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Crystalline polymer: Some reminiscences over the years☆

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Abstract

This paper is concerned with reminiscences of 50 years of research with crystalline polymers. It begins with the early days and the establishment of the basic thermodynamics of fusion of semi-crystalline polymers up to the present. In between are works involving crystallization kinetics, nucleation theory appropriate to polymers and the strong influence of molecular weight on the crystallization process and the resulting morphology, structure and properties. The problems and controversy regarding regularly folded chain and the crystallite interfacial structure, and their resolution was central to a great deal of activity during this time period.

I wish to thank all of you, former students, colleagues and friends for being here today and participating in this Symposium. It is both a sentimental and memorable event for Berdie and myself to see you all once again and renew old times together. In particular, I wish to thank Prof. Rufina G. Alamo of FAMU/FSU Department of Chemical Engineering and Dr. Carin A. Helfer of the University of Akron for your efforts and hard work on arranging the Symposium and related matters. I would like to go back in time this morning and reminisce about some of the highlights that we experienced over the last 50 years in our research with crystalline polymers.

My introduction and interest in crystalline polymers was kindled in my postdoctoral days in Paul Flory's Laboratory at Cornell during the period 1949–1952. If one can think back to that early period, there was very little, if any, basic understanding of crystalline polymers. Matters such as the nature of the fusion process, crystallization kinetics and mechanisms and the relation of morphology and structure to macroscopic and microscopic properties were virtually non-existent. It was a very exciting time to be involved. During this period we were able to establish some important basic concepts that underly the crystallization behavior of polymers. They are, in the main, still valid today. Some of the principles that were established during this period are as follows.

It was widely recognized then and now that a polymer was not completely crystalline. However, we were able to establish that the transition of a semi-crystalline polymer to the completely liquid state could be treated by the classical methods of phase equilibrium. In fact it was shown that one was dealing with a first-order phase transition, albeit a diffuse one. All the dictates of such a transition was followed. The basic concepts and conclusions of the statistical mechanical theory of polymer crystallization were verified [1].

On the basis of phase equilibrium the existence of an equilibrium melting temperature was proposed. At that time this was a revolutionary proposal, but it has stood the test of time. It was recognized, however, that true equilibrium would be difficult to attain. Thus, the usual semi-crystalline polymer represents a metastable state. This was a well known fact that has recently been rediscovered. The direct determination of the equilibrium melting temperature has, however, been elusive to this day. Several extrapolative methods have been proposed but a significant uncertainty in the true value of the equilibrium melting temperature remains [2].

During the time at Cornell we also undertook a study of crystallization kinetics of a variety of polymers, as poly(ethylene oxide), polyesters and polyamides using dilatometric techniques. (Differential scanning calorimetry was not as yet available.) We found, not at all surprising today, but very surprising to us at the time, that there was a strong negative temperature coefficient for the onset of crystallization. Also, a plot of the extent of the isothermal transformation against the log time gave a sigmoidal shape isotherm. An understanding of what was going on completely eluded us for a long time. This situation is difficult to

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imagine considering what we know now. A resolution to our difficulties became clearer by a fortunate circumstance. Around that time, Dr. David Turnbull, then at the General Electric Research Laboratory, presented a lecture at Cornell describing his classical work on the nucleation of mercury droplets [3]. It became quite apparent that his report was related to our work. In a subsequent discussion Dr. Turnbull introduced us for the first time to general nucleation theory and the Avrami type analysis of kinetic isotherms. It did not take us very long to apply these concepts to polymers. The moral of this experience is go to seminars, you never can tell what you will learn.

The first quantitative application of general nucleation theory to polymer was accomplished and the results published in 1954 [4]. In this initial application of nucleation theory the nucleus was represented by a cylinder with the chain lying parallel to the long axis. The free energy of forming such a critical size nucleus could be calculated from the saddle point of the free energy surface. Steady state nucleation theory was invoked and a satisfactory explanation of the temperature coefficient was obtained. Thus the major objective of this work, namely to explain the unusual negative temperature coefficient was accomplished. Since then other types of nuclei have been proposed for specific situations, all of which give the negative temperature coefficient [5–7].

