene polymers (104) containing varying amounts of the crystallizing

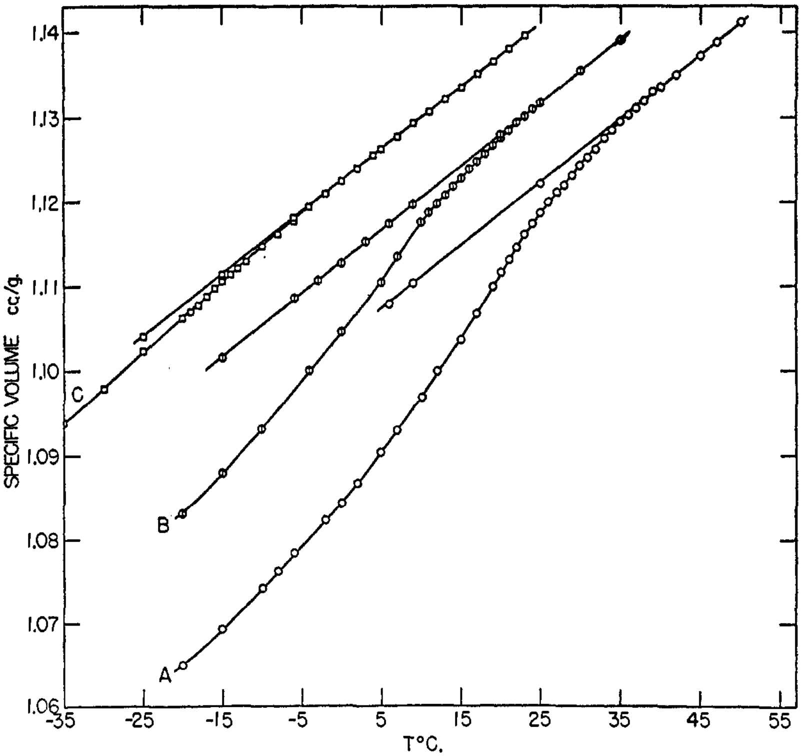


FIG. 4. Plot of specific volume vs. temperature for polybutadienes. Curve A for polymer prepared at −20°C.; curve B for polymer prepared at 0°C.; curve C for polymer prepared at +50°C. Curves B and C are arbitrarily displaced upward along the ordinate; for the actual specific volume subtract from the ordinate 0.01 for curve B and 0.02 for curve C (104).

trans 1,4 units are given. These plots are typically sigmoidal and crystallinity disappears over a wide temperature range. The melting range is increased as the amount of non-crystallizing component is increased, and the volume change on melting is simultaneously decreased. The inherent difficulty in experimentally determining an accurate melting temperature in copolymers can be seen from this figure. As an aid in locating T_m one must have recourse to the establishment of a supercooled liquid line. It should be emphasized that the broad temperature range over which crystallinity disappears is not a general characteristic of homopolymers, as has been assumed (121), but is caused by the incorporation of non-crystallizing copolymeric units into the chain.

Condensation-type copolymers are usually of the random type and are the most logical with which to examine the validity of equation 29-1. According to this equation, for a series of copolymers having a common crystallizing unit, a plot of $1/T_m$ against $\ln X_A$ should be linear, irrespective of the nature of the non-crystallizing units. The slope of this plot will depend on ΔH_u, a property of the crystallizing unit. In figure 5 results of a study by Evans, Mighton, and Flory (41) of the melting temperature of decamethylene sebacate copolyesters with various coingredients are plotted. The data are well represented by a straight line; similar results have been obtained for other copolyesters (39, 40, 41), copolyamides (41, 56), and diene-type polymers where only one of the structural units is capable of crystallizing (104, 114). These results substantiate the validity of equation 29-1 in describing the dependence of the melting point of a copolymer on its composition. However, from the slope of the straight line in figure 5 a value of ΔH_u of 4700 cal. per mole of repeating unit was obtained for polydecamethylene sebacate, while from an analysis of the depression of the melting point of this polymer by diluent a value of 12,000 cal. per mole was deduced (41). Thus an analysis of the copolymer data yields an appreciably lower value for ΔH_u. As indicated in table 2, for many polymers the value of ΔH_u obtained by the copolymer method is appreciably lower than that obtained by the diluent method.

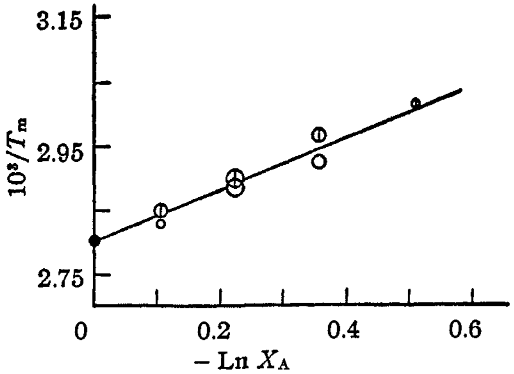


FIG. 5. Plot of $1/T_m$ vs. $-\ln X_A$ for decamethylene sebacate copolyesters. Coingredients: decamethylene isophthalate (⦶) and *cis*-1,4-cyclohexamethylene sebacate (○) (Evans, Mighton, and Flory (41)).

TABLE 2

Comparison of the copolymer and diluent methods in determining the heat of fusion

Polymer	ΔH_u		References
	Copolymer method	Diluent method	
	cal./mole	*cal./mole*	
Decamethylene adipate	3800	10,200	(41, 99)
Decamethylene sebacate	4700	12,000	(41)
N, N'-Sebacoylpiperazine	5000	6,200	(56)
Chloroprene	1350	2,000	(114)
Decamethylene sebacamide	7800	8,200	(10, 41)

Though equation 29-1 appears to be an adequate empirical description of the dependence of the melting temperature on copolymer composition, the value of ΔH_u that is deduced is low by varying amounts. This situation occurs because even sensitive methods of determining T_m cannot detect the disappearance of the small number of crystallites composed of very long sequences of the A units. The temperature at which these crystallites disappear is the one required by equation 29-1. As the concentration of the crystallizing units is decreased, the difference between the experimentally detectable melting temperature and that required by theory systematically increases. The melting-point depressions appear to be greater than they actually are; hence a lower value of ΔH_u is deduced. Though the value of ΔH_u deduced from the melting of copolymers is deemed unreliable, it is still a useful parameter in describing the dependence of the observed melting temperature on composition.

When the different units of the copolymer appear in long sequences, as in a block copolymer, the melting-point depressions should not be so great as predicted by equation 29-1. Striking evidence of this fact is seen in the observations of Coffey and Meyrick (32), who investigated the melting temperatures of copolymers of ethylene sebacate and ethylene adipate which were prepared as either random or block copolymers. Invariably the block copolymers possessed a higher T_m than the corresponding random-type copolymers. For example, for copolymers having equal molar compositions T_m for the random copolymer was 52°C., while that of the corresponding block copolymer was 20° higher. Similar effects are observed (33) for block copolymers of ethylene terephthalate and polyoxyethylene glycol, where only slight depressions in the melting temperature of polyethylene terephthalate occur. Verification of equation 29 has also been obtained for the system α-methylstyrene–fumaronitrile, where there is a strong tendency for the units to alternate (141).

If the B units are also capable of crystallizing and are structurally dissimilar to the A units, then as the proportion of B units is increased a eutectic-type minimum will be observed in the melting-point–composition curve (30, 39, 40, 83). If the two units are crystallographically similar, then cocrystallization can result; this phenomenon has been observed for copolymers of hexamethylene terephthalamide and hexamethylene adipamide and is indicated by a monotonic increase in melting temperature (39). Indications of cocrystallization of different units have also been found in partially substituted cellulose derivatives (98).

D. THERMODYNAMIC QUANTITIES

Since polymers are not completely crystalline, portions of a given molecule are capable of participating in several different crystallites. Thus the thermodynamic quantities directly measured during the fusion process will by necessity depend on the semicrystalline state of the system, and hence will not be of very general utility. The more significant and useful quantities will be those characteristic of the chain repeating unit; these parameters are the equilibrium melting temperature, the heat of fusion, and the entropy of fusion, T_m^0, ΔH_u, and ΔS_u, respectively. In table 3 these quantities are given for those polymers where reliable measurements have been made. The melting points were determined by methods which directly measure changes in the amount of crystallinity and, since slow heating rates were employed, are deemed accurate. ΔH_u was deduced from the measured melting-point depression of polymer–diluent mixtures and ΔS_u was taken from the ratio $\Delta H_u/T_m^0$. The polymers listed in table 3 vary in their chemical nature and in the size of the structural repeating unit; hence the wide variation observed for ΔH_u and ΔS_u is not surprising. It can be expected that a major contribution to the entropy of fusion is the increased gain in configurational freedom by the chain segments on melting. ΔS_u would then be expected to increase as the number of chain atoms in a repeating unit increases. A more rational basis of comparison between different units might then be achieved by dividing the observed ΔS_u by the number of single bonds in the repeating unit. These values are given in the last column of table 3. However, it must be realized that besides the configurational freedom gained on melting there can be other contributions to the entropy of fusion. In particular, one

TABLE 3

Thermodynamic quantities characterizing the fusion of polymer

Polymer	T_m^0	ΔH_u	ΔS_u per Unit	ΔS_u per Bond	Reference
	°C.	*cal./mole of unit*			
Polymethylene	137	785*	1.90	1.90	(100)
Polyethylene oxide	66	1,980	5.85	1.95	(97)
Natural rubber	28	1,050	3.46	1.15	(139)
Gutta percha†	74	3,040	8.75	2.92	(102)
Polychloroprene (1,4-*trans*)‡	80	2,000	5.7	1.9	(114)
Polydecamethylene adipate	79.5	10,200	29	1.60	(99)
Polydecamethylene sebacate	80	12,000	34	1.55	(41)
Polydecamethylene azelate	69	10,000§	29	1.40	(10)
Polydecamethylene terephthalate	138	11,000	26.8	1.9	(87)
Polyhexamethylene terephthalate	160.5	8,300	19.1	1.9	(87)
Poly-*N*,*N*′-sebacoylpiperazine	180	6,200	13.7	1.25	(56)
Polydecamethylene sebacamide	216	8,200	16.8	0.76	(10)
Polydecamethylene azelamide	214	8,700	17.9	0.85	(10)
Polychlorotrifluoroethylene	210	1,200	2.50	1.25	(18)
Cellulose tributyrate	207	3,000	6.2	3.1	(98)
Cellulose trinitrate	>700	900-1500	<1.5	<0.75	(53)
Cellulose 2.44-nitrate	617	1,350	1.51	0.76	(124)

* Extrapolated value from data for low-molecular-weight paraffins.

† For the higher-melting, thermodynamically stable polymorph.

‡ Extrapolated to the hypothetical all-1,4-*trans* polymer.

§ Approximate value.

must give consideration to the contribution due to the volume change that occurs on melting.

The ultimate aim of many physicochemical studies is the description of physical properties in terms of the chemical and molecular structure. Since T_m is defined by ΔH_u and ΔS_u, an interpretation of these latter two quantities in terms of structure is highly desirable. This is admittedly a rather formidable task, since the quantities in question depend on differences between the liquid and the crystalline states. Furthermore, the possibility also exists that the heats and entropies of fusion are themselves correlated. Despite the obvious difficulties in attempting to achieve this ultimate goal, the thermodynamic parameters that have been deduced so far deserve some consideration in terms of structure, particularly since they focus attention on some salient points.

