On the Annealing of Polyethylene Crystals Formed from Dilute Solution[1]

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ABSTRACT: The critical annealing temperature, defined as the temperature at which crystals formed in dilute solution and then dried undergo major alterations in thermodynamic and morphological properties, has been accurately determined as a function of the initial crystallite thickness. This temperature is shown to obey the theory for the melting of crystals of small size and thus can be identified with the melting temperature. It is, therefore, not necessary, as has been proposed, to endow the chain units within the interior of the crystals with any extraordinary mobility. The well-known changes in properties that are observed upon annealing are merely consequences of the fusion process and recrystallization.

It is well established that when crystals prepared from dilute solutions of long-chain molecules are separated from the mother liquor, major alterations occur in morphological and thermodynamic properties when the samples are heated above a certain temperature.[2-6] These changes in properties include as much as a three- to fourfold increase in crystallite thickness as well as a substantial elevation of the dissolution temperature[4] (melting temperature in a dilute solution.) Two quite different points of view have been expounded to explain these observations. On the one hand, it has been proposed[7-10] that a regularly folded chain type of interfacial structure is initially present and maintained during the heating (annealing) process. Therefore, in order to explain the increase in thickness, the polymer molecule must possess an extraordinarily high and coordinated mobility within the crystalline phase.[2,7-10] Such mobility would be an extraordinary characteristic of a crystalline polymer. In contrast, it has also been proposed[4,5,11,12] that the observations in question are a consequence of either melting or of partial melting followed by recrystallization from the molten state. Measurements of the changes in density, birefringence, and wide angle X-ray diffraction patterns during isothermal annealing[4] support this concept. Further confirmation of this hypothesis is found in the calorimetric properties of these crystals during fusion[12] and the observation of Nagai and Kajikawa[13] that after annealing, in the temperature range of interest, the orientation of the crystallographic axis has become random.

A resolution of this problem could be obtained by the direct measurement of the melting temperature in the pure state and comparison of this temperature with that which causes the properties to change on annealing. However, the required melting points cannot be easily obtained directly because of rapid recrystallization in the melting range and the concomitant change in structure that occurs.[14,15] Therefore, very rapid heating rates have to be employed.[16,17] There is, however, an indirect approach to this problem which alleviates these difficulties. If the crystallite size and interfacial free energy are given, it is then a straightforward procedure to calculate the expected melting temperature T_m of the crystals formed from dilute solution. The required interfacial free energy has already been determined from the analysis of the dependence of the dissolution temperature on crystallite size.[18] Hence, if an accurate determination can be made of the annealing temperature at which the properties change, a comparison of these two temperatures should help resolve this problem. The present paper is concerned with the experimental determination of this critical annealing temperature and the analysis of the data in terms of the proposition set forth.

Experimental Section

Two molecular weight fractions of linear polyethylene, $M_\eta = 46{,}500$ and 365,000, prepared and characterized in the manner previously described,[19] were isothermally crystallized from a 0.08% xylene solution for long time periods.[18,20] Isothermal crystallization was conducted over the tempera-

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[2] W. O. Statton and P. H. Geil, *J. Appl. Polym. Sci.*, 3, 357 (1960).

[3] W. O. Statton, *J. Appl. Phys.*, 32, 2332 (1961).

[4] E. W. Fischer and G. F. Schmidt, *Angew. Chem.*, 1, 488 (1962).

[5] J. B. Jackson, P. J. Flory, and R. Chiang, *Trans. Faraday Soc.*, 59, 1906 (1963).

[6] M. Takayanagi and F. Nagatashi, *Mem. Fac. Eng., Kyushu Univ.*, 24, 33 (1965).

[7] D. H. Reneker, *J. Polym. Sci.*, 59, 539 (1962).

[8] N. Hirai, Y. Yamashito, T. Mitshata, and Y. Tamura, *Dept. Res. Lab. Surface Sci., Far. Sci., Okayama U.*, 2, 1 (1961).

[9] A. Peterlin, *J. Polym. Sci., Part B*, 2, 279 (1963); *Polymer*, 6, 25(1965).

[10] J. D. Hoffman, *Soc. Plastic Eng.*, 4, 315 (1964).

[11] L. Mandelkern, A. S. Posner, A. F. Dioro, and D. E. Roberts, *J. Appl. Phys.*, 32, 1509 (1961).

[12] L. Mandelkern and A. L. Allou, Jr., *J. Polym. Sci., Part B*, 4, 447(1966).

[13] H. Nagai and N. Kajikawa, *Polymer*, 9, 177 (1968).

[14] A. Nakajima, F. Hamada, S. Hayashi, and T. Sumida, *Kolloid-Z.*, 222, 10, 124 (1968).

[15] H. E. Bair, R. Salovey, and T. W. Huseby, *Polymer*, 8, 9 (1967).