In the 1954 paper [4], we were also able to make the first quantitative adoption of the Avrami concept to polymers. The fact that the transformation of polymers was never complete was taken into account. This procedure is now widely used in analyzing crystallization isotherms. However, time has taught us that as far as polymers are concerned the Avrami treatment has no real advantage over the Gölen-Sachs "free growth" approximation [8]. Chain entanglements, and other topological defects, which are relegated to the non-crystalline region as the transformation progresses has been shown to play a major role in influencing the course of the crystallization [9].

There was also a discussion in the 1954 paper of the reasons for the maximum that was observed in the crystallization rate. It was then estimated that the ratio of the temperature of the maximum rate to the equilibrium melting temperature should be $\simeq 0.8$. This conclusion fit the sparse data available then and has stood the test of time as more data became available [9].

After a stay at the then National Bureau of Standards, I accepted a Professorship in 1962 in the Department of Chemistry, Florida State University. Early during this period I was invited to participate in an ACS Lecture Tour covering Tennessee and Alabama. After a few lectures at different locations in Tennessee I noticed the same gentleman in the audience. He finally introduced himself one evening as a representative of Perkin-Elmer. He further stated that he was out to sell me a calorimeter. Having recently come from the Bureau of Standards, where there was a great deal of adiabatic calorimetry activity involving all kinds of substances I told him that you could not do much research of scientific interest with polymers because of the large quantities involved. It was to work with well characterized fractions to make any progress. He responded by telling me the instrument he was trying to interest me in only required a few milligrams. This really got my interest and he explained to me the principles of the operation of the differential scanning calorimeter. He then asked if I was interested in buying one. My answer "sure, but I do not have any money." "How about if I lend you an instrument?" was his response. I quickly accepted his offer. Shortly thereafter he sent me a DSC-1 which we were able to keep for about a year. Dr. Jose Fatou, a post-doctoral in my lab at that time, learned how to operate the instrument. What followed was an extremely fruitful research period. We published one of the very early, if not the first, paper utilizing DSC to study the melting of a semi-crystalline polymer, in this case linear polyethylene [10]. Of particular interest was the observation of multiple endotherm, quite unusual for that time and were able to offer a rational explanation.

During the course of our early work at Florida State, it became apparent that molecular weight plays an important role in crystallization behavior. Based on this thinking, we undertook a major program of molecular weight fractionations and characterization of linear polyethylene. Due to Herculean efforts by Jose Fatou and Ertugal Ergoz, as well as others in the laboratory at that time, we were able to prepare and characterize fractions over the range $M \simeq 10^3$ to greater than 10^6 [11]. These efforts lead to important results with respect to the role of chain length on a variety of properties of some crystalline polymers [12]. These include the crystallinity level, not only of linear polyethylene, but other polymers as well [12]; thermodynamic properties [11,13]; crystallization kinetics [11,14,15]; supermolecular structure [16–19]; spectral properties [20–23]; lamellar structure and organization [24,25] and tensile properties among others. [16,27]. Of particular interest was the finding that spherulites, and other type supermolecular structures, are not universally observed in homopolymers [16]. Molecular weight and polydispersity are important structures that governed whether such factors could be observed. It was also found that above about $M \simeq 20{,}000$ molecular weight fractionation does not occur during isothermal crystallization from the pure melt [27a]. On the other hand fractionation occurs during crystallization from dilute solution. This is a convenient procedure to obtain a wide range of molecular weight fractions. In retrospect, the decision to work with molecular weight fraction was worthy of the effort involved as a great deal of important information was obtained.

In an unusual observation we found that isotactic poly(propylene) displayed significant isothermal melting kinetics [27b]. This phenomenon can be attributed to the homoepitaxy displayed by this polymer. It then becomes very difficult to involve any of the standard extrapolation methods to obtain the equilibrium melting temperature of this polymer. It also explains in part the wide range in the equilibrium melting temperature that has been reported for isotactic poly(propylene).

