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History of Crystalline Polymers

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ABSTRACT

The history of crystalline polymers closely parallels the development of polymer science itself. This paper discusses, in historical perspective, the work that led to the recognition that crystalline polymers exist and to the understanding of the structure, morphology, and properties that evolved. A chronological approach is taken and the cornerstones of major discoveries delineated. Initially there was a period where significant physical observations were made but could not be explained because the concept of polymers, no less crystallinity, was unheard of. Early x-ray diffraction work was extremely difficult to interpret for similar reasons. When it was established that polymers existed as bona fide molecular entities, structural analysis using classical diffraction methods soon followed. The principles of crystallization kinetics and the thermodynamics of fusion were firmly established by theory and experiment and found to have the same scientific basis as similar phenomena in low molecular weight substances. Modern emphasis has been directed to the influence of crystalline morphology on properties. The internal, interfacial, and external structures of the elementary lamella crystallite have been subject to divisive discussion for about two decades. Facts and fantasies associated with this problem are separated by considering recent experimental and theoretical results. Finally, emerging areas of research and unifying concepts are presented.

INTRODUCTION

Studies of the physical properties of crystalline polymers actually pre-date the time that polymers were accepted as molecular entities of very high molecular weight. They were not, of course, recognized as such at the time. These studies indicated the differences in properties between what we now recognize as crystalline and amorphous polymers as well as the contractility characteristics of the crystalline state. The study of crystalline polymers, and the development of this subject, parallels very closely the development of polymer science itself. Actually, some of the early studies of crystalline polymers, and the deductions therof, were very important in the development of the macromolecular hypothesis and the concept of chain molecules [1].

In this discussion of the history of crystalline polymers, we shall adopt essentially a chronological approach. Emphasis will be placed on the major cornerstones or turning points which led to and which constitute the basis of our understanding today. These major points and the underlying principles covering them will be pointed out and described in detail. The key events leading to our understanding of crystalline polymers will be emphasized, at the expense of some very important and interesting detail, due to space and time limitations. The discussion will bring us to the modern day, where some of the current problems and controversies that still remain will be described.

INITIAL PERIOD

In the early nineteenth century there was a period of very keen experimentation where some very significant physical observations were made. These are more important in light of today's understanding, for naturally they could not be interpreted on any molecular basis at that time because the concept of polymers—no less crystallinity—was unheard of. These observations can now be interpreted in a straightforward manner; and, in retrospect, their significance is quite remarkable. Some of these observations are discussed in Flory's Principles of Polymer Chemistry in connection with the development of the theory of rubber elasticity [2]. However, it is best from the point of view of a historical discussion of crystalline polymers that we examine these pioneering observations in somewhat more detail here.

In 1806 Gough reported on his three now-classical experiments [3]. The first two of these experiments are self-consistent and concerned with completely amorphous rubber. They are beautiful examples of deductions from the Second Law of Thermodynamics, even though at the time the Second Law had not yet been enunciated. The molecular significance of these experiments was not appreciated until at least 150 years later. The result of Gough's third experiment was described as follows:

> If a thong of Caoutchouc be stretched, in water warmer than itself, it retains its elasticity unimpaired; on the contrary, if the experiment be made in water colder than itself, it loses part of its retractile power, being unable to recover its former figure; but let the thong be placed in hot water, while it remains extended for want of spring, and the heat will immediately make it contract briskly.

This result was obviously concerned with crystallization and melting of natural rubber under stress. Later in his report Gough describes the increase in density that took place upon crystallization. These observations must certainly represent some of the very first to describe the crystallization of a polymer, although they are not directly described as such.

C. G. Page, a medical doctor and professor of chemistry at the National Medical College in Washington, D.C., reported the results of his experiments with natural rubber in 1847 [4]. This endeavor may very well represent the onset of interdisciplinary research activity involving macromolecules. The highlights of Page's observations are as follows:

> If when the strip of rubber is in the stretched condition, it be quickly cooled ... it will be found to have lost its elasticity, and may be left for an indefinite time without regaining its elastic property. It resembles a piece of frozen rubber in some respects, although not quite so rigid. A piece of this substance, which has become stiff and inelastic by exposure to a great degree of cold soon regains its elasticity by immersion in an atmosphere of 70° Fahr., or even much below this.

* * *

> A curious sensation is experienced if it be inclosed in the hand, like the creeping of an insect. If successive portions of the inelastic strip be pinched between the thumb and finger, it contracts powerfully in these parts, leaving the others unaffected, and presenting the appearance ... of a string of knots or beads, which may be preserved in this state for any length of time, if not handled, and kept at a moderate temperature.

* * *

> It is somewhat remarkable that the interesting substance, gutta percha, appears very much like the India rubber when rendered inelastic .... When placed in water at 110°, no effect is produced upon it, except that it receives the impression of the nail more

> readily; but when the temperature is raised to 145° or upwards, it gradually becomes so soft and pliant.... When in the soft state, it possesses all the elasticity of common India rubber, but it does not retain this property long. It soon begins again to grow hard, and in a short time, varying according to the temperature and the size of the piece operated upon, regains its original hardness and rigidity. May not this be a case of isomerism, in which the different arrangement of atoms determines these physical distinctions?

In the first of his observations, Page describes the crystallization of rubber under stress, producing in the process what is now known as "racked rubber" [5, 6]. His description of melting not only is interesting, but it demonstrates the contractile properties of oriented crystalline polymers. It can be considered to be a precursor to all experiments in which phase equilibrium is established and studied [7]. In the last of the observations, he gives a comparison of the properties of gutta percha and natural rubber; a description of melting, supercooling, and recrystallization of gutta percha; and the rather important and, indeed, interesting conjecture for that time that gutta percha and natural rubber might very well be isomeric to one another. What remarkable intuition was displayed.

The classical studies of thermoelasticity by J. P. Joule, covering a wide variety of materials, were published in 1857 and 1859 [8, 9]. His major findings pertaining to polymers are summarized in the following quotations:

> The experiments on the stretching of solids showed, in the case of the metals, a decrease of temperature when the stretching weight was applied, and a heating effect when the weight was removed.... With gutta-percha also a cooling effect on extension was observed; but a reverse action was discovered in the case of vulcanized india-rubber, which became heated when the weight is laid on, and cooled when the weight was removed.