[16] B. Wunderlich, P. Sullivan, T. Arakawa, A. B. Dicyan, and J. F. Flood, *J. Polym. Sci., Part A*, 1, 3581 (1963).

[17] E. Hellmuth and B. Wunderlich, *J. Appl. Phys.*, 36, 3039 (1965).

[18] J. F. Jackson and L. Mandelkern, *Macromolecules*, 1, 546 (1968).

[19] J. G. Fatou and L. Mandelkern, *J. Phys. Chem.*, 69, 417 (1965).

[20] J. F. Jackson and L. Mandelkern, *J. Polym. Sci., Part B*, 5, 557 (1967).

ture range 75–92.5° to ensure as wide a range as possible in the resulting crystallite sizes.[18] The crystal suspension was collected in the form of a thin mat, by slow filtration, and subsequently vacuum dried at about 40°. The dried mats for each sample were divided into eight to ten portions, each was wrapped in aluminum foil, and they were then further evacuated for 48 hr. The samples were then placed in sealed evacuated tubes which were immersed in silicone oil thermostats maintained at the desired temperature. A fresh sample was used at each annealing temperature. This annealing was carried out for 48 hr, except for certain specific experiments which were designed to investigate time effects. To define adequately the temperature of interest, the annealing was conducted at temperature intervals of 1–2°.

After being heated for the requisite time, the sample was rapidly cooled to room temperature and examined by low-angle X-ray diffraction using a Rigaku-Denki camera. The crystallite thickness was obtained from the well-defined maxima and was converted to a linear dimension by means of Bragg's law. The experimental uncertainty in the crystallite size is estimated to be ±2 Å.

Results and Discussion

The low-angle X-ray diffraction patterns of the original unannealed samples were similar to those reported by other investigators.[21,22] The maxima are relatively sharp and at least two orders of diffraction are easily discerned. This characteristic diffraction pattern is maintained upon heating until a temperature is reached which is about 2° below that which causes the major changes in properties. At this point, although the patterns become more diffuse, the original spacing is still observed. Upon heating above this critical temperature, however, both the original sharp pattern and the spacings are altered. The patterns characteristically become very diffuse and the magnitude of the spacings increase. For a sufficiently high annealing temperature, the diffraction pattern in completely lost. Two typical sets of data, representing the change of spacing with annealing temperature, are given in Figures 1 and 2. The initial crystallite thickness of these samples are 129 ± 2 and 154 ± 1 Å, respectively. At low temperatures the diffraction maxima remain invariant over a wide range. However, it is clear from these figures that above a critical temperature, designated as T^*, major changes in the low-angle spacings take place. For the type of experiment reported here this temperature can be defined to within ±1°. We have not observed the decrease in spacing with temperature and time that has been reported to occasionally occur by Calleja, Bassett, and Keller[23] and by Nakajima, *et al.*[24]

A summary of the results obtained, for different initial crystallite sizes, are given in Table I. The major result is that the critical temperature monotonically increases with the initial crystallite thickness. For the two molecular weight fractions studied, M_η = 46,500 and 365,000, identical results are obtained. The lower molecular weight fraction was included primarily because studies of its fusion, by means of differential calorimetry, showed that two distinct peaks could be resolved.[12] This is characteristic of melting, recrystallization, and final melting.

TABLE I
RELATION BETWEEN CRITICAL ANNEALING TEMPERATURE AND CRYSTALLITE SIZE

M_n	Temp of crystn, T_c, °C	Initial thickness, Å	T^*, °C
365,000	75	115 ± 1	114.0 ± 2
365,000	85	126 ± 1	118.5 ± 1
365,000	85	128 ± 2	119.5 ± 1
46,500	85	129 ± 2	119.5 ± 1
365,000	88	145 ± 1	122.5 ± 0.5
365,000	90.0	154 ± 1	124.2 ± 0.5
365,000	92.5	172 ± 1	126.8 ± 0.5

Since the purpose of the detailed annealing studies is to detect the temperature at which changes occur, it is important to establish whether adequate time (48 hr at each temperature) has been allotted for this purpose. An analysis of the detailed isothermal time studies of Fischer and Schmidt[4] and Takayanagi and Nagatoshi[6] indicate that the procedure adopted here is adequate. This conclusion is further substantiated by the following additional experiments. In one set, a sample having an initial thickness of 130 ± 2 Å and a critical temperature of 120° was heated at 1–2° below this temperature for periods of time ranging from 30 min to 11,500 min. No variation in the low-angle spacing was observed with the heating time in this case. In contrast, a sample whose initial spacing was 129 ± 2 Å was an-

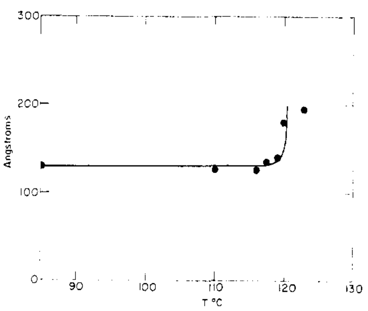

Figure 1. Plot of low-angle spacing in ångströms against annealing temperature for sample M_η = 46,000 crystallized at 85° in xylene.