Crystallization of homopolymers formed from dilute solution are lamellar-like with thicknesses of the order of 100–200 A and where chain axis are preferentially oriented normal to the basal plans of the lamellae. This very important observation was initially reported at about the same time by several groups of investigators [28–31]. Subsequently similar observation was reported for melt crystallized linear polyethylene [32]. Except for very low molecular weights the crystallite thickness is always much less than the extended chain length. Thus, some type of chain folding must take place. With the discovery of the lamellar-like crystallites, it was widely heralded that the chains crystallized in a regular folded array with complete adjacent reentry in a crystallographic plane. Thus, the basal plane was presumed to have a very smooth interfacial structure. With both few exceptions this concept became a matter of faith. The arguments regarding the interfacial structure were passionate and in some instances vitriolic. The issues involved are summarized in a Faraday Society Discussion, held in Cambridge, England (1979) [33]. The basis for regular folding was the interpretation of electron micrographs. However, the resolving power of the electron microscope was not sufficient to resolve this problem. Further support for a regular folded chain structure was the adoption of monomeric nucleation theory and the underlying assumption that nuclei were comprised of regularly folded chains [7]. The argument with regard to regular chain folding then became a circular one. The lamellar-like crystallites that are observed need not be identified with regularly folded chains. The gross morphological form that is observed is compatible with other types of chain structures. Nuclei with regularly folded chains are not necessary for lamellar crystallite to develop [34].

Our laboratory was heavily involved in this controversy. Several important contributions were made to clarify the problem and help resolve the controversy. Today, several decades after the discovery of lamellar-like crystallites, the problem is well on the way to resolution. A variety of experimental techniques demonstrate that a disordered overlayer is associated with the crystallite formed in dilute solution [35,36]. It is estimated that 15–20% are located in a disordered centerfacial region. Of particular interest is the fact that such crystallites display well-defined glass temperatures which correspond to the values from the corresponding melt crystallized polymers [37]. Since the glass temperature is the property of the amorphous region must be concluded that dilute solution crystals contain a significant amorphous overlayer.

A variety of experimental methods demonstrate that there is a partially disordered interphase that is associated with polymer crystallized from the pure melt [38]. These methods include density, wide and small-angle X-ray diffraction, thermal analyses, Raman spectroscopy, small-angle neutron scattering, dielectric relaxation and nuclear magnetic resonance involving different nuclei and techniques. The evidence for a non-regular interfacial structure is overwhelming for the polymers that have been studied so far. The experimental evidence is supported by theoretical studies. It is estimated that the interfacial region is about 10–30 Å thick, depending on the polymer and crystallization conditions and can comprise up to 30% of the system for modest to high molecular weights.

The availability of high molecular weight *n*-alkanes allowed for a connection to be made between molecular crystals, all molecules having the same chain length, and polymers [39–41]. The availability of such materials allows for a connection to be make between the crystallization behavior of low and high molecular weight chains. In collaboration with Prof. G. Wegner from Mainz, we were able to examine some important problems. We found that the chain length at which low molecular weight fractions of linear polyethylene and the corresponding *n*-alkane form fold chain crystallites are close to one another for crystallization from either the pure melt or dilute solution [42]. Pre-melting due to end sequence disordering (not attributable to impurities) is observed during the fusion of the *n*-alkanes [43,44]. The crystallization isotherms of the *n*-alkanes follow the Avrami formulation of about 60% of the transformation, with an exponent $n = 4$, similar to low molecular weight linear polyethylene fractions [43]. We learned that in studying kinetics, as well as other properties, it is important to distinguish between crystallites formed directly from the melt and not those transformed from it [45]. Otherwise significant errors can be made in interpretation. One of the most important results to come from the study of the high molecular weight *n*-alkanes was the fact that the interfacial free energy for nucleation, that is associated with the basal plane, was independent of whether the mature crystallite consisted of either folded or extended chains [46]. This conclusion was reached by applying nucleation theory pertinent to chain molecules of low molecular weight to the growth rate reported for $C_{246}H_{494}$ [47].

In this reminiscence we have, because of time, only briefly touched basically on crystallization from dilute solution and have neglected the crystallization of copolymers. There are still major problems that remain to be resolved with respect to the crystallization of homopolymers. These include, among many, a correct theoretical and reliable experimental method to obtain the equilibrium melting temperature; a determination of the temperature dependence of primary and secondary nucleation; a detailed structure of the interfacial region and the relation between mechanical properties and molecular and superstructure.

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