* * *

> When, by keeping india-rubber at rest at a low temperature for some time, it has become rigid, it ceases to be heated when stretched by a weight, and, on the contrary, a cooling effect takes place as in the metals and gutta percha.

* * *

> The third experiment described by Mr. Gough has indicated the means of using this substance in the production of textile fibers.

* * *

> ... a piece of india-rubber, softened by warmth, may be exposed to

> the zero of Fahrenheit for an hour or more without losing its pliability; but ... a few days rest at a temperature considerably above the freezing-point will cause it to become rigid.

* * *

> When the band was stretched to six times its original length, little further elongation took place by increasing the tensile force....

In Joule's first observation, he points out the similarity in the thermoelasticity between ordinary crystalline solids and gutta percha, which implies a similarity in the state or structure of these substances. He also points out that vulcanized natural rubber has a quite different thermoelastic behavior under mild deformation. We would now interpret this property to be characteristic of an amorphous, liquidlike substance which does not crystallize under mild deformation because of vulcanization [2]. In his next observation, the crystallization of natural rubber upon cooling is described. It becomes a rigid substance, and its thermoelastic behavior becomes similar to metals and gutta percha. Joule points out that Gough's experiment has shown a way of using natural rubber in the production of textile fibers. He has recognized that fibers require oriented crystallinity. He also recognized the negative temperature coefficient of the crystallization process (without deformation). He thus essentially anticipates the more quantitative studies of Wood and Bekkedahl [10] which were reported almost a century later. Joule also noted that when vulcanized rubber is stretched, there is an upsweep in the stress-strain curve at large deformations. This result is now recognized as being a quite common effect of crystallization on the modulus of elasticity induced under stress [2].

These very early results with natural rubber and gutta percha quite obviously represented some very fundamental observations concerned not only with the properties of polymers but specifically with crystalline ones. It was unfortunate that the significance of these observations was not recognized and pursued at that time. One can only speculate how much further along in the study of polymers we would be today if, after the enunciation of the Second Law, the obvious differences in the properties of certain classes of molecules had been recognized and studied as such. Rather they were relegated and ignored until the advent of the macromolecular hypothesis. It is of course interesting to note in the present context that some of the rather important physical and mechanical properties of crystalline polymers were recognized as long ago as the early to mid 1800s.

CRYSTAL STRUCTURE DETERMINATION

The discovery by von Laue and by Bragg in 1911 and 1912, respectively, that simple crystalline substances diffract x-rays and give a method by which to determine crystal structures was very shortly thereafter applied to the study of what we now recognize as polymeric substances. This experimental method, the x-ray diffraction at wide angles, provides the most direct evidence for the occurrence of three-dimentional, long-range order, i.e., crystallization in polymers. These studies represent the first systematic investigations of crystalline polymers. From the initial work in this field, taking place in the early and mid 1920s, it became apparent that many naturally-occurring substances, now recognized as polymers, diffract x-rays. These early studies included chitin, ramie fibers, other forms of cellulose, collagen, and stretched as well as only cooled natural rubber [11-15]. This kind of experimental observation was (and still is) extended to a wide variety of natural and synthetic polymers. It is still a very important and powerful technique in the modern day of polymer research. During this early period of x-ray diffraction studies, it was noted that there was a class of substances which would not diffract x-rays under what were considered "normal conditions." These were termed "amorphous" substances. Some of these were shown to very definitely diffract x-rays when stretched beyond a critical length [12, 16].

Although most of the detailed structures that were carried out in these early years were not always exact, and in some cases were completely incorrect, in retrospect the important matter was the very important principles that were established by these pioneers. These can be summarized as follows: 1) normal bond distances, bond angles, and other elements of structure appear to be the general rule; 2) the role of the chemical repeating unit in polymers is analogous to that of molecules in crystals of low-molecular-weight organic compounds; 3) it is not uncommon to find more than one chain passing through the unit cell; and 4) the unit cells are usually composed of from one to eight chain units. As has been described by Flory [1], the realization that a unit cell need not contain a complete molecule was one of the very important concepts that led to the development of the macromolecular hypothesis, namely that a polymer consists of a succession of chain units joined by covalent bonds.

A very serious dilemma presented itself in the original x-ray diffraction analysis with respect to this latter point. As was discussed by Katz [17] and by Mark [18], the unit cells of all the crystals studied, though thought to be of high molecular weight, did not have molecular weights greater than 800 times that of a hydrogen atom. This would then appear to be contrary to the emerging, but not yet widely accepted, concept of natural and synthetic high-molecular-weight substances. This dilemma was resolved in 1926 by a botanist, O. L. Sponsler [19], who was interested in the structure of cellulose and published his results in the Journal of General Physiology. He satisfactorily worked out the complete structure of the cellulose molecule and, in particular, the unit cell. The chemical repeating unit, the pyrranose ring, with the side chain CH_2OH being alternately to the left and right of the units, formed glucosidic connecting bonds giving an ordered chain molecule. It was apparent that the molecule would be much larger than the unit cell, but one could still quantitatively describe all of the observed x-ray diffraction characteristics [19]. There was no a priori reason for the complete molecule to be placed in the unit cell. Further refinement of this concept was given by Meyer and Mark [20] in their classic paper on the x-ray diffraction of polymers. Indirect confirmation of this hypothesis can be found in the work of Mie and Hengstenberg, working with Staudinger [21], who studied both the small- and wide-angle x-ray scattering of low molecular weight oligomers of polyoxymethylene. The wide-angle spacings remained constant, but the small-angle scattering was proportional to the chain length.