The heats of fusion of the various polymers listed in table 3 fall generally into two classes. In one class the values of ΔH_u are of the order of several thousand calories per mole of repeating unit and in the other category they are about 10,000 calories per mole of repeating unit. Except for the derivatives of cellulose the lower values of the heats of fusion are characteristic of the non-polar polymers, while the higher values of ΔH_u are characteristic of the more polar polymers. The melting temperature does not directly follow the variation in ΔH_u, indicating that the entropy of fusion must play a significant role in determining T_m. It is reasonable to assume that an increase in the intermolecular forces will be reflected in an increased value of ΔH_u. Attempts to correlate intermolecular forces with chemical structure have been made by calculating the cohesive energy of the repeating units by various schemes (23c, 25, 106). Although some correlation appears to be attained, comparison with the measured value of ΔH_u is not too good. For example, values of ΔH_u for the *cis*- and *trans*-polyisoprenes differ by a factor of about 3, while the cohesive energy densities of the two appear to be identical. Similarly, although the values of ΔH_u for the aliphatic polyesters and polyamides are comparable, the cohesive energy density calculated for the polyamides is appreciably greater. Thus an effective correlation between the cohesive energy densities and the heats of fusion has not as yet been attained.

The melting temperature of polyethylene oxide is less than that of polymethylene, although it possesses an appreciably greater heat of fusion. The larger entropy of fusion of polyethylene oxide can be due to its greater flexibility in the liquid state as a result of periodic introduction of ether linkages along the chain. As has been noted, ΔH_u for gutta percha, the 1,4-*trans*-polyisoprene, is approximately three times as great as that for the *cis* polymer, natural rubber. Since the melting temperatures are comparable on an absolute scale, there is a drastic difference in their respective entropies of fusion. The heats of fusion of the aliphatic and aromatic polyesters appear to be similar, yet their melting points differ by about 100°C. The chain rigidity caused by the *p*-phenylene linkage is thus reflected in a much higher entropy of fusion.

The heats of fusion of the polyamides are about the same as those of the corresponding polyesters, despite the appreciable difference in melting points that exists. Thus the polyamides have relatively low entropies of fusion when compared to other polymers. Cellulose derivatives are high melting and considered to be very polar, but we again find surprisingly low values for the heats of fusion. The extremely high melting points of the cellulose trinitrate are again clearly a result of low values for the entropy of fusion. The entropy of fusion of cellulose tributyrate is somewhat higher, presumably owing to the contributions from the relatively large butyrate side group.

The important role played by the entropy of fusion in determining the location of the melting temperature is apparent despite the relatively small amount of data available. The entropy of fusion, being the difference in entropy between the liquid and the crystalline states, will depend on any disorder that may be present in the crystal as well as on the flexibility of the molecule in the liquid state, the latter most probably being the more important factor. Some interesting and rather suggestive qualitative correlations exist between the molecular configuration of a polymer in the liquid state and its melting temperature. For example, polydimethylsiloxane has a very low T_m (165) and is also a very flexible molecule (55). Similarly, nitrocellulose in the liquid state is a fairly extended molecule, it possesses a relatively low entropy of fusion, and it is consequently high melting (79, 81). Studies of the solution properties of polyhexamethylene adipamide (96) indicate that it may be a relatively extended molecule, which can account, in part, for the low entropy of fusion observed for the polyamides. The almost threefold difference in the entropies of fusion between natural rubber and gutta percha may be related to the greater relative extension in space of natural rubber as compared to gutta percha (162). Since at present no quantitative relationship exists between molecular configuration and entropy of fusion the qualitative observations will have to suffice.

Flory (52a) has recently shown that polymer chains which are only partially flexible can be arranged in a state of parallel order as a consequence solely of the influence of intramolecular forces. The critical amount of inflexibility necessary to achieve this condition is surprisingly small, and the transition from the ordered to the disordered state resembles a first-order transition. Hence for chains arranged in parallel order only relatively weak intermolecular forces would be required to achieve a state of three-dimensional order. It is therefore quite plausible for relatively stiff chains to possess high melting temperatures accompanied by low heats of fusion.

For a majority of the polymers listed in table 3 ΔS_u is of the order of R calories per single bond, a value which is suggestive of the hole theory of melting (74). This theory might be applicable if the only contribution to ΔS_u is the configurational freedom which is gained on melting. However, there are other contributions, particularly that due to the latent volume change that occurs on melting. Thus at constant temperature the change in entropy with change in volume can be given (128, 149) by

$$(\partial S/\partial V)_T = -\alpha/\beta \tag{31}$$

where α is the volume–temperature coefficient at constant pressure and β is the volume–pressure coefficient at constant temperature. At the melting temperature equation 31 can be written as

$$\Delta S_v = -(\alpha/\beta)\Delta V_u \tag{32}$$

where ΔV_u is the latent volume change on melting per repeating unit and ΔS_v is the corresponding entropy change. Natural rubber is the only polymer for which all the quantities necessary to evaluate ΔS_v are available. Taking at the melting temperature $\alpha = 7.42 \times 10^{-4}$ cm.^{3}/g./degree (11), $\beta = 60 \times 10^{-6}$ cm.^{3}/g./bar (148), and $\Delta V_u = 0.098$ cm.^{3}/g. (19, 139), $\Delta S_v = 1.8$ cal./deg./mole of repeating unit. The entropy of fusion of natural rubber was found to be 3.46 cal./deg./mole, so that the volume change that occurs on melting makes a rather significant contribution to the observed entropy of fusion. A similar contribution from ΔS_v can be reasonably expected for other polymers (102). Assuming that ΔS_u can be approximated by the sum of ΔS_v and ΔS_c, where ΔS_c is the configurational contribution, for natural rubber $\Delta S_c = 1.7$ cal./deg./mole. According to the lattice theory of polymer solutions the entropy change on completely disordering a mole of segments at constant volume is given by

$$\Delta S_c = R \ln \left[(Z - 1)/e\right] \tag{33}$$

where Z, the lattice coordination number, is a measure of the packing of the segments in the liquid state. Direct comparison between the observed ΔS_c and equation 33 cannot be made, since both the lattice coordination number and the relation between the structural repeating unit and the size of the segment in the equivalent freely jointed chain must be known. However, the value of ΔS_c calculated for natural rubber is not incompatible with equation 33 when reasonable values for the parameters are used. These results indicate that the contribution of ΔS_v to ΔS_u is significant and must be considered before attempting to quantitatively relate the entropy of fusion and the configurational freedom gained on melting.

E. FURTHER APPLICATIONS OF THERMODYNAMICS

1. Polymorphism

The arrangement of the atoms in the unit cells can occur in different modifications similar to the polymorphism exhibited by crystals of low-molecular-weight materials. For example, from stereochemical considerations Bunn (19) has predicted the possibility of four different crystalline modifications of gutta percha. Three of the polymorphs have actually already been identified (19, 44); two of these polymorphs can be formed solely by cooling the polymer to an appropriate temperature, while the third form crystallizes only upon stretching. Polymorphic modifications have also been observed in the polyamides polyhexamethylene adipamide and polyhexamethylene sebacamide (27) and polycaproamide (78), poly-α-butylene (122, 123), and poly-p-xylene (85). Polyesters of trimethylene glycol and dibasic acids possess a polymorphic transition on stretching (62) which is similar to that observed in proteins (4, 5) and the synthetic polypeptides (8).

The relative thermodynamic stability of the polymorphs can be described by utilizing the previously developed description of a semicrystalline polymer. At a given temperature the polymorph which possesses the greatest free energy of fusion per repeating unit will be the most stable. Since ΔF_u can be approximated by $\Delta H_u(1 - T/T_m^0)$, determination of the melting points and of ΔH_u at the respective polymorphs defines ΔF_u and hence the stability. This method has recently been applied in describing the relative stability of two crystalline modifications of gutta percha which form simply upon cooling (102). For this case it was deduced that the lower-melting polymorph is a metastable one at all temperatures.

2. *Effect of hydrostatic pressure*

The thermodynamic principles governing the melting of polymeric systems should, of course, also be valid when applied to a one-component system. Thus the Clapeyron equation describing the variation of the melting temperature with applied hydrostatic pressure can be appropriately written as

$$\mathrm{d}T_m^0/\mathrm{d}p = T_m^0 \Delta V_u/\Delta H_u \tag{34}$$

Systematic experiments to check the validity of equation 34 are not available. The variation of the melting temperature with applied hydrostatic pressure has been observed for polytetrafluoroethylene (109). However, since neither ΔV_u nor ΔH_u was independently determined, a verification of equation 34 could not be achieved. An indication of the validity of appropriately applying the Clapeyron equation to the melting of polymers is seen in the data for natural rubber. Dow (37) has observed that T_m for natural rubber at 1230 atm. is 77.5°C. According to equation 34 T_m^0 is predicted to be 84°C. for this polymer (139). The difference between the observed and predicted melting temperatures is well within experimental error and these observations, though sparse, indicate the validity of equation 34.

3. *Crystallization from dilute and moderately concentrated solutions*

If a sufficiently poor diluent is mixed with the polymer, then at a concentration of diluent less than a critical value the melting temperature remains invariant with composition. Such behavior has been observed with polychlorotrifluoroethylene (18) and with poly-N,N'-sebacoylpiperazine (56) when mixed with the appropriate diluents. In the concentration range where this invariance occurs the mixtures form two immiscible liquid phases (diluent and liquid polymer) upon melting, and equation 13 is no longer valid. Hence, as a consequence of the phase rule, the melting temperature must be invariant with composition. On further heating such a system the two liquid phases become completely miscible at a well-defined temperature. The boundary of this liquid miscibility can be experimentally established (56, 135) and displays the typical characteristics of polymer systems (45, 80) having a maximum at low polymer concentrations.

When a thermodynamically favorable solvent is mixed with the polymer the melting temperature will monotonically decrease as the concentration of diluent increases (56, 135, 160), even in extremely dilute solutions. However, in dilute solutions equation 14 is no longer an adequate representation for the chemical potential of a chain unit, since the lattice model does not satisfactorily account for the non-uniform concentration of polymer segments (50d). In calculating the theoretical relation between melting temperature and composition in this concentration range recourse must be had to the thermodynamic theories applicable to dilute polymer solutions (49, 54). However, when this is accomplished no appreciable change results in the relations between melting point and composition. Though crystallization and melting have been observed in dilute solutions, adequate systematic quantitative investigations have not as yet been reported to describe the melting behavior in the dilute range.

Heterogeneous polymers are usually separated into various molecular-weight species by fractional precipitation from dilute solution. This procedure is used because the solubility of polymers decreases with increasing molecular weight. It is of extreme importance that the separation which occurs during the fractionation process be the separation of two immiscible liquid phases, and in attempts to fractionate a semicrystalline polymer it is necessary to ascertain that the above-mentioned conditions are fulfilled. If instead of liquid–liquid separation crystallization occurs, the fractionation process can be very inefficient because the melting temperatures are not very sensitive to changes in molecular weight. Large supercooling effects are possible, so that crystallization kinetics can actually govern the separation process. Thus the molecular-weight fractionations of many crystalline polymers, such as the high-melting cellulosics, the polyamides, and polyvinyl chloride, have been relatively unsuccessful when compared to the non-crystallizing amorphous polymers. Liquid–liquid type separation can be distinguished from crystallization by a phase diagram study. In the former case the separation temperature displays a characteristic maximum when plotted against concentration (in a one-component solvent), while for the latter case the separation temperature monotonically increases with concentration.