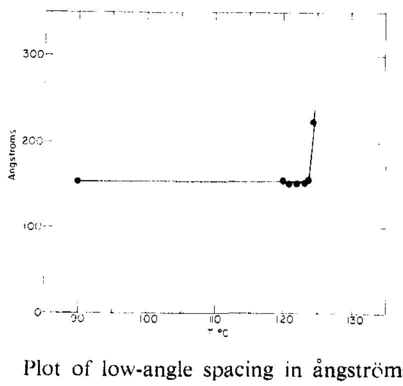

Figure 2. Plot of low-angle spacing in ångströms against annealing temperature for sample M_η = 365,000 crystallized at 90° in xylene.

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(21) A. Keller, *Phil. Mag.*, **2**, 1171 (1957).

(22) E. W. Fischer, *Z. Naturforsch.*, **12**, 753 (1957).

(23) F. T. Balta Calleja, D. C. Bassett, and A. Keller, *Polymer*, **4**, 269 (1963).

(24) A. Nakajima, S. Hayashi, and H. Nishimura, *Kolloid-Z.*, **229**, 107 (1969).

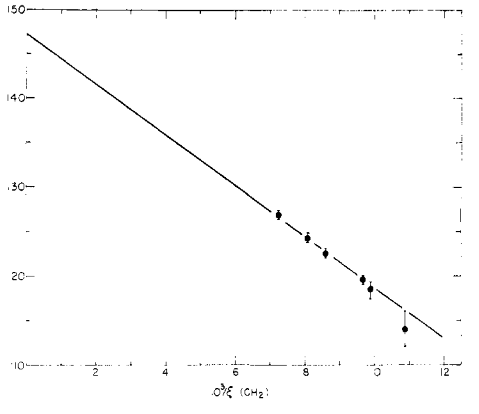

Figure 3. Plot of critical annealing temperature T^* against reciprocal of initial crystallite thickness in CH_2 units.

nealed at 123° for 2888, 5540, and 11,175 min, respectively. The low-angle diffraction maxima was found to be 180 ± 5 Å in all cases. Hence, for the present purpose of delineating T^* the heating schedule adopted is more than adequate.

By analyzing the data in Table I it is now possible to test the premise as to whether T^* can be identified with the melting temperature T_m. Utilizing the general theory for the melting of crystals of finite size, it is readily shown that for lamella-like crystallites

$$T^* = T_m^0\left[1 - \frac{2\sigma_{ec}}{\Delta H_u \zeta}\right] \qquad (1)$$

(in the derivation of this equation no assumption needs to be made as to the molecular nature of the interface). Here T^* has been identified with T_m, the melting temperature of the actual crystallites, T_m^0 is the equilibrium melting temperature, σ_{ec} is the interfacial free energy per mole of sequences emerging from the 001 basal plane of the crystallites, ζ is the crystallite thickness in CH_2 units, and ΔH_u is the enthalpy of fusion per repeating unit. The data from Table I are plotted in Figure 3 according to the suggestion of eq 1. The predicted linear relation results when T^* is plotted against $1/\zeta$. When the data are extrapolated to $1/\zeta = 0$, T_m^0 is found to be 147 ± 1°. This extrapolated equilibrium melting temperature is in excellent accord with the theoretical value of 145.5 ± 1 predicted by Flory and Vrij[25] for linear polyethylene. It is also in good accord with the value of 146 ± 0.5° which was determined from an analysis of the dependence of the melting temperature on the crystallization temperature for the bulk polymer,[26] and on the directly observed value of 146.5 ± 0.5° for annealed specimens, prepared by high-speed stirring from solution.[27] Thus, the identification of T^* with T_m is directly substantiated.