This early work and the perceptions that were involved utilized standard methods. None of the techniques or concepts used were unique to polymers. These led in subsequent years to major advances in the enunciation of the crystalline structure, i.e., the ordered structure of chain molecules. Much of this work on polyolefins, diene-type polymers, polyesters, and polyamides was pioneered by C. W. Bunn, an expert practitioner of crystallographic science [22-24]. The same principles of bonded and nonbonded interactions are involved with polymers and low-molecular-weight substances. This generalization is epitomized by the fact that Bunn's determination of the crystal structure of high-molecular-weight polyethylene [25], the orthorhombic unit cell, and its lattice parameters follows in a very natural fashion as a continuation of the crystalline structure of the higher homologs of the n-paraffins.

In discussing these early x-ray diffraction results, our attention has been concentrated on the discrete reflections. However, as was pointed out by Katz [12] and Ott [15], virtually all polymeric systems studied also display diffuse reflections or amorphous halos. This fact was first noted in early studies of natural rubber and is discussed in detail in a very definitive review on x-ray diffraction by Gehman in 1940 [26]. These observations were the first indications that crystallization was not complete, i.e., the system was not 100% crystalline. Crystalline and liquidlike or amorphous regions coexisted in varying and as yet undefined amounts.

In all major outward appearances, the pattern of frozen (unstretched) rubber originally studied by Katz [12, 17] can now be generalized to all crystalline polymers in that they resemble the pattern obtained from powdered organic crystals. It represents a structure of very small crystallites in random arrangement, i.e., a set of Debye-Scherrer rings and a diffuse amorphous halo is observed [26].

Katz reported [12, 17] that when rubber is stretched beyond a critical elongation, it gives a fiber type of diagram instead of concentric Debye-Scherrer rings. Discrete spots are observed similar to the rotation diagram of a crystal, with the axis of rotation corresponding to the stretching direction. Again, we have an analogy to simple organic systems. However, for polymers the diffraction spots are superposed on the amorphous halo which is still present. The lattice spacings for the Debye-Scherrer rings agree with the spots observed for stretched rubber. This result indicates that the same crystal structure exists for both cases, which is now a quite general result for virtually all polymers.

For natural rubber (which happened to be studied first) the density of the unit cell, as determined from the x-ray diffraction structure analysis, is much greater than that determined for the macroscopic sample [27]. Similar results were found later for other crystalline polymers. These general results indicate that the sample is not completely crystalline. This conclusion is consistent with the diffuse halos found in the x-ray patterns.

In brief summary, by 1940 it was established that many polymers will diffract x-rays, yielding discrete rings or spots. The crystal structures can be determined by standard methods. The presence of diffuse halos and a comparison of unit cells with macroscopic densities are consistent with incomplete crystallization, indicating the semicrystalline nature of such systems.

The synthesis of stereoregular polymers by Natta in the 1950s yielded new classes of crystalline and crystallizeable polymers [28]. The methods and techniques for the determination of ordered structures were already established, verified, and ready for use. Various types of helical ordered crystal structures were deduced for the isotactic and syndiotactic polymers that were produced [29]. At approximately the same time, the ordered structures of polypeptides and polynucleotide chains were also found to be helical [30, 31]. We might note, for historical perspective, that the first postulated ordered, helical structure for a chain molecule was given for polyisobutylene [31a].

The determination of the crystalline or three-dimensional structures of the ordered regions of semicrystalline polymers can now be considered to be a relatively standard, virtually routine matter. This aspect of the problem, the wide-angle x-ray scattering, so vital now and so controversial in the formative years of polymer recognition and structure determination, is now a classical procedure. History thus teaches us that problems get resolved and basic principles established as long as the scientific method and procedures are obeyed. Some of the controversies involving the crystal structure of chain molecules and what was thought to be an audacious act in studying such materials will be reminiscent of some of the controversies that developed subsequently in elucidating the properties of crystalline polymers.

OTHER ASPECTS OF THE PROBLEM

The crystallographic aspect of structure is now relatively well understood and is in a fairly tranquil state. There does not appear to be any reason why this subject should not remain so. However, there are many other areas which are also of fundamental importance in the understanding of crystalline polymers. These include the thermodynamics and kinetics of melting/crystallization, the molecular description or chain structure of the basic crystallite, the crystalline morphology or supermolecular structure, i.e., the arrangement of the crystallites relative to one another, and the relation of these phenomena to microscopic and macroscopic properties. There is a subtle but discernible relation among these various aspects of the total problem, which should be recognized as we follow the historical development. They can be looked at as follows: 1) properties are related to molecular morphology, 2) molecular morphology is determined by the crystallization mechanisms, 3) the crystallization mechanisms are deduced from studies of crystallization kinetics, and 4) crystallization kinetics requires an understanding of the thermodynamics of the system.

In the 1940s, two major advances were made in the realm of thermodynamics and kinetics of crystallization. Wood and Bekkedahl [10] reported the results of an experimental study of the crystallization kinetics and melting of natural rubber. Flory [32] presented a statistical mechanical theory of the fusion of polymers which had very important theoretical and experimental consequences for future work.

Wood and Bekkedahl [10], following the earlier classical calorimetric studies of Bekkedahl [33] and some fragmentary kinetic data in the literature, showed that the physics and physical chemistry of crystalline polymers could be studied quantitatively using methods and concepts which were well known for low-molecular-weight crystalline substances. Despite the fact that the data itself could not be properly interpreted until much later, three major points—now found generally for all crystalline polymers—were observed and their significance realized. The first of these was the shape of the kinetic isotherms, as illustrated in Fig. 1. Initially there is a time lag for the crystallization, followed by an increase in crystallinity at an accelerated rate. Toward the completion of the process, there is a leveling off of the amount of crystallinity at a well-defined pseudo-equilibrium value. Thus a typical sigmoidal-shaped isotherm results. They also found a very characteristic temperature coefficient to the kinetics of crystallization. There is a strong negative coefficient in the crystallization rate in the vicinity of the melting temperature, a maximum in the rate at somewhat lower temperatures, and a retardation in the crystallization rate as the glass temperature is approached. The dependence of the melting temperature, and course of fusion, on the crystallization temperature for natural rubber is shown in Fig. 2. Similar results have now been found for all homopolymers [34]. Unfortunately, these initial results led in the early days to the erroneous concept that natural rubber did not possess and equilibrium melting temperature and by inference that the same situation existed for other polymers. This kind of observation, which is fairly widespread for many polymers, can now be given a straightforward interpretation in terms of the crystallite structure. Unfortunately, it led to the