The crystallization of many polymers in dilute or moderately dilute solutions imparts a high viscosity and rigidity to the mixture and such systems have been popularly termed gels. This type of gel formation occurs because of insolubility, i. e., the temperature of observation is below the melting temperature of the mixture, and should not be confused with the gelation that occurs during the polymerization of multifunctional comonomers (50e). The criterion for gelation to occur is distinctly different in the two cases. Many mixtures of semicrystalline polymers with diluent, such as polyvinyl chloride in dioctyl phthalate (165), nitrocellulose in ethyl alcohol (125), and polyacrylonitrile in dimethyl formamide (12, 13), are relatively rigid even in dilute solution. In fact, it appears as though the gelation of gelatin itself can be treated as a phase transition (14, 154). In harmony with this view the rate of "gel formation" in these systems is very temperature-sensitive, as is the crystallization rate of polymeric systems (see Section IV), and appreciable supercooling can be achieved. The physical properties of these systems, such as their high viscosity, rigidity, and elastic behavior, can be explained if the crystalline regions act as effective cross-links. Care must be exercised in the interpretation of physicochemical measurements prior to the actual observation of the gels, since nuclei or crystallites too small to be seen can be present. This can be a troublesome phenomenon, particularly in thermodynamic measurements in dilute solutions. For example, Doty, Wagner, and Singer (36) observed and recognized some rather unusual behavior in their light-scattering and osmotic pressure studies of polyvinyl chloride in dioxane, a poor solvent. At high temperatures the osmotic pressure–concentration curves were of the normal variety and when extrapolated to infinite dilution gave molecular weights which were in agreement with that obtained in good solvents. As the temperature was lowered the molecular weight appeared to be appreciably higher (both the number average and weight average). At the same time the second virial coefficient decreased to zero with decreasing temperature and eventually became negative at a sufficiently low temperature. This peculiar thermodynamic behavior could be the result of a slow crystallization process.

F. CRYSTALLIZATION OF DEFORMED NETWORKS

For crystallization to occur it is necessary that the product of the absolute temperature and entropy of fusion be equal to or less than the heat of fusion. These conditions can be achieved merely by cooling the system and the problems considered heretofore have been concerned solely with crystallization induced by cooling. Alternatively, the criteria for crystallization can be realized by deforming the polymer at constant temperature, as, for example, by stretching. Under these conditions less entropy will be lost on crystallizing as compared to the undeformed state. Deformation processes thus enhance the tendency of polymers to crystallize, particularly in cross-linked systems which possess a network structure, since the imposed orientation cannot be easily dissipated by viscous or relaxation processes. These considerations are in accord with the widespread observation that many polymers such as polyisobutylene and vulcanized natural rubber, which do not readily crystallize simply upon cooling, do so quite easily when stretched. A statistical thermodynamic treatment of the crystallization of polymer networks held in simple extension has been given by Flory (46). Because of simplifications that are introduced, the results are not completely quantitative. Despite this shortcoming the analysis provides a rather keen insight into the nature of the problem and has pointed out a significant experimental approach. In the calculation the semicrystalline state is hypothetically reached by first stretching the polymer to an extension ratio α at a temperature sufficiently high to prevent the occurrence of crystallization. The network is then cooled to a temperature where crystallinity can develop while the relative extension ratio is maintained constant. It is assumed that the direction in which the chains traverse the crystallite is parallel to the stretching direction, which is designated as the z direction. The free-energy difference is calculated between the stretched semicrystalline network and the completely crystalline polymer taken as the standard state. The usual contribution from the heat of fusion is realized and there are two significant contributions due to the resulting change in entropy. By participating in the crystallization a segment sacrifices all its configurational freedom and the entropy decreases. Also, upon crystallization the end-to-end distance of the segments in the intervening amorphous regions is altered, causing an additional entropy change. The contribution of this entropy change is quite significant and its computation presents the major problem encountered.

By using Gaussian statistics to express the chain configurations in the amorphous regions and assuming that all chains traverse the crystallite in the same direction as the z displacement of one end of the chain with respect to the other, Flory (46) has derived an expression for the free-energy change that occurs. When the equilibrium condition $(\partial \Delta F/\partial \lambda)_\alpha = 0$ is applied to this expression, the fraction of the polymer that is amorphous is found to be

$$\lambda = \{[3/2 - \phi(\alpha)/[(3/2 - \Theta)]\}^{1/2} \tag{35}$$

where

$$\phi(\alpha) = (6/\pi)^{1/2}\alpha/n^{1/2} - (\alpha^2/2 + 1/\alpha)/n \tag{36}$$

and

$$\Theta = (\Delta H_u/R)(1/T_m^0 - 1/T) \tag{37}$$

where n is equal to the number of segments between cross-links and T_m^0 is the melting temperature of the undeformed network. These expressions for the equilibrium fraction crystalline should be considered only approximate, owing to the oversimplification of the model, but should hold at low degrees of crystallinity. Equation 35 is obviously inadequate at low elongations, for at $T = T_m^0$ and $\alpha = 1$ (no deformation) a finite amount of crystallinity is indicated. This is, of course, a physically untenable conclusion. At higher elongations the expression for λ should be more reliable and indicates that the degree of crystallinity induced by stretching is never excessive. This conclusion is borne out by experimental observations of Goppel and Arlman (69) and of Nyburg (127) on stretched vulcanized natural rubber.

The dependence of the melting temperature on the extension ratio can be found by setting $\lambda = 1$ in equation 35 so that

$$1/T_m^0 - 1/T_m = -(R/\Delta H_u)\phi(\alpha) \tag{38}$$

An inconsistency again arises since at $\alpha = 1$, T_m is predicted to be less than T_m^0. At higher extension ratios, when equation 38 can be expected to hold, the elevation of the melting temperature by stretching will depend on the nature of the chain unit as typified by ΔH_u, and on the network structure as described by n, the number of segments between cross-links. Direct experimental investigations of the variation of T_m with α have not as yet been accomplished. However, experiments have been performed, using vulcanized natural rubber (2, 57), where the variation of the incipient crystallization temperature with elongation has been observed. Identification of this temperature with T_m leads to rather good agreement with equation 38. The values of ΔH_u deduced from these studies were 800 (57) and 1030 (2) cal. per mole of repeating unit, results which are in excellent agreement with the value obtained from studies of the melting temperature of natural rubber–diluent mixtures (139). These results cannot be taken as a complete verification of equation 38, since the melting temperatures of the undeformed networks were not determined, and the incipient crystallization temperature could be appreciably lower than the true melting temperature, owing to supercooling effects. Equation 38 also adequately describes the variation of the melting temperature of oriented collagen with extension ratio when immersed in either formamide or water (173).

Subsequent to crystallization the retractive force of the stretched rubber f is equal to $(\partial \Delta F/\partial \alpha)_\lambda$ and can be expressed as

$$f = \sigma RT[(\alpha - 1/\alpha^2) - (6n/\pi)^{1/2}(1 - \lambda)]/\lambda \tag{39}$$

where σ is the number of chains which participate in the crystallite and the equilibrium degree of crystallinity $1 - \lambda$ is specified by equation 35. In the absence of crystallinity the retractive force of the stretched network is given by the usual expression

$$f = \sigma RT[\alpha - 1/\alpha^2] \tag{40}$$

Thus as crystallinity develops at constant extension ratio the tension should decrease. This prediction has been verified by many investigators (65, 113, 115, 172). In fact, equations 35 and 39 indicate that under appropriate conditions the stress will decay to zero and can even become negative. The observation of Smith and Saylor (150) that upon cooling stretched natural rubber to -25°C. there is an elongation of about 4 per cent is in qualitative accord with the theory.

The theoretical analysis and experimental verification of the decrease in tension upon the development of crystallinity would appear to be in contradiction to the widely observed stress–strain curves of natural rubber networks. The retractive force of a system which crystallizes while being stretched is much greater than if there is no crystallinity. This apparent paradox can be resolved (46) by realizing that equations 39 and 35 apply only to conditions of thermodynamic equilibrium, such conditions not being realized when the crystallization develops during the deformation process. The crystallites formed during the isothermal stretching can act as additional points of cross-linkage. Thus, on further stretching, the chain segments in the amorphous regions can be oriented much more than normal. A proportionately larger decrease in the entropy will occur which will result in an increase in the retractive force. Since further crystallization will occur with subsequent elongation, this effect will be enhanced and the increase in the tension accelerated.

G. DEGREE OF CRYSTALLINITY

Many physical and mechanical properties of polymers depend on the fraction of the polymer which is crystalline. It is, therefore, important that this quantity be reliably determined. Since true equilibrium is rarely attained in these systems the degree of crystallinity depends not only on the temperature of observation but to a large extent on previous thermal treatment. Of particular importance are the crystallization conditions and the heating rate employed. Since a determination of the proportion of the material that is crystalline can be obtained by a variety of methods, it is of the utmost importance that the polymer receive the same thermal history prior to each measurement, if a comparison is to be made of the results obtained by the different methods.

The degree of crystallinity can be determined from the measurement of the density or the specific volume by assuming that the specific volume of a semicrystalline polymer is the result of the additive contribution of its crystalline and amorphous portions. Thus

$$\lambda = (\bar{V}_A - \bar{V})/(\bar{V}_A - V_c) \tag{41}$$

where $\bar{V}_A$ is the specific volume of the amorphous polymer at the temperature under consideration, $\bar{V}_c$ is the specific volume of the all-crystalline polymer, and $\bar{V}$ is the specific volume of the semicrystalline polymer. The specific volume of the crystalline regions is obtained from the size and the number of chain units in the unit cell. The structure of the unit cell of the crystal is determined by x-ray diffraction methods. The specific volume of the amorphous region is obtained by extrapolating the specific volume–temperature curve obtained above the melting point to the temperature of interest.

An analysis of the relative intensity of the x-rays diffracted by the crystalline and amorphous regions can also provide a measure of the extent of crystallization. This method is based on the principle that the total x-ray scattering by a substance is independent of the degree of crystallinity. The pioneering work of Goppel (68) and Goppel and Arlman (69) in determining the degree of crystallinity of natural rubber has led to widespread use of this method (71, 72, 95, 107). A review of the various experimental techniques and theoretical methods of analyzing the x-ray diffraction data has recently been given by Nichols (126). If absorption bands which are independently sensitive to the amorphous and crystalline content are present in the infrared spectrum of a semicrystalline polymer, then an absolute determination of the degree of crystallinity can be made. This is the case for polyethylene, where the absorption spectrum has a strong doublet at 725 cm.$^{-1}$, the low-frequency component being characteristic only of the amorphous or liquid portions. Thus, analysis of the infrared absorption spectrum has been used to determine the extent of crystallinity for this polymer (136). If, however, the absorption bands of a polymer are sensitive only to changes in crystallinity, then an absolute method is not available.