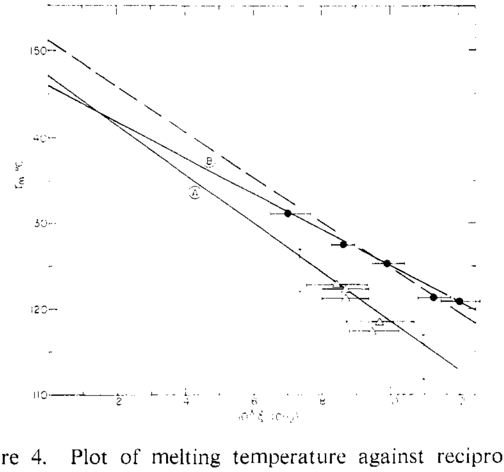

Figure 4. Plot of melting temperature against reciprocal crystallite thickness in CH_2 units. Line *A* from Figure 3: I from Calleja, *et al.*;[23] —Δ— from Wunderlich, *et al.*;[16] line *B* and —●— from Bair, Huseby, and Salovey.[21]

Further confirmation of this conclusion is obtained from the interfacial free energy deduced from the data in Figure 3. According to eq 1, from the slope of the straight line the interfacial free energy can be calculated. Utilizing $T_m^0 = 147°$ and $\Delta H_u = 980$ cal/mol of units,[28] the interfacial free energy characteristic of the actual mature crystallites is found to be 3400 ± 100 cal/mol. This set of units corresponds to 125 ergs/cm.[2] This value for the interfacial free energy is identical with that obtained previously from an analysis of the dissolution temperature–crystallite size relations.[18] In these latter experiments, this quantity has been shown to be independent of the crystallizing solvent.[18,29] Thus, the same interfacial free energy is obtained from two completely different and independent studies. These results thus give strong support to the proposition that the major changes in properties observed on annealing the dried specimen are a direct consequence of melting and recrystallization. The linear relations obtained in both sets of experiments indicate no significant temperature variation of the interfacial free energy over the range of study. It should be noted, however, that the samples studied were crystallized at sufficiently elevated temperatures so that the process took place isothermally.[18] The determination of the dissolution experiments involve very rapid heating rates,[18] while the annealing experiments described in the present work require relatively slow heating. As long as reliable melting temperatures are determined, the interfacial free energy deduced is independent of the heating rate employed, assertions to the contrary not withstanding.[30]

The results presented in Figure 3 and the interpretation thereof are further substantiated by data that have been reported in the literature. These latter results are summarized in Figure 4. In this figure the lower solid straight line, designated A, is a reproduction of the line from Figure 3 and thus represents the present experimental results. Two points from the paper of Calleja, *et al.*,[23] represent T^* for two differential initial crystallite sizes. Although, unfortunately, the critical temperature was only determined over a 5-deg range by

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(25) P. J. Flory and A. Vrij, *J. Amer. Chem. Soc.*, **85**, 3548 (1963).

(26) M. R. Gopolan and L. Mandelkern, *J. Phys. Chem.*, **71**, 3833 (1967).

(27) A. M. Rijke and L. Mandelkern, *J. Polym. Sci., Part A*, in press (1969).

(28) F. A. Quinn, Jr., and L. Mandelkern, *J. Amer. Chem. Soc.*, **80**, 3178 (1958).

(29) R. K. Sharma, L. Mandelkern, and J. F. Jackson, Abstract of paper presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(30) T. W. Huseby and H. E. Bair, *J. Appl. Phys.*, **39**, 4969 (1968). See also reference therein to paper to be published by J. D. Hoffman, *et al.*

them, their data fall on our line. There is also plotted in this figure the directly observed melting temperatures of solution crystals that were reported by Wunderlich, *et al.*[16] The melting temperatures were determined by light microscopy and rapid heating rates, greater than 10°/min, were utilized in order to avoid structural reorganization. Their data are seen to be coincident with the same straight line. The somewhat larger variation in the crystallite thickness than is usually observed has been attributed by the investigators to the deliberate nonisothermal crystallization procedures that were adopted at the high temperatures.[16] It is clear that within the uncertainty of the crystallite size determination these directly observed melting temperatures are virtually identical with the critical temperatures determined from annealing experiments. They yield the same value for $T_m{}^0$ and σ_{ee} and confirm the conclusions that have been made above.

Bair, Huseby, and Salovey[15,31] have attempted to determine the melting temperature of solution formed crystals by utilizing differential calorimetry at heating rates of 10°/min. However, prior to fusion, the samples were subject to very high irradiation doses. The underlying reason for this procedure is the assumption that was made[15] that lamella thickening, and other structural reorganizations, would be retarded without altering any of the thermodynamic quantities governing fusion. Their melting temperature determinations are also given in Figure 4. The solid straight line, designated B, representing these data, has been transposed from their original paper. As is indicated in the plot, the melting points determined by this procedure are from 4 to 6 deg higher for comparable values of ζ than is obtained by the other methods indicated. However, the extrapolated value obtained for $T_m{}^0$ is 145.8°.[31] The basis for the difference in the melting points appears to reside in either the method of measurement or in the introduction of the crosslinks into the highly crystalline system. It still remains to be established that at the heating rates employed structural reorganization is prevented by this procedure and furthermore that no other changes occur by virtue of the cross-linking. It is known, for example, that the enthalpy of fusion is changed by this process.[32] It is also theoretically expected that the cross-linking of a highly crystalline system should result in an elevated melting