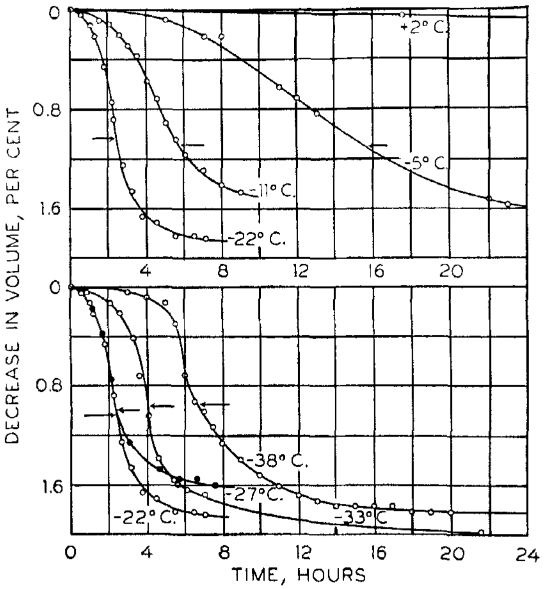

FIG. 1. Volume-time relations at indicated temperatures during the crystallization of natural rubber [10].

concept that no equilibrium melting temperature existed. However, it was subsequently shown that an equilibrium melting temperature exists for natural rubber [35] as well as for other polymers [36]. These general observations were correct, and they can now be given a proper and consistent interpretation. The experimental results of Wood and Bekkedahl [9] were subject to a great deal of discussion and thought, being the only reliable quantitative and systematic data then available. It is an understatement to say that they served as a great stimulus for further experimental and theoretical studies.

The theory developed by Flory [32] represents the beginning of the quantitative understanding of the properties and behavior of crystalline polymers. The major conclusions from this theory were that: 1) a well-defined equilibrium melting temperature exists; 2) melting-crystallization is a first-order phase transition, albeit a very diffuse one; and 3) the melting temperature is depressed in a systematic manner, depending on the concentration of added diluent, on copolymer composition and copolymer sequence distribution, and on molecular weight, for systems with a most probable distribution. These concepts were later extended to the molecular weight dependence for uniform chain length [37]. These theoretical conclusions were somewhat revolutionary in their time and were thus prone to be controversial. However, all the major conclusions and predictions of this theory were

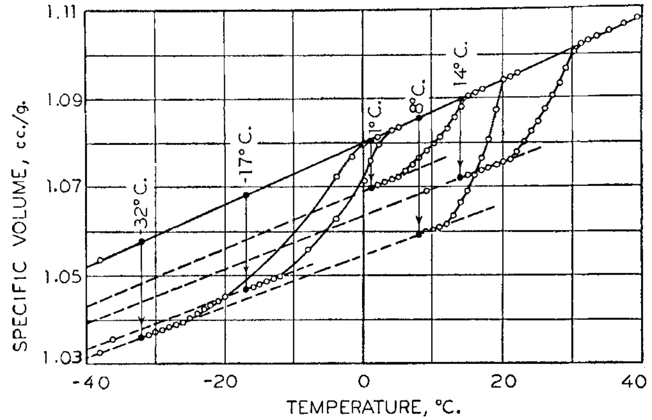

FIG. 2. The melting of natural rubber crystallized at different temperatures [10].

subsequently substantiated by experiment. The diluent effect allowed the enthalpy of fusion per repeating unit to be determined as well as related thermodynamic parameters [38]. The importance of sequence distribution in determining the melting temperature of copolymers was vividly demonstrated [39]. Two-phase equilibrium was demonstrably established below T_m [40]. Predictions of the melting temperature for infinite chains [37] were verified for linear polyethylene [41, 42]. Thus a very basic substantive theory was made available for use in interpreting experimental data.

Experimental studies of the course of fusion during this period showed that depending on molecular weight, molecular weight distribution, and the crystallization conditions, the fusion range could be very broad. Melting-recrystallization processes were very commonplace prior to complete melting [36]. (By the same token, by careful sample preparation and isothermal crystallization conditions, melting of low and moderate molecular weights could be relatively sharp [40, 43].) This phenomenon, melting and recrystallization, until it was recognized as such, was one of the major stumbling blocks in developing a quantitative understanding of the problem. It was incorrectly used as evidence against the concept of polymer crystallization being a first-order phase transition.

The concept of a first-order phase transition and the existence of an equilibrium melting temperature is a necessary requisite for the application of nucleation theory. The importance of nucleation theory has proven to be a crucial and cogent idea in understanding crystallization kinetics of polymers and the properties that result [34]. It was first recognized and identified as such by the very strong negative temperature coefficient of the crystallization rate of several polymers in the vicinity of T_m [44]. This type of temperature coefficient is characteristic of nucleation control of the crystallization and is invariably found in polymer crystallization [34]. It then leads to a straightforward interpretation of the earlier kinetic studies of Wood and Bekkedahl [10]. The importance of nucleation control of polymer crystallization cannot be overemphasized in any study of the problem. It became apparent in subsequent kinetic studies of the overall crystallization process as well as of individual crystallite growth rates [45, 46]. Unfortunately, the very general grounds upon which this conclusion is reached preclude the deduction of any unique molecular description of the nucleation process and, most important, the chain structure within the nucleus [47]. This serious restriction prevents the structure of the nucleus from being deduced solely from kinetic studies, as has been attempted and widely publicized [48].

In the early formative stages of the study of crystallization kinetics, it was shown that the overall crystallization process from the pure melt [44], from polymer-diluent mixtures [49], and more recently from very dilute solutions [50] follows the general mathematical formulation for the kinetics of phase changes as developed by Avrami for metals [51] and modified for applicability to polymers [34, 44]. More recently the growth rate of crystallites [46] was found to follow a theory developed by Hillig [52] for low-molecular-weight substances. It is not unique to polymers [47].