Calorimetric measurements can also be used to determine the amount of crystallinity. The ratio of the heat of fusion of the semicrystalline polymer ΔH_u^* measured calorimetrically to ΔH_u (deduced from studies of the melting-point depression with diluents) should be equal to the proportion of the polymer that is crystalline. This method has been used to determine the degree of crystallinity of natural rubber (139), polychlorotrifluoroethylene (75), and polyethylene (35, 130). Recently the degrees of crystallinity of polyethylene and polytetrafluoroethylene were also determined from nuclear magnetic resonance studies (167).

In comparing the values of the degree of crystallinity of a polymer obtained by different methods, it must be realized that the minimum amounts of crystallinity detected by the various methods will differ. Thus it should not be expected that the different methods will give concordant results at low degrees of crystallinity. An analysis of the available data for natural rubber (139) crystallized by cooling at 0°C. indicated that the heat of fusion data, density data, and the x-ray method give concordant results within the experimental error. When crystallization is induced by stretching natural rubber vulcanizates, good agreement has been obtained for the extent of crystallinity by both x-ray and density methods (69, 127). Over a wide temperature range the degree of crystallinity of polychlorotrifluoroethylene obtained by the heat of fusion method agreed to within ±6 per cent with that estimated from density measurements (75). Despite the agreement of the various methods just cited, results on polyethylene, the most widely studied polymer, are discordant (23d, 35) over a wide range in temperature and degrees of crystallinity. Results obtained by the heat of fusion method for this polymer are not in agreement among different investigators (35, 130), owing to the use of different values of the heat of fusion per repeating unit; different estimates of this value are being made from the data for the normal paraffins of low molecular weight. This confusion may exist because of the existence of three different crystalline forms of the low-molecular-weight normal paraffins (76, 144). In some investigations the x-ray and density measurements give reasonable agreement (95), while in other cases (82, 107) these same techniques may give widely different results. One reason for the discordant results is inherent in the nature of the polymer, since it is branched. The degree of crystallinity that can be ultimately attained will depend on the amount of branching, and it is not at all clear that the same samples or types of samples have been compared. Since the melting range of polyethylene is very broad, the degree of crystallinity will be very sensitive to previous thermal treatment and it is imperative for this polymer that these conditions be identical in order for rational comparisons to be made. The experimental results have not substantiated the oft made claim of the importance of fringe regions of the crystallites, since in careful experiments the different methods give reasonably concordant results for the degree of crystallinity.

IV. Crystallization Kinetics of Polymeric Systems

A. GENERAL CONSIDERATIONS

If a polymeric liquid of sufficient regularity is at a temperature below T_m^0 crystallization should ensue. However, similar to the behavior of low-molecular-weight substances, a polymer may be supercooled below T_m or if cooled sufficiently rapidly to a very low temperature can become a glass and crystallinity will be effectively prevented from occurring. Thus, though crystallization is thermodynamically favored at temperatures below T_m, kinetic factors will determine whether any crystallinity will be detected during an experiment. Although it has been demonstrated that the transition from the crystalline to the amorphous state may be treated by thermodynamic methods, at temperatures well below T_m true equilibrium is only very slowly approached. The physical properties of a semicrystalline polymer under these conditions will depend primarily on the kinetic factors prevailing during the crystallization rather than on any considerations of thermodynamic equilibria. An understanding of the mechanisms involved in the crystallization process is thus of prime importance in explaining the properties of this class of polymers.

The experimental observations of the crystallization kinetics in polymeric systems have consisted of two general types of measurements. One type of observation has been concerned with the determination of the total amount of crystallinity developed as a function of time at constant temperature (1, 11, 31, 94, 97, 101, 117, 117c, 132, 133, 142, 161, 170, 171), and a variety of experimental techniques have been employed. On the other hand, by direct microscopic observation the isothermal rate of spherulitic formation and growth has been determined (110, 117, 117c, 129). For a variety of polymer types, the isothermal development of crystallinity follows a very similar if not universal pattern first observed by Bekkedahl (11) for natural rubber. When a polymer sample is quickly transferred from a temperature above T_m to the desired crystallization temperature, a well-defined "apparent induction time" occurs before crystallization becomes observable. After the onset of observable crystallization the process proceeds at an accelerating rate and eventually a pseudo-equilibrium degree of crystallinity is approached. The typical sigmoidal-shaped isotherms that result at various temperatures are illustrated in figure 6 for polyethylene oxide, where

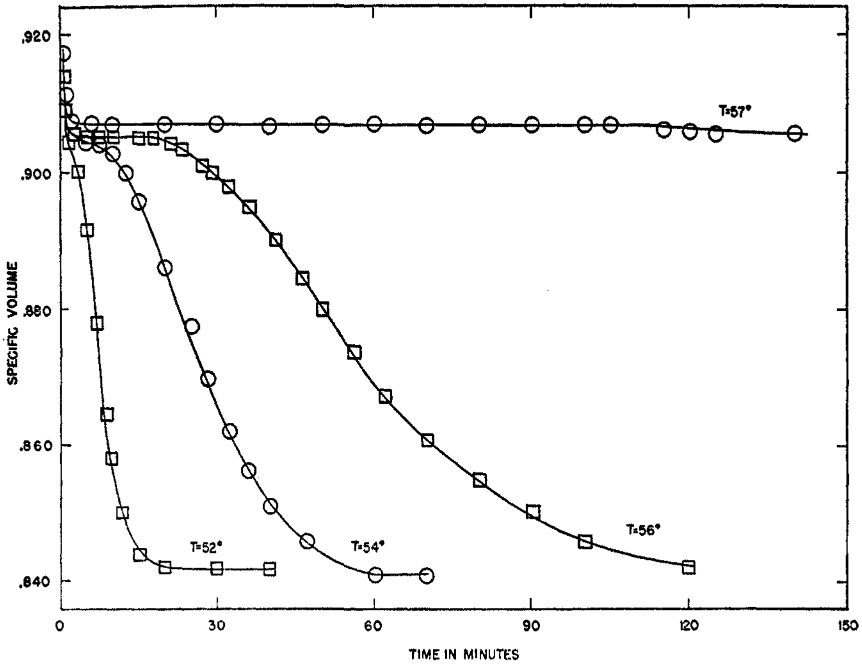


FIG. 6. Plot of specific volume vs. time for polyethylene oxide at various temperatures (Mandelkern, Quinn, and Flory (101)).

in this case the crystallization process was followed by observing changes in the specific volume.

Besides displaying the characteristic isotherms, the crystallization process in polymeric systems has in general been found to be very dependent on temperature. At temperatures just below T_m the crystallization rate is extremely slow; as the temperature is decreased further the rate increases, passes through a maximum, and when the temperature is lowered sufficiently the rate assumes low values once again (31, 117, 171). The extreme sensitivity of the crystallization rate to temperature in the vicinity of T_m can also be seen in figure 6. The time at which crystallization is first observed, τ_i, varies by a factor of 100 for a five-degree temperature interval. The shape of the crystallization isotherms and the temperature variation of the crystallization rate of polymers are reminiscent of the pioneering work of Tammann (151) on the crystallization kinetics of low-molecular-weight materials.

For a phase transformation to occur there must be both an initiation and a propagation of the new phase within a mother phase. The birth of a new phase is termed nucleation and its subsequent development is called growth. The kinetics of an isothermal transformation can usually be explained by an adequate description of the nucleation and growth mechanisms. To be effective in the transformation nuclei exceeding a thermodynamically defined critical size must be formed. These nuclei can be formed within the bulk of a homogeneous supercooled liquid by statistical thermal fluctuations (9, 15, 77, 158). However, foreign bodies, cavities, or other heterogeneities will facilitate the rate at which nuclei are formed (9, 158) and certain types of cavities will even allow the embryo of a phase to be stable at temperatures above which the bulk material is unstable. When the latter type of heterogeneity is present, the crystallization kinetics is sensitive to previous thermal history, so that the behavior at a temperature ΔT degrees below T_m depends on how many degrees above T_m (ΔT^+) it was heated (77).

When the crystallization kinetic experiments in polymeric systems are conducted in such a manner that prior to the crystallization the sample is maintained at a temperature above T_m in order to melt all the crystallites, and if no degradation occurs, the resulting isotherms are extremely reproducible at a specified temperature below T_m and independent of the initial temperature at which the sample was held (94, 101). Although there appears to be a tendency for spherulites to appear in the same position in the field of view after successive crystallization (28, 129, 137), Richards and Hawkins (137) observed that if the above-mentioned conditions are fulfilled spherulites that are subsequently formed do not appear in the same position. These observations are strong evidence that homogeneous nucleation can occur quite generally in polymeric systems. According to Turnbull (156) this situation is often realized in supercooled organic liquids of high viscosity in which crystal growth is relatively slow at temperatures where homogeneous nucleation is measurable. However, there are many instances where the above-mentioned reproducibility and independence of the initial heating temperature are not easily achieved in polymeric systems (1, 117,

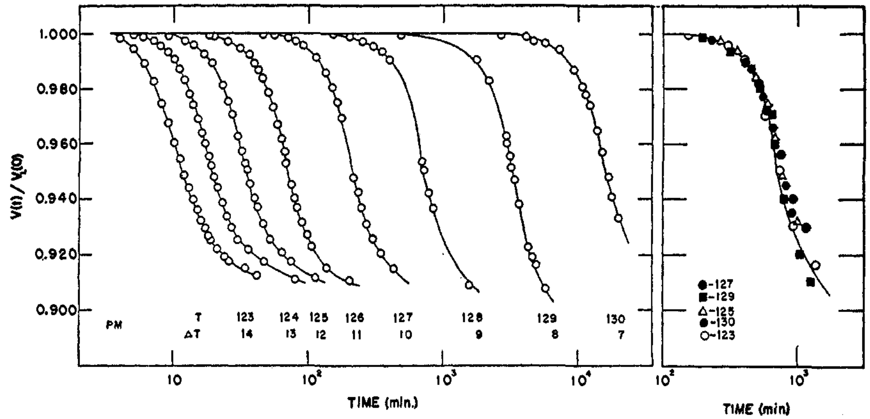


FIG. 7. Left: ratio of specific volume at time t to that at zero time, plotted against log time for polymethylene at various temperatures. Right: superposition of isotherm to isotherm at 128°C. (103).

117c, 129) and in these cases a heterogeneous nucleation process appears to be operative. In some of the cases the heterogeneous nucleation is clearly due to the fact that the samples were incompletely melted (1, 117, 117c) or is due to bubble formation within the bulk of the sample (1). Obviously if fragments of crystallites are retained in the supercooled liquid a heterogeneous process will be favored. Heterogeneous nucleation in these cases is a consequence of inadequate thermal treatment rather than an inherent property of the polymer itself. The strong influence of impurities in governing the course of the crystallization in polymers has recently been demonstrated (66), wherein it has been shown that certain impurities can act as nucleation catalysts in promoting the crystallization of natural rubber.