Some very important principles concerned with equilibrium and crystallization kinetics, fundamental to the comprehension of the properties of crystalline polymers, were established. Formally the crystallization of long chain molecules follows the same basic scientific principles that were established for other crystalline substances, despite the superficial molecular complexities. However, many important questions, unique to polymers, still would remain unanswered if recourse had been made only to these basic principles. The reason for this is that polymer crystallization does not occur at, or even near, equilibrium conditions. Early studies showed that, in order to occur at a finite rate, polymer crystallization must be conducted at temperatures well below the melting temperature [34, 44], i.e., at relatively large undercoolings. Hence a nonequilibrium polycrystalline state results with different crystalline morphologies, which strongly influence properties. Therefore, the next major area that needs to be considered in our development of a perspective on the subject is that of morphology. It is important, however, to recognize that to be meaningful the morphology needs to be developed on a molecular basis as contrasted with gross microscopic observations. The morphology is concerned with the structure of the individual crystallites; their relative arrangement one to the other, termed the supermolecular structure; and the extent of crystallinity. Of prime importance is the relation of macroscopic properties to the morphology.

STRUCTURE AND MORPHOLOGY

The description of the morphology and the interpretation of properties of semicrystalline polymers has been subject to a very deep and divisive debate for more than two decades [47, 53-60]. This situation could have been avoided if some of the basic principles that were involved had been understood and the rudimentary elements of scientific standards and of objectivity had been followed [47]. Historically, one of the conclusions that was deduced from the analysis of the x-ray diffraction patterns of polymers was that the crystalline regions were quite small and crystallinity was not complete. This subject has been discussed at some length by Bunn [23]. It was deduced from the breadth of the diffraction lines that the dimensions of the crystalline regions were of the order of hundreds of angstroms in all directions. This conclusion, as well as the incomplete crystallinity, led to the concept of the "fringed micelle" as the primary crystalline or morphological form. This model is illustrated in Fig. 3. The basic idea is that the crystalline dimensions are small and that any given molecule will pass through a number of crystalline regions in the course of its trajectory. The portion of the molecules between the crystallites constitutes the amorphous regions. This two-phase, fringed micelle model enjoyed widespread recognition and popularity, although its oversimplification was recognized by most investigators [23]. It became fashionable in subsequent years to use this concept as a convenient whipping boy.

In the mid 1950s a major advance was made in the understanding of the crystallite structure by the results reported from several laboratories [61-64]. It was found that homopolymers crystallize from dilute solution in the form of platelets or lamella-like crystallites, as is illustrated in the electron micrograph of Fig. 4 for linear

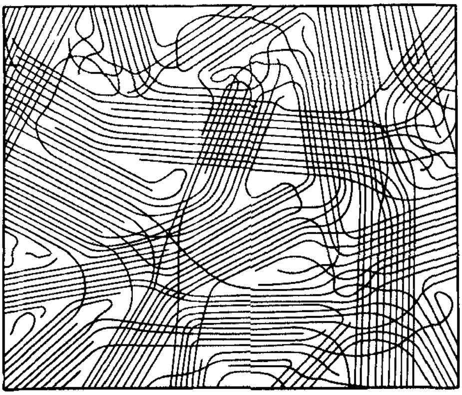

FIG. 3. Fringed micelle model of crystallite structure.

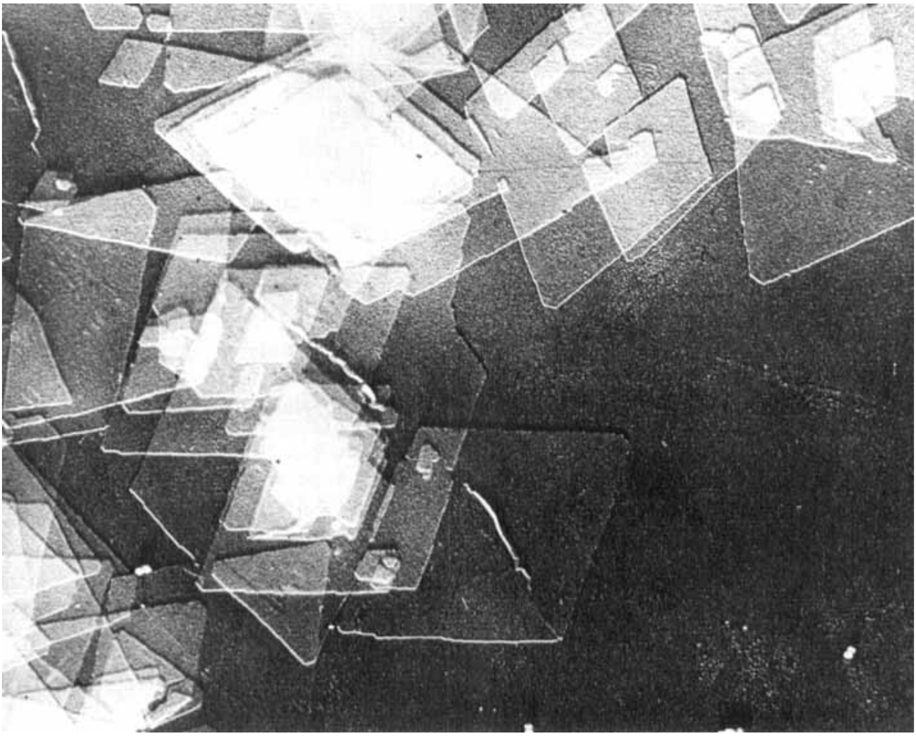

FIG. 4. Typical crystals of linear polyethylene grown from dilute solution.

polyethylene. Typically such crystals are several microns in lateral dimensions and of the order of 100-200 Å thick. Most important, the chains within the crystalline platelets are preferentially oriented perpendicular to the wide face of the crystal. Since the platelets are usually no more than the order of a few hundred angstroms thick and the molecular chains are many orders of magnitude greater in length, it is necessary that a given molecule transverse a crystallite many times in order to satisfy the orientation, chain length, and crystallite thickness. Thus some type of folding must take place. These structures have been observed for all homopolymers studied [57, 65] and have been termed "single crystals," which appears to be a misnomer.

These observations recalled the virtually neglected report of Storks in 1938 [66] concerned with an electron diffraction study of very thin films of gutta-percha and polyethylene sebacate which were prepared by evaporation from dilute solution. Storks found that unstretched films of gutta-percha "are composed of relatively large crystallites which are precisely oriented with their fiber axis directions normal to the film surface. It is presumed that the macromolecules are folded back and forth upon themselves in such a way that adjacent sections remain parallel." This conclusion of Storks appears to be the first enunciation of regular chain folding. However, he also reported that the unstretched films of polyethylene sebacate "consist of relatively small crystals believed to be oriented with their fiber axis directions approximately in the plane of the films but with limited rotation around the fiber axis direction." We note that the chains within the crystal of this polymer had a completely opposite orientation from that of gutta-percha. (In the modern resurrection of Storks' work, the results obtained with gutta-percha are widely quoted; those with polyethylene sebacate are completely ignored.)

With the habit for dilute solution crystals being well established, the detailed structure of the interface associated with the basal plane of the lamellae becomes a matter of interest. This structure is not at all obvious. What is obvious is that the reentry requirement demands some type of "folded chain." Based on the external shape of the platelets and the apparent smoothness of the basal plane, all being the result of direct microscopic examination, it was postulated that the chains were regularly folded, with hairpinlike connections between the crystalline sequences, yielding essentially a completely crystalline sample [53-56, 63]. Alternatively, it was suggested that adjacent reentry of the chain was not required; the crystalline sequences were connected more or less at random with connecting loops of random lenth [67, 68]. This concept was soon popularly termed "the switchboard model." Both of these models were and are completely compatible with the direct electron microscopic observations. Intermediate structures, essentially modifications of these two extremes, can also be envisaged. It becomes clear that molecules and their trajectories are not observed by this type of electron microscopy. Other means and other types of arguments are needed to resolve the nature of this interfacial structure. This kind of discussion has now been going on for more than 20 years. As we trace the history of this problem, we will see that many of its aspects are now clearly at the point of resolution [47, 60].

One of the major consequences of the crystal habits formed from dilute solution were its implications to the structure of bulk-crystallized polymers. In this case, lamella-like crystallites can also be directly observed by electron microscopic study and inferred from other observations such as the maxima in low-angle x-ray scattering, the internal structure of spherulites, and an examination of the residue left after selective oxidation of a crystalline sample. An example of the observation of lamellae by direct electron microscopy of surface replicates is shown in Fig. 5 [69]. In this early example the lamella thickness was of the order of 100 Å. These results were thus immediately equated with the interfacial structure of solution crystals, since they were comparable in thickness. It was unfortunate that

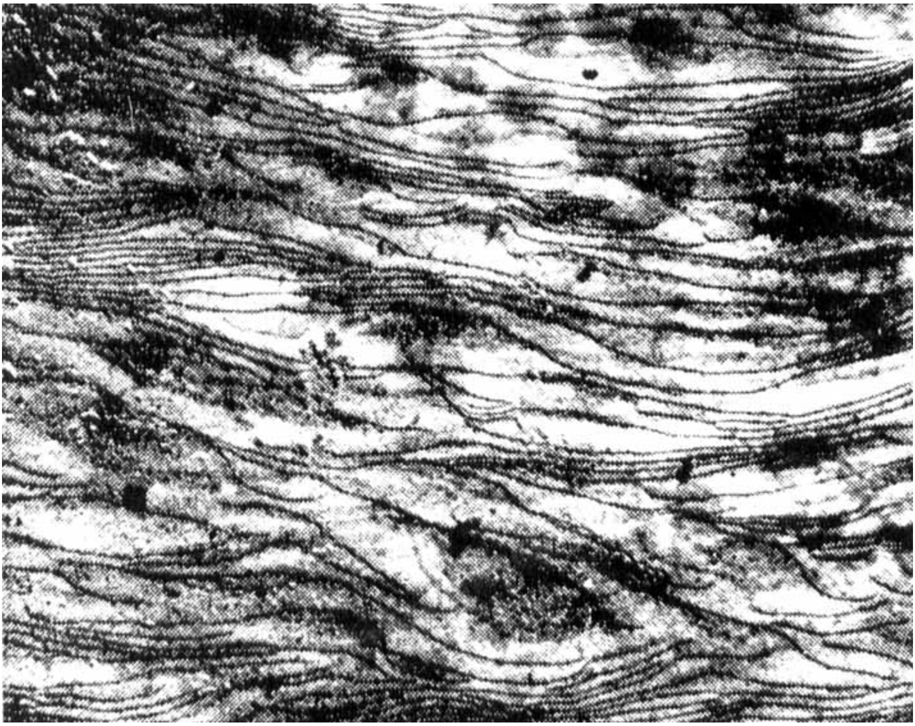

FIG. 5. Electron micrograph of surface film of linear polyethylene [69].

these kinds of micrographs, with such small dimensions in the chain direction, were those initially reported. Later work showed that in bulk crystallization lamella thicknesses up to the order of 1000 Å or greater could be observed [70-72]. The lamella thickness depends on the molecular weight and the crystallization conditions under atmospheric pressure. Thus the dimensional characteristics of the lamellae are quite different from those in dilute solution. A great deal of the difficulties in understanding and resolving the controversial issues would have been avoided if the thicker lamellae had been those that were initially observed.

Despite the observation of larger crystallite dimensions, it was very strongly and vociferously argued through the 1960s and much of the 1970s that the chains were regularly folded in bulk-crystallized polymers. This became a very popular and widespread point of view, as can be discerned by many reviews written on the subject that appeared at that time [53-56]. Contrary views, although voiced, were more often than not ignored [58, 59, 73-75].