When the ratio V_t/V_0 of the specific volume at time t to the initial volume is plotted against log t for various temperatures not too far below T_m, it is found that the individual isotherm for the given polymer can be brought into coincidence merely by shifting each of these curves an appropriate distance along the horizontal axis (101, 142). This has been observed for a variety of homopolymers and is illustrated in figure 7 for polymethylene (103). The individual isotherms are given in this plot, and in the right-hand box they have all been superimposed on to the 128° isotherm.[1] It can be seen that the superposition of the isotherms is maintained for the entire crystallization process from zero time to completion. Though most of the detailed studies have been limited to temperatures in the vicinity of T_m, the results of Russell (142) for vulcanized natural rubber and a replot of the data of Wood and Bekkedahl (171) for natural rubber indicate that the superposition may be maintained over the complete temperature range provided crystallinity develops from a true supercooled liquid. Recently Gent

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[1] Though the superposition has been observed for all homopolymers studied it does not appear to be valid when applied to the crystallization of copolymers. The published work of Kovacs (94) on polyethylene supports this view as do unpublished kinetics studies from the author's laboratory on polyethylene and polybutadiene.

(67) has observed in the case of natural rubber studied over a wide temperature range, that if one starts in all cases from the supercooled liquid, the isotherms are indeed superposable.

When the initial state is an incompletely melted liquid or is the glassy state the superposition does not hold over any appreciable temperature range (117, 117c). This is not surprising, because when the sample is first quenched to the glass and then brought to the crystallization temperature the process is quite different from that occurring when the crystallization proceeds directly from the melt. In the former case it has been noted that no well-defined spherulites appear (117, 117c, 129) and the pseudo-equilibrium density increases with increasing temperature (31).

B. ISOTHERMAL CRYSTALLIZATION

A consequence of the superposability of the isotherms is that the temperature coefficient is invariant throughout the course of the process. This observation gives strong support to the assumption that the nucleation and growth processes are concurrent, the same assumption employed by Mehl and Johnson (111), Avrami (6), and Evans (42) in their consideration of the crystallization kinetics in metals, and serves as a convenient starting point in the development of theoretical isotherms for polymeric systems. We then assume that the steady-state rate of nucleation is reached at $t = 0$ and that growth is initiated at $t = 0$. There has been a tendency to identify τ_i, the time at which crystallinity is first observed, with the time necessary for the steady-state rate of stable nuclei production to be reached (1, 142). It is evident (101, 157) that τ_i will depend on the sensitivity of the crystallinity detector used; if less sensitive methods were used τ_i would of course occur at later times while the crystallization rate remains invariant. Thus τ_i will depend on the sensitivity of the crystallinity detector and on the nucleation and growth rates. The nucleation incubation time is probably only a small fraction of τ_i.

The major consideration in calculating theoretical isotherms is accounting for the effect of the impingement of growing centers upon each other and the fact that complete crystallinity is not attained in polymers. In polymeric systems there may be other restraints to the development of crystallinity, such as the presence of diluents or the presence of non-crystallizing units along the chain. These effects can all be treated in a similar fashion by following the methods developed by Avrami (6, 19, 101).

A hypothetical analog is assumed wherein nuclei are allowed to form and grow throughout the entire mass of the system. Some of these nuclei are, of course, fictitious, but the actual crystallization rate is calculated by considering only that portion of the increase of mass of an average growing center which takes place in space not already transformed. This somewhat artificial procedure enables the effect of impingement of growing centers upon each other and other retardations of growth to be conveniently accounted for. We let dW'_c be the mass of the system that is transformed during time dt, assuming that there are no restraints of any kind to the growth of a center. Because of the various retardations to growth possible, the actual mass transformed, $\mathrm{d}W_c$, will be less than $\mathrm{d}W'_c$. Since nuclei, both real and hypothetical, have been formed at random throughout the entire mass, the shells of transformed material are in random regions. Therefore in the vicinity of the growing center the fraction of the mass available for transformation is the same as the total fraction available. Then the actual mass transformed is

$$\mathrm{d}W_c = \mathrm{d}W'_c[1 - U(t)] \tag{42}$$

where $U(t)$ is the "effective fraction" of the mass transformed at time t. It is that fraction of the total mass, at time t, in which further crystal growth cannot occur. The effective fraction transformed is assumed to be proportional to the actual fraction transformed, the proportionality factor being $1/X_w$, the reciprocal of the mass fraction of the total system which is crystalline at the completion of the process. Then

$$\mathrm{d}W_c/\,\mathrm{d}W'_c = [W_0 - (1/X_w)W_c]/W_0 \tag{43}$$

where W_c is the mass crystalline at time t and W_0 is the total mass.

If $W'_c(t, \tau)$ is the mass at time t of a given center which was initiated at time τ ($\tau \leqq t$) and A' is the rate of formation of nuclei per unit of mass

$$W'_c = A'W_0 \int_0^t W'_c(t, \tau)\,\mathrm{d}\tau \tag{44}$$

$$= AW_0(\rho_c/\rho_l) \int_0^t v'_c(t, \tau)\,\mathrm{d}\tau \tag{44-1}$$

where A is the nucleation rate per unit volume, $v'_c(t, \tau)$ is the volume transformed at time t of a center initiated at time τ, ρ_l is the density of the polymeric liquid, and ρ_c is the density of the completely crystalline polymer.

By substituting equation 44-1 into equation 42 and performing the indicated integration there is obtained

$$\ln\{W_0/[W_0 - (1/X_w)W_c]\} = (1/X_w)(\rho_c/\rho_l)\,A \int_0^t v'_c(t, \tau)\,\mathrm{d}\tau \tag{45}$$

To evaluate the integral appearing in the right-hand side of equation 45 it is necessary to specify both the rate at which a center grows and the geometric pattern that is evolved subsequent to nucleus formation.

If crystallite growth is controlled by the diffusion of polymer segments in the amorphous portions, then the radius of a growing center should be proportional to the square root of time (34, 58, 157, 166). On the other hand, if the growth is not limited by diffusion but is controlled by processes which occur at the crystallite–liquid interface, then the radius will vary linearly with time (34, 157, 166). Direct microscopic observations of the growth of spherulites (110, 117, 117c, 129) indicate that the radius of the growing centers increases linearly with time. Thus the rate of volume increase of the transformed material is proportional to its surface area, which is in accord with the accelerated manner in which the total amount of crystallinity develops. It thus appears reasonable to assume a lineal growth rate for polymeric systems (101, 117). Various growth geometries have been considered (101, 117) but for illustrative purposes we shall limit ourselves to spherical and disk-type growth. In the latter case the centers grow along their radii with the polymer chains being normal to the plane of the disk. For spherical lineal growth equation 45 becomes

$$\ln \{W_0/[W_0 - (1/X_w)W_c]\} = (\pi/3)(1/X_w)(\rho_c/\rho_l)AG^3t^4 = k_st^4 \qquad (46\text{-}1)$$

where G is the rate of change of the radius with time. For a disk of thickness l_c growing along the radius

$$\ln \{W_0/[W_0 - (1/X_w)W_c]\} = (\pi/3)(l_c/X_w)(\rho_c/\rho_l)AG^2t^3 = k_dt^3 \qquad (46\text{-}2)$$

For comparative purposes, if the growth is diffusion controlled so that G is proportional to the square root of time,

$$\begin{aligned}\ln \{W_0/[W_0 - (1/X_w)W_c]\} &= (\pi/15)(1/X_w)(\rho_c/\rho_l)AG^3t^{5/2} \\ &= k_s't^{5|2} \qquad (46\text{-}3)\\ \ln \{W_0/[W_0 - 1/X_w)W_c] &= (\pi/2)(1/X_w)(\rho_c/\rho_l)AG^2t^2 \\ &= k_d't^2 \qquad (46\text{-}4)\end{aligned}$$

In equations 46 k_s and k_d can be considered the crystallization rate constants. An identical set of isotherms can be obtained following the method developed by Evans (42), involving the theory of expanding circles and spheres. Again, a completely random distribution in the origin of nuclei must be assumed, and if various retardations to growth are considered in a similar manner to that used in Avrami's method, identical isotherms are obtained.

The nucleation process will be promoted by any heterogeneities that are present in the liquid, and in the extreme case of incomplete melting stable nuclei may already be present. At a given temperature heterogeneities have the effect of appreciably increasing the nucleation rate relative to that for homogeneous nucleation. Certain types of heterogeneities allow crystallite fragments to be stable at temperatures above the melting temperature of the bulk phase. In this situation the crystallization behavior below the melting temperature is very sensitive to the superheating history (155).

If at $t = 0$, a fixed number, $\bar{N}$, of stable nuclei are present and the subsequent transformation is a consequence only of the lineal growth of these centers. Avrami (6) and Evans (42) have shown that isotherms similar to equation 46 are obtained. Similar results are also obtained where the rate of growth is proportional to the square root of time. Though the time dependence of the crystallization process is still mainly governed by the shape of the growing center, the exponent of the time is lowered by a power of 1 for this type of nucleation and growth as compared to the homogeneous process previously considered. Specifically,

$$k_s^* = (4\pi/3)(1/X_w)(\rho_c/\rho_l)G^3\bar{N}t^3 \qquad (47\text{-}1)$$

for spherical lineal growth and

$$k_d^* = \pi l_c(1/X_w)(\rho_c/\rho_l)G^2\bar{N}t^2 \tag{47-2}$$

for disk-type lineal growth. However, as Avrami (6) pointed out, if the probability $\bar{n}$ of the growth of the nuclei is relatively small, so that the growth of all the centers is not initiated at $t = 0$, then the rate constants are, respectively,

$$k_s^* = (\pi/3)(1/X_w)(\rho_c/\rho_l)G^3\bar{N}\bar{n}t^4 \tag{48-1}$$

and

$$k_d^* = (\pi/3)(l_c/X_w)(\rho_c/\rho_l)G^2\bar{N}\bar{n}t^3 \tag{48-2}$$

and the exponent of the time is the same as in the homogeneous case. Equations 47 and 48 describe two extreme situations. The former represents the situation of complete exhaustion of nuclei at the onset of the process; the latter equation the persistence of the initially present nuclei throughout the process. When the nuclei are depleted at some intermediate stage, the power dependence of the time will be somewhat between these two extremes. Since the nucleation rate and the growth rate have been assumed to be independent of time, equations 46 and 47 are in accord with the observation that isotherms at different temperatures are superposable merely by rescaling the time. Equations 48 are in accord with this observation only when the product $G^3\bar{N}$ is independent of time, the so-called isokinetic range of Avrami (6).

The methods used in calculating equations 46 to 48 require that both real and fictitious nuclei be allowed to form throughout the entire mass. Though this is a convenient procedure in calculating the total overall rate at which crystallinity develops, it has the disadvantage of not allowing the specification of regions where nuclei are physically prohibited from forming. As an example, the use of these isotherms does not allow one to assess the effect of cross-linking on either the nucleation or the growth rates separately, but only on the overall rate at which crystallinity develops. The variation with time of the mass transformed is very similar for all the cases considered. The crystallization rate constant can be generally expressed as a constant times t^n, the major difference between the various mechanisms being in the value of n appropriate to a given situation. Unfortunately, the assignment of a given value of n does not uniquely describe both the nucleation and the growth processes; various combinations of both are consistent with a given value. The fact that with sufficient care reproducible isotherms independent of the superheating condition can be obtained is strong evidence for the consideration of homogeneous nucleation.

The isotherms calculated by the methods outlined above are expressed directly in terms of the mass transformed, notwithstanding the fact that this quantity is seldom directly observed. Thus, to obtain experimental verification of the theoretical isotherms they must be recast in terms of the type of measurement being made. Since measurements of the specific volume are a convenient and also a very accurate method for studying the development of crystallinity, equations 46 to 48 will for illustrative purposes be formulated in these terms. For the general case it is found (97, 101) that

$$\ln \{(V_\infty - V_t)/(V_\infty - V_0)\} = (-1/X_w)kt^n$$

or

$$(V_\infty - V_t)/(V_\infty - V_0) = \exp \{-(1/X_w)kt^n\} \tag{49}$$

or, if expressed in terms of the relative volume shrinkage,

$$a(t) = (V_0 - V_t)/V_0$$

equation 49 becomes

$$1 - a(t)/a(\infty) = \exp \{-(1/X_w)kt^n\} \tag{50}$$

For a given nucleation and growth process the crystallization rate is determined by specifying k. The crystallization rate can also be specified by either τ_i or $t_{1/2}$, the time necessary for half the crystallization to occur, since either of these quantities depends on critical values of the arguments of the logarithm in equation 49. A simple way of determining kt^n is to first construct a set of theoretical plots (for different values of n) of $(V_\infty - V_t)/(V_\infty - V_0)$ against $\log \tau^{1/n}$, where $\tau = (k/X_w)t^n$. Then another plot using the experimental data is prepared using $\log t$ as the abscissa. If the two graphs are superimposed and shifted horizontally until the best fit is obtained, both n and k/X_w can be obtained. A set of experimental data can also be analyzed by plotting

$$\ln \ln [(V_\infty - V_t)/(V_\infty - V_0)]$$

against $\ln t$, and from the slope and intercept of the resultant straight line n and k are obtained. Besides the lack of sensitivity in taking the double logarithm, this method bars consideration of the rather important time interval where crystallinity is not detected.

In figure 8 theoretical isotherms are plotted in accordance with equation 49 for values of n equal to 1, 2, 3, and 4. All the curves have several features in common. Initially there is an interval where only very small volume changes are observed for appreciable values of the variable τ. Then as the crystallinity develops the volume decrease occurs at an accelerated rate, and finally levels off as V_∞ is approached. These features are in qualitative accord with the previously described experimental observations. As n increases from 1 to 4, the times at which the onset of crystallinity is detected become greater. However, beyond the onset of detectable crystallinity, the rate of volume decrease is greater the higher the value of the exponent. All the curves have a common point of intersection at $\tau^{1/n} = 1$; beyond this point the completion of the process is more rapidly approached for larger values of n. The plots in figure 8 indicate quite clearly that in analyzing experimental data it will be a difficult matter to decide whether $n = 3$ or 4 or possibly even 2. This will be particularly true for the early stages of the process; unfortunately, this is the region where the most reliable experimental data are obtained.

In figure 9 typical isotherms for three different homopolymers are plotted according to the suggestion of equation 49. The solid lines represent the experimental isotherms, and the corresponding theoretical isotherms for $n = 3$ are

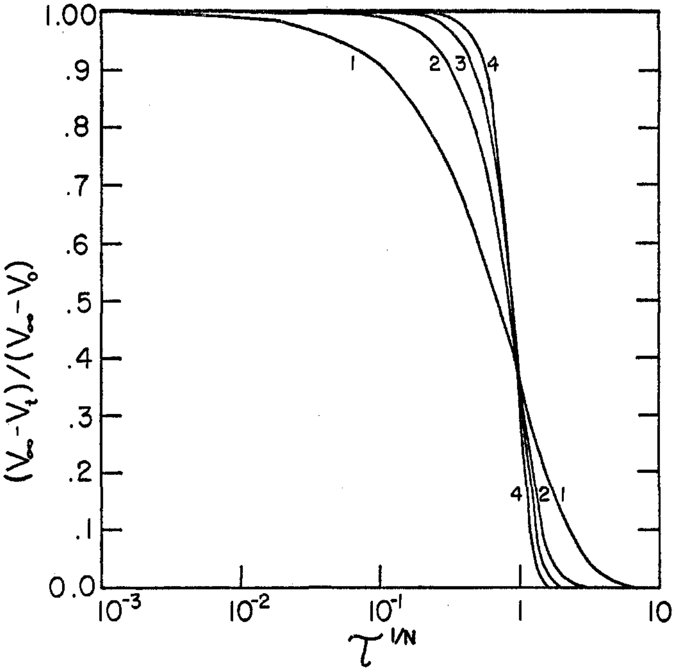

FIG. 8. Theoretical plot of $(V_\infty - V_t)/(V_\infty - V_0)$ vs. $\tau^{1/n}$ for $n = 1, 2, 3$, and 4

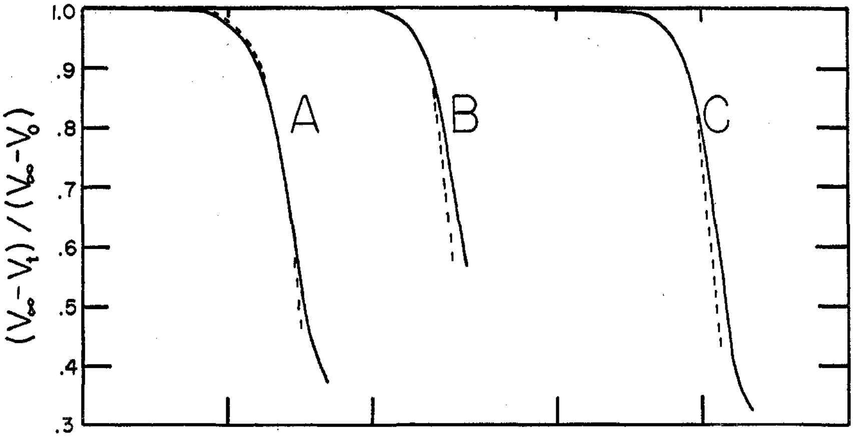

FIG. 9. Fit of experimental data to theoretical curves. Plot of $(V_\infty - V_t)/(V_\infty - V_0)$ vs. log time. Solid lines, experimental results; dotted lines, theoretical curves for $n = 4$. Curve A for natural rubber crystallized at −11°C. (171). Curve B for polyethylene oxide crystallized at 57°C. (101). Curve C for polydecamethylene adipate crystallized at 70°C. (101).

indicated by the dashed lines. As has been generally observed (1, 65, 97, 101), good agreement can be obtained for the early stages of the process, but as the crystallization proceeds the calculated amount of crystallinity is systematically greater than the observed. The studies of Morgan *et al.* on polyethylene terephthalate (117) and polyhexamethylene adipamide (117c) would appear to be exceptions to this observation, since equations of the type indicated by equation 49 give good agreement for the complete crystallization process. The assumptions inherent in the development of equation 49 are in accord with the generally observed disparity with experiment beyond the early stages of the process. In low-molecular-weight materials the assumption that the nucleation rate is invariant with time might be a valid one, since each of the molecules can act independently; on the other hand in polymeric systems, since the segments which comprise the nucleus are connected to each other by covalent bonds, the nucleation rate will be expected to depend on the amount of crystallinity already present and thus not be invariant with time. In attempting to account for the various retardations that a growing center encounters, the assumption was made that the proportionality factor between the effective fraction transformed and the actual fraction transformed is independent of time. The validity of this assumption is very difficult to assess. Dunning (38) has recently analyzed the final stages of the crystallization process as the pseudo-equilibrium degree of crystallinity is approached. He concludes that the log of the volume decrease should be directly proportional to the time in this region, which though in agreement with experimental results for rubber vulcanizates (38, 142) is not in agreement with results for polyethylene (94). It must be borne in mind, however, that this is a region most inaccessible to reliable experimental observation.

Despite the various shortcomings, the theoretical isotherms adequately describe the early stages of the process. Since the isotherms at different temperatures are superimposable over their complete extent, the causes of the discrepancies between theory and experiment depend only on the amount of crystallinity that has developed and are independent of temperature. The basic assumption of the concurrence of nucleation and growth processes is further supported by the interpretation of the overall temperature coefficient and the effect of various external parameters

C. TEMPERATURE COEFFICIENT OF THE CRYSTALLIZATION RATE

Though at a given temperature critical size nuclei are formed through the growth of smaller sized nuclei, a steady rate of production of critical nuclei is quickly reached. Becker and Döring (9) and Turnbull and Fisher (158) have shown that in condensed systems the steady-state rate of nucleation can be expressed as

$$A = A_0 \exp \{-E_D/RT - \Delta F^*/RT\} \tag{51}$$

where A_0 is a constant that is only slightly temperature-dependent and E_D is the activation energy required for transport across the nuclei–liquid interface. The free-energy change involved in the formation of a nucleus within the bulk of a mother liquor is the resultant of the contribution of the change in the bulk free energy (which is negative), the surface free energy (which is positive (9, 15, 158)), and the strain free energy (which arises from the volume change). As a consequence, the total free-energy change possesses a maximum with respect to the size of the nucleus. The value at the maximum is ΔF^*, the height of the free-energy barrier that must be surmounted for stable nuclei to be formed. The nucleus size at this maximum is the critical size nucleus; nuclei greater than this critical value can grow spontaneously, while those smaller are unstable and will disappear. In calculating ΔF^* for a nucleus composed of segments of polymer molecules advantage is taken of Flory's (48) statistical theory of polymer crystallization (38, 97).

Consider a disk of length L and radius R comprised of ρ polymer chains, the chains being aligned parallel to the length of the disk. If ζ is the number of repeating units along the length of the disk, $\zeta\rho_s$ the number of repeating units on the surface, and γ_u the surface free energy per repeating unit, then the free energy of forming such a disk from the supercooled polymeric liquid can be written as

$$\Delta F_d = \zeta\rho_s\gamma_u - \Delta F_f \tag{52}$$

where the first term on the right represents the lateral surface energy due to the crystallite liquid interface and ΔF_f includes both the bulk free energy of fusion and the surface free energy of the ends of the disk, the strain free energy being neglected in this approximation. For a system comprised only of N polymer molecules, each of x repeating units, equation 6 can be written as

$$\frac{\Delta F_f}{xN} = (\zeta\rho/xN)\Delta F_u + RT\left\{(1/\lambda)\ln\,[1 - \zeta\rho/xN\rho/xN + \rho/xN\left[\ln D + \ln\frac{(x - \zeta + 1)}{x}\right]\right\} \tag{53}$$

Since in the nucleus $\zeta \ll x$, equation 53 becomes

$$\Delta F_f \cong \zeta\rho\Delta F_u + RT\rho\ln D \tag{54}$$

where ΔF_u is the bulk free energy per mole of repeating unit and D is a parameter whose value is constrained to be between 0 and 1, as discussed in Section III. Since ρ_s is equal to $2\sqrt{\pi\rho}$, equation 52 can be written as

$$\Delta F_d = 2\zeta\gamma_u\sqrt{\pi\rho} - \zeta\rho\Delta F_u + RT\rho\ln D \tag{55}$$

ΔF^* is then the value of ΔF_d at the saddle point of the surface described by equation 55. At the saddle point

$$\zeta = \zeta^* = \gamma/\Delta F_u\,; \qquad \rho = \rho^* = \frac{4\pi\gamma_u^2}{\Delta F_u^2}$$

so that

$$\Delta F^* = 4\pi\gamma\gamma_u^2 T_m^2/\Delta H_u^2(\Delta T)^2 \tag{56}$$

where $\gamma \equiv RT\ln D$ is identified with the surface energy of the ends of the nucleus and to a good approximation can be considered temperature-independent. Aside from numerical factors equation 56 is identical in form to the expression obtained when the polymeric nature of the system is not specifically taken into account (9, 15, 158).