The major principles that were widely enunciated to support regularly folded chains in bulk crystallized polymers were that 1) the chain units in crystalline homopolymers should be assigned to either the interior of the crystallites or to the smooth interface; 2) chain units connecting crystallites were rare events and, if they existed at all, adopted ordered conformations; and 3) deviations in properties from those expected from macroscopic crystals were widely known and accepted. Contributions from the interface and from defects within the interior of the crystal were postulated to account for the observed properties [53, 55, 76]. In retrospect, it should be recalled that at the time the concepts outlined above, although extremely popular, were never proved but were tacitly assumed.

In connection with the above model, it is obvious that the more conventional amorphous regions were disavowed and that what came to be termed a "crystalline defect model" was extensively publicized and advertised as representing the crystalline state of polymers. Those who disagreed were thought to be either heretics or ignorant or incapable of understanding the complexities in interpreting the electron micrographs. Upon close scrutiny, the only evidence—experimental and theoretical—for the inspiration of the aforementioned model were the electron micrographs. In summary, in this model a crystalline polymer is viewed as consisting of disordered units (or defects) imbedded within a classical crystalline matrix.

Alternatively, it was recognized by some that the presence of chain units external to the crystalline region is not incompatible with lamella-like crystallites. It was only the ad hoc assumption of regularly folded chains which placed the complete burden of explaining properties on internal defects in concentrations which were unprecedented relative to other crystalline substances. The question as to which model is appropriate and correctly represents the molecular morphology of the crystalline state is obviously fundamental to the comprehension of the properties of crystalline polymers. The question then became, how can this matter be resolved? There have been essentially two general approaches to this problem which do not involve microscopic observations.

One approach to this problem has been to study the properties of molecular weight fractions and deduce structure in a consistent manner from such experiments. A large number of different properties have been studied, obligatory for interpretable results, over a wide range of molecular weight fractions. The results that have been obtained with polyethylene and polyethylene oxide are detailed elsewhere [47, 58, 77]. In summary, it has been found that properties systematically vary with molecular weight. The idea of a degree of crystallinity, all but discarded by some of these newer concepts of the time, was shown once again to be a very quantitative concept. The level of crystallinity for a given polymer can vary from more than 90% to less than 50%, depending upon the molecular weight and crystallization conditions. The properties cannot be described in any unified, comprehensible manner without requiring a substantial

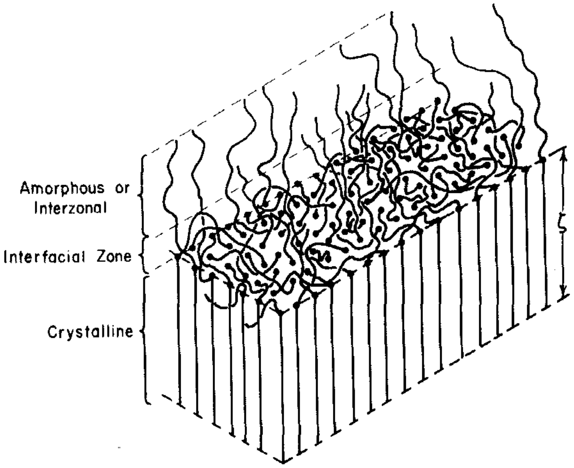

FIG. 6. Schematic representation of crystallite [74].

content of amorphous regions with chain units in disordered array. The unit cell parameters were found to be invariant over a large range of macroscopic densities [78], ruling out the possibility of any massive concentrations of internal defects to explain properties. Melting temperature measurements require high interfacial free energies [70, 71], suggesting the presence of a diffuse interfacial zone [32, 70]. This interpretation of the thermodynamic measurements is supported by spectroscopic results [79, 80].

From these results a schematic representation of a rudimentary lamella crystallite has emerged [74]. This crystallite consists of three major regions, as is illustrated in Fig. 6. There is a lamella-like crystalline region, which represents the three-dimensional ordered structure, containing internal defects of the same order of magnitude as comparable crystalline low-molecular-weight substances. There is an interfacial region which is very diffuse and whose structure gradually changes between that of the two regions it connects. This interfacial zone is not a sharp or clearly-defined boundary. Details of structure still need to be worked out, but there must be some type of anisotropic orientation in this region close to the basal plane. There is therefore a major difference between this type of interface and those of monomeric systems, and it is obviously unique to the crystallization of chain molecules. The third region is the amorphous, or interzonal, region, where the chain units are in nonordered conformation and connect the crystallites. The properties of this region are very close, if not identical, to those of the pure melt [58, 65, 75].

This model, which is consistent with the electron micrographs of bulk-crystallized polymers, explains virtually all properties. It requires a lamella-like structure while it still retains some elements of the previous "fringed micelle" model. The main resemblance is the presence of the amorphous or nonordered regions. In addition to the lamella-type crystallite, which was the major new contribution, there is also a diffuse, high free energy interface which is not compatible with the regularly folded chain model. The schematic crystallite illustrated in Fig. 6 is consistent with properties and does not require that each individual molecule crystallize independently from another. This process is the only way that regular chain folding could occur. It is not only improbable because of chain statistics but also very difficult to envisage mechanistically as taking place from a melt of entangled high-molecular-weight chains.

Another method of attacking this problem has been by analyzing the small-angle neutron scattering (SANS) of a deuterated polymer in a protonated host. This is a relatively new and extremely potent technique that has been rapidly developing as the major facilities that are required have become more generally available. The acceptable scattering experiments, i.e., those devoid of aggregation, for several polymers—polyethylene, polypropylene, and polyethylene oxide—have ruled out the possibility of any regularly folded structures or any significant adjacent reentry for bulk crystallization. With minor exception [81], there is a consensus of opinion on this point [60, 82-85]. In 1976 Shelten et al. found that for rapidly crystallized polyethylene (to avoid species segregation) the radius of gyration of a chain in the crystalline state is the same as that found in the melt [86]. The same result was subsequently obtained for polyethylene oxide crystallized by slow cooling [84, 85], as well as for quenched and isothermally crystallized polypropylene [87]. For polypropylene the radius of gyration in the crystalline state is proportional to $M^{1/2}$. The significance of these results is far-reaching and is incompatible with regular folding with adjacent reentry throughout. Detailed analysis of the shape and intensity of the scattering curves also renders this thesis untenable [60, 82]. The conformational relaxation of the chain in the melt precludes the transformation of the randomly coiled molecule to a regularly folded crystalline structure within the time span that it can be enveloped by a growing crystal face [88]. Recent efforts to circumvent this conclusion by postulating that a crystallite can "reel in" individual molecules from the entangled melt, so that each chain crystallizes individually in a regularly folded array [89], have been shown to be hopelessly inadequate [90].