The steady-state nucleation rate can then be expressed as

$$A = A_0 \exp\{-E_D/RT - 4\pi\gamma_u^2\gamma T_m^2/\Delta H_u^2(\Delta T)^2RT\} \tag{57}$$

and has the property of being zero at 0°K. and at T_m and attaining a maximum value at an intermediate temperature (15). The dependence of the nucleation rate on temperature is illustrated in figure 10, where log A/A_0 is plotted against T. For this example T_m^0 was taken at 300°K., E_D as 10^4 cal. per mole, and $4\pi\gamma_u^2\gamma/R\Delta H_u^2$ as 128 deg.$^{-1}$ At temperatures just below T_m the nucleation rate has a very large temperature coefficient due, primarily, to variation of the term $\exp\{-\Delta F^*/RT\}$. As the temperature is decreased further the nucleation rate increases at a much slower rate, reaches a maximum, and then decreases. As the absolute zero in temperature is approached, a positive temperature coefficient is indicated in the nucleation rate. The extreme sensitivity of the nucleation rate to temperature can be illustrated by the observation of Turnbull (156) that a mercury sample can be held 1 hr. at a temperature $\Delta T = 43°$ without detectable change, but completely solidifies within a minute when the temperature is lowered three degrees to $\Delta T = 46°$. Similar time effects in the detection of the onset of crystallization in polymeric systems have already been indicated. If the nucleation process is assisted by the presence of foreign bodies or by surface heterogeneities, then the temperature dependence of the nucleation rate will be the same as in the homogeneous case (155), although the numerical factors will differ. If the crystallization process consists only of the growth from stable nuclei that are initially present, then the temperature coefficient of the process will, of course, be only that of the growth process.

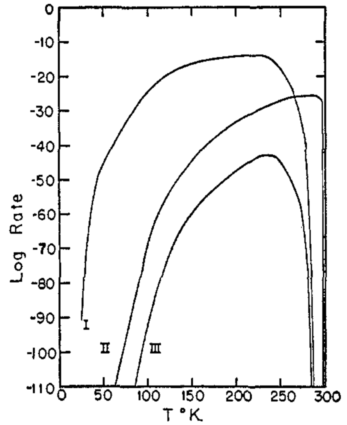

FIG. 10. Plots of temperature coefficient of crystallization rate according to equations 57, 58, and 59. Curve I, log (A/A_0); curve II, log $(G/G_0)^3$; curve III, log k_s.

The formulation of the temperature dependence of the growth is decidedly hampered by the lack of detailed knowledge of the mechanism of crystal growth in polymers. The assumption of a lineal rate of growth is in agreement with the observed rate of spherulitic growth (110, 117, 117c, 129) and satisfactorily accounts for the sigmoidal-shaped isotherms and their characteristic accelerated regions. However, the molecular mechanism by which this lineal growth rate is achieved has not as yet been ascertained and its elucidation must await future experimental observations before definite formulation can be given to the growth step. The simplest consideration is that the growth is controlled by transfer across the crystallite–liquid interface and the growth rate will then depend on the free-energy difference between the two phases. The growth rate can then be expressed as (156, 161):

$$G = G_0 \exp\{-E_D/RT\}[1 - \exp\{-\Delta H_u \Delta T/RTT_m\}] \qquad (58)$$

Thus, according to equation 58 the growth rate also has the property of being zero at $T = T_m$ and at 0°K. and possesses a maximum at an intermediate temperature. In figure 10 there is also plotted a curve of log $(G/G_0)^3$ against temperature. T_m was again taken as 300°K. and E_D and ΔH_u were each assigned the value 10^4 cal. per mole. According to this formulation the cube of the growth rate steadily increases as the temperature is increased above absolute zero, levels off to a broad maximum, then precipitously drops to zero at temperatures very close to T_m. Thus there is only a very small temperature region, which is an experimentally inaccessible one, where the growth rate would have a substantial negative temperature coefficient. Volmer (161) pointed out some years ago that these conclusions are in contradiction to the observed growth rate of low-molecular-weight materials and led him to postulate that growth is governed by surface nucleation. The conclusions drawn from equation 58 are also in contradiction to the experimental observations of the temperature coefficient of spherulitic growth of polychlorotrifluoroethylene (129), polyethylene terephthalate (117), polyhexamethylene adipamide (117c), and polydecamethylene sebacate (110). For these polymers strong negative temperature coefficients of the growth are observed at temperatures well below T_m. For example, for polychlorotrifluoroethylene (129), which has a melting temperature of approximately 210°C., the lineal rate of spherulitic growth increases by a factor of 20 as the crystallization temperature is decreased from 190°C. to 170°C. For polyhexamethylene adipamide an even larger negative temperature coefficient of spherulitic growth has been observed (117c). Recently, McIntyre and Flory (110) have studied the rate of spherulitic growth in polydecamethylene sebacate over a narrow temperature interval just below T_m. ΔT ranged from 8° to 13°, and over this five-degree interval the growth rate increased by a factor of 1000 as the crystallization temperature was decreased. The large negative temperature coefficient that is observed for the growth is strongly suggestive of growth by nucleation (110).

An explicit formulation for the temperature coefficient of the overall rate at which crystallinity develops would obviously be premature until more details of the growth process are available. If equation 58 is used in conjunction with the steady-state nucleation rate (equation 50) the crystallization rate constant becomes

$$k_s = k_s' \exp\left\{\frac{-4E_D}{RT}\right\}\left[1 - \exp\left\{\frac{-\Delta H_u \Delta T}{RTT_m}\right\}^3 \exp\left\{\frac{-4\pi\gamma_u^2\gamma T_m^2}{\Delta H_u^2(\Delta T)^2 RT}\right\}\right] \qquad (59)$$

where

$$k_s' = (\pi/3)(1/X_w)(\rho_c/\rho_l)A_0G_0^3$$

and a corresponding equation can be written for k_d. In figure 10, k_s as described by equation 59 is plotted against T, and the shape of the curve is qualitatively similar to that obtained in the few instances where the rate of crystallization of a polymer has been studied over a wide temperature range (31, 161, 171). Superficially, equation 59 appears to be an adequate description of the temperature dependence, despite the fact that the temperature coefficient employed for the growth process is inadequate.

In the vicinity of T_m (ΔT = 6–20°C.) the rather phenomenal negative temperature coefficient that is observed suggests that in this region the process may be nucleation controlled and hence

$$\text{Log } k_s = A - \frac{4\pi\gamma_u^2\gamma}{2.3}\,\frac{T_m^2}{(\Delta H_u)^2(\Delta T)^2RT} \qquad (60)$$

where

$$A = \log\left\{k_s' \exp\,(-4E_D/RT)\left[1 - \exp\left\{\frac{-\Delta H_u\,\Delta T}{RTT_m}\right\}\right]^3\right\}$$

The data in this temperature range for polyethylene oxide, polydecamethylene adipate, and three different molecular-weight samples of the polyamide poly-N,N'-sebacoylpiperazine (101) are plotted in figure 11 according to the suggestion of equation 60. For the small temperature interval that is involved, ΔT = 6–13°C. for polyethylene oxide, ΔT = 5.5–10.5°C. for polydecamethylene adipate, and ΔT = 12–25°C. for the polyamides, the crystallization rate constants vary by about 12 decades. The results for the polyamides can be approximated by straight lines, but the data for polyethylene oxide and polydecamethylene adipate are definitely curved. The abscissas in these plots are extremely sensitive to small errors in ΔT. As has been previously seen, an uncertainty exists as to the absolute value of T_m. The dotted lines of figure 11 indicate the resulting plot if three degrees are added to the assigned T_m. Within the experimental uncertainty of locating T_m the temperature coefficient of the crystallization process in this temperature region can be explained by the temperature coefficient of the steady-state nucleation rate. However, the curvature in the plots could also be attributed to the contribution from the growth process, as has been indicated by recent experimental investigations. Regardless of the cause of the curvature, the large negative temperature coefficient of the crystallization process at temperatures just below the melting temperature can be clearly attributed to the temperature coefficient of the nucleation process.

In the temperature interval just below T_m the magnitude of the rate constant depends primarily on temperature and is essentially independent of the chemical nature of the polymer molecule or its crystal structure. However, at temperatures well below T_m, k_s depends very markedly on the structural unit comprising the polymer chain. For example, for natural rubber (171) at the temperature at

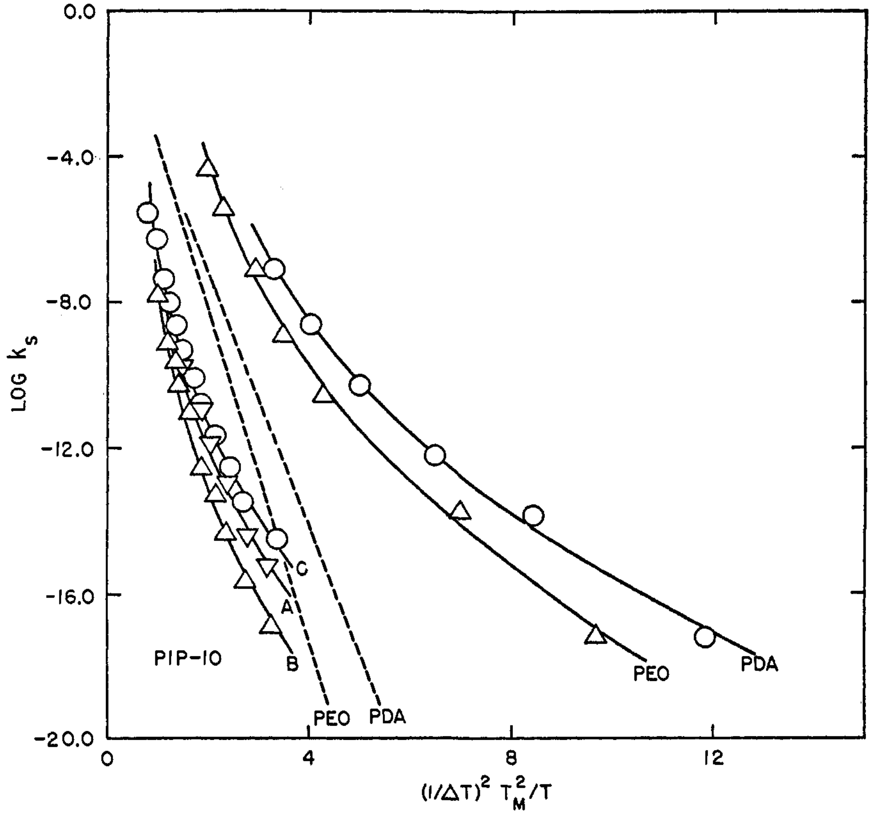

FIG. 11. Plot of log k_s vs. $(1/\Delta T)^2(T_m^2/T)$ for various polymers. PDA indicates polydecamethylene adipate; PEO indicates polyethylene oxide; Pip-10 A, B, and C indicates poly-*N*,*N'*-sebacoylpiperazine of three different molecular weights. Dashed lines represent results obtained using values of T_m three degrees higher than those obtained dilatometrically (Mandelkern, Quinn, and Flory (101)).

which the crystallization is most rapid, the crystallization is essentially complete after 8 hr. On the other hand, for polyethylene terephthalate (31) at its temperature of maximum rate of crystallization the process is complete in a matter of minutes, while polyethylene and polymethylene can be supercooled only a few degrees.