The current status of the structure of bulk-crystallized polymers can be summarized by the fact that two quite different major approaches to the problem, the study of properties and the SANS analysis, yield essentially the same conclusion with respect to the nature of the lamella crystallites and their associated regions. Disordered amorphous regions exist, as does a diffuse interfacial region associated with the basal plane. Efforts to maintain <u>any</u> vestiges of a regularly folded chain structure, for this mode of crystallization, have not met with very much success in view of these modern experiments and their comprehension and interpretation in a unified manner.

Another important characteristic of bulk-crystallized polymers is the crystalline morphology or supermolecular structure, which is concerned with the relative arrangement of the crystallites to one another. An example of such structures is spherulites, which were well known in inorganic crystals and in many low-molecular-weight organic solids [91, 92]. In polymers they were originally found in natural rubber by Smith and Saylor [27] and in polyethylene by Bunn [93]. The fact that spherulites were observed in a very wide variety of crystalline polymers, as the subject developed, led to the concept that such structures represent a universal mode of polymer crystallization. However, systematic studies of the factors governing the supermolecular structure have only recently been reported [40, 93-95]. From these studies it becomes abundantly clear that spherulites are in fact not a universal mode of crystallization. A variety of different morphologies can actually be observed, depending on molecular weight (when fractions are used) and on crystallization temperatures. These morphological studies are in a formative stage, with the different constitutional and crystallization factors which govern the supermolecular structure being sorted out. It appears to be a major subject area for future development.

A comprehensive and detailed summary of the current status of both crystallite and supermolecular structure, i.e., the nature of the crystalline state for bulk-crystallized polymers, including a discussion of the remaining areas of disagreement, can be found in the proceedings of a recent Discussions of the Faraday Society on The Organization of Macromolecules in the Condensed Phase [104].

We return now to the history of the properties and structure of crystals formed from dilute solution, such as those illustrated in the electron micrograph of Fig. 4. A variety of theories was immediately proposed [48, 96-98] as to why the chains in such crystals should be regularly folded. A study of the rise and, in some cases precipitous, fall of some of these theories makes interesting reading [47, 57]. One theory, with minor variants [14, 48] and additions thereto [89], the so-called "kinetic theory of folding" (for both dilute and bulk crystallization), has persisted because of repetitious usage and application. It purports to explain why chains are regularly folded in mature crystallites because of a nucleation requirement. Several different investigators have pointed out over many years that this theory assumes what it sets out to prove [47, 99, 100] and also that it has inherent shortcomings. It is in fact nothing more than the classical nucleation theory [101] with an assumption. It has nothing to do with folded chains except by decree. There is in fact no substantive theoretical base for the concept and support of regularly folded chains. As soon as this underlying fact is recognized, more progress will be made in this field. These theoretical shortcomings were recognized by some, and studies aimed at understanding the crystallite structure again proceeded along two main lines.

In studying the properties of solution-formed crystals, a rather important and general deduction made from kinetic studies was that crystallization was nucleation-controlled and the crystallite thickness was also nucleation-controlled [57]. The properties of the crystals have been summarized in detail elsewhere [57, 102]. The results of extensive studies have brought forth incontrovertible evidence, with only very minor exceptions, that a disordered interface is required in order to sustain the data. About 15-20% of the chain units must be in disordered conformation. A regularly folded array is incompatible with the data and thus represents an unacceptable model.

The SANS studies of solution crystals are in the very early stages of development. Although the consensus has not as yet reached the stage of bulk-crystallized systems, the major aspects of the structure, deduced from this technique, are emerging. The radius of gyration of solution-grown crystals of linear polyethylene is much smaller than their melt-crystallized analogs and, consequently, than that of the pure melt. They are only slightly dependent on the molecular weight [103]. Based solely on the results for the radius of gyration, a model termed the "superfolded model" has been propsed [103]. Here the folding of a chain is not confined to a single layer but adjacent reentry is assumed for each growth layer. This model can explain the radius of gyration results; but as has been pointed out, to properly interpret such experiments the nature of the experimental scattering function also has to be explained [60]. According to Yoon and Flory [60], the reproduction of both the form and the intensity of the scattering functions for such crystals requires an array of crystalline stems which are confined to several layers of the crystal but which are not densely packed in any of them. Therefore, the crystalline sequence of a given molecular chain may occur at small distances but not adjacent to one another in the growth plane. Reentry is indicated to occur nearby but not in direct adjacency. These investigators have also been able to show that the low incidence of adjacent reentry from solution-formed crystals is consistent with the configurational statistics of the chain [60]. Although much remains to be done by neutron scattering, a definitive structure will only be deduced when the results for both the radius of gyration and the complete scattering function are taken into account.

As we enter the 1980s we can recognize that the problems of crystallite structure and crystalline morphology which have plagued progress in the field of crystalline polymers now seem well on their way to being resolved [47]. Up until just a few years ago the concept of regular chain folding for both solution- and bulk-crystallized polymers was taken in many quarters to be so very well proven and established that all knowledge was taken to stem from that doctrine. As the most recent Discussions of the Faraday Society has revealed [104], the rhetoric may still be there, but it is being dimmed. The doctrine is now in serious question, movement away from it is clear, and a great deal of equivocation is evident.

From a historical viewpoint, problems involving crystalline polymers should be examined in broad perspective. It should be recognized that complex problems and controversies have been associated with this area since the inception of serious investigations. However, time and the scientific method have always led to a resolution of the difficulties.

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