The results plotted in figure 11 give strong support to the concept of an equilibrium melting temperature. The strong temperature variation of k_s arises mainly from the factor $(1/\Delta T)^2$ in the second term of equation 60, which varies with temperature solely because the melting temperature has been taken as a fixed point.

In a formal manner the temperature at which the crystallization rate is a maximum can be obtained from equation 59. This temperature of the maximum will then depend on ΔH_u, E_D, and the nucleation parameters. Equation 59 appears to predict results which are in qualitative agreement with experiment (101). At temperatures below the maximum, crystallization is once more retarded and becomes imperceptible at temperatures where the supercooled liquid might be expected to transform to a glass. This may be a consequence of the fact that the relaxation processes involved in crystal growth are similar to those responsible for the occurrence of the glassy state (51, 86, 138).

D. CRYSTALLIZATION KINETICS OF POLYMER–DILUENT MIXTURES

The addition of a low-molecular-weight diluent to a semicrystalline polymer would be expected to drastically alter the rate of crystallization at a given temperature as compared to that of the corresponding homopolymer because of the effect of the diluent in altering the nucleation and growth rates. Careful experimental observations on the crystallization rate of polymer–diluent mixtures are at present limited to studies in the temperature interval just below T_m (97). In this temperature range the isotherms that are observed are very similar to those of bulk polymers in that they are superposable and exhibit very large negative temperature coefficients. Thus the isothermal crystallization kinetics of a given polymer–diluent mixture can be represented by a composite curve obtained by shifting all the isotherms to a common one. In figure 12 the solid curves represent these composites for mixtures of polyethylene oxide with varying amounts of diphenyl ether as diluent. Although the general shapes of these composites are the same, as the amount of diluent is increased sufficient differences are observed to preclude the possibility of constructing a realistic composite which is independent of concentration. The dashed lines in figure 12 are the theoretical isotherms for spherical growth, and similar results are obtained if

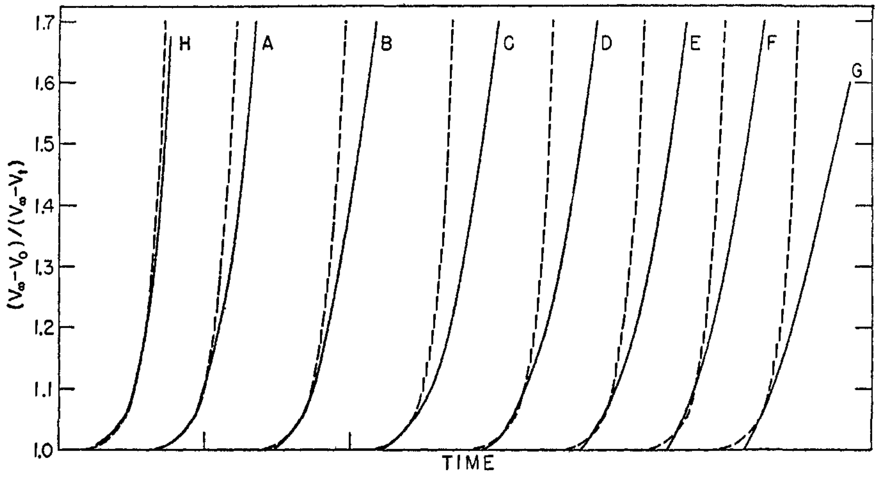

FIG. 12. Fit of experimental data to theoretical curves for the crystallization kinetics of polymer–diluent mixtures. Plot of $(V_\infty - V_0)/(V_\infty - V_t)$ vs. log t for mixtures of polyethylene oxide with diphenyl ether. Solid lines represent the composite isotherm for each mixture. Curve A, $v_1 = 0.094$; curve B, $v_1 = 0.182$; curve C, $v_1 = 0.295$; curve D, $v_1 = 0.398$; curve E, $v_1 = 0.494$; curve F, $v_1 = 0.601$; curve G, $v_1 = 0.689$; curve H, $v_1 = 0.000$. The dashed line represents the theoretical isotherm for $n = 4$. The position of each isotherm relative to the abscissa is arbitrary; short vertical marks along the abscissa indicate the length of one decade (97).

disk-type growth is assumed. The deviations between the theoretical and observed isotherms are such that crystallinity develops at a slower rate than calculated, the disagreement becoming greater as the diluent concentration is increased. As the polymer concentration is decreased the diffusion of polymer segments to the crystal–liquid interface may play a more prominent role in the crystallization than in the more concentrated systems.

The very marked negative temperature coefficients that are observed in the vicinity of T_m strongly suggest that in this region the crystallization is again controlled by nucleation. For a polymer–diluent mixture ΔF^* can be calculated in a similar manner to that for bulk polymers, and to a good approximation it is found that (97)

$$\Delta F^* = \frac{4\pi\gamma_u^2\gamma T_m^2}{(\Delta H_u)^2(\Delta T)^2} \tag{61}$$

where γ can be defined more generally as $-RT \ln v_2 D$ and T_m is the melting temperature of the mixture. Hence if all the other terms entering into the rate constant were invariant with composition, as v_2 decreased ΔF^* would increase and the rate of crystallization would decrease because of the decrease in the nucleation rate.

For mixtures of polyethylene oxide and diphenyl ether, it has been observed that for v_1, up to 0.50, the rate constant is invariant with composition when compared at the same values of ΔT. As the diluent concentration is increased further there is a decrease in the rate constant, which is reflected in the fact that longer times are required before crystallinity is detected. Thus up to moderate concentrations of diluent, the effects of the diluent on the different terms in equation 61 nullify one another, leaving the crystallization rate invariant. As further diluent is added the term containing ΔF^* appears to predominate, causing the decrease in rate constant.

E. THE EFFECT OF CROSS-LINKING AND DEFORMATION

The introduction of chemical cross-links between units of different polymer chains will also alter the crystallization behavior. Since the units involved in the cross-linking will not possess the same structure as the rest of the chain, the melting point will be depressed as if a non-crystallizing copolymeric unit were introduced. Similarly, the rate at which crystallinity develops from the supercooled liquid will be altered as a consequence of the influence of the cross-links on both the nucleation rate and the growth rate. Natural rubber which has been cross-linked or vulcanized by reaction with sulfur, sulfur–accelerator mixtures, or ditertiary butyl peroxide is the only cross-linked polymer for which the crystallization kinetics has been investigated (65, 142, 170).

The crystallization isotherms for these systems have the characteristic shape typical of polymers and are describable by equations of the form given by equations 46 to 48. As in the case of non-cross-linked polymers, good agreement is obtained between the theoretical expression and experiment for the early stages of the process, but the crystallization eventually proceeds at a slower rate than is calculated (65). Russell (142) has studied the rate of crystallization of various vulcanized rubbers at four different temperatures and found that there is a maximum in the rate at about −26°C. similar to that for unvulcanized natural rubber. He found that the isotherms for a given vulcanizate were superposable when plotted in a manner similar to the plots of figure 7. These experimental observations indicate that the crystallization process in a cross-linked system is similar to that of homopolymers.

These studies have shown quite conclusively that at a fixed temperature as the amount of cross-linking is increased, the crystallization rate decreases rather markedly. For example, Wood and Bekkedahl (170) observed that at 2°C. half of the crystallization of natural rubber occurred in about 6 days. However, combining 0.4 per cent of sulfur with the rubber increased the half-time to 37½ days, and similar effects have been observed for other types of vulcanizing agents. This retardation of the rate has been attributed solely to a decrease in the steady-state nucleation rate (65, 142). Since only the overall development of crystallinity is observed, it is difficult to assess the separate effects of nucleation and growth in causing the retardation in rate. In particular, cross-linking would be expected to also impede the internal segmental mobility, which could have a pronounced effect on the growth rate. When a cross-linked polymer is subjected to a stress, the course of the crystallization of the deformed network will depend on the amount and type of deformation that are imposed. Recently Gent (65) investigated the crystallization kinetics of natural rubber networks held in simple extension at −26°C. with the extension ratio varying from 1 to 3. He found that the crystallization could be followed equally well by measuring either the decrease in volume or the rate of stress relaxation. The isotherms were once again describable by equations similar in form to equations 46 to 49. However, the integer n appearing in the exponential term varied from 3 to 1 as the extension ratio was increased from 1 to 3. This indicates that the nature of the growth process changes with increasing extension ratio, so that at the highest extension ratio studied the growth appears to be uniaxial, probably along the stretching direction.

The application of hydrostatic pressure raises the melting temperature and will thus tend to increase the steady-state nucleation rate. However, the application of pressure decreases the internal segmental mobility; this would increase the activation energy for transport across the crystal–liquid interface and thus act to retard the crystallization process. As Wood (168) has observed, at a given temperature there would be an optimum pressure at which crystallization would be most rapid. At temperatures (at atmospheric pressure) where the process is not very dependent on the nucleation rate, the application of hydrostatic pressure would act solely as a retardant. Systematic studies of the effect of hydrostatic pressure on the crystallization rate are not available, but the observations of Thiessen and Kirsch (152, 153) and of Dow (37) are in qualitative accord with these considerations. For example, for natural rubber at 0°C. crystallization is more rapid upon the application of 10–30 bars than it is at 1 atm. However, at the same temperature when a pressure of 7840 bars was applied, crystallinity was not detected after two weeks.

F. THE EFFECT OF MOLECULAR WEIGHT

It has been previously noted that at temperatures just below T_m the crystallization rate is independent of molecular weight over a wide molecular-weight range for poly-N,N'-sebacoylpiperazine when comparison is made at the same value of ΔT. These experiments were conducted in a temperature range where the crystallization rate appears to be determined by the thermodynamic terms appearing in the steady-state nucleation rate and hence is independent of molecular weight. However it has been observed (161) that for fractions of polyethylene succinate the crystallization rate depends very markedly on molecular weight over a rather extended temperature range. At a given temperature the crystallization proceeds much more rapidly for the polymers of lower molecular weight. Similar effects, though not covering as extensive a temperature range, have been observed for polyethylene terephthalate (117) and polyhexamethylene adipamide (117c). The molecular weights of the fractions studied were such that a dependence of the melting temperature on molecular weight could be expected and was actually observed in one case (161). Hence, a more rational understanding of the effect of molecular weight on the crystallization kinetics would result from these experiments if the melting temperatures were accurately determined and if, for comparative purposes, the crystallization temperatures were appropriately adjusted for variation of the melting temperature with molecular weight.

Grateful acknowledgement is made to the Cornell University Press, Journal of Polymer Science, The Journal of the American Chemical Society, and Journal of Applied Physics for permission to reproduce figures orginally appearing in these publications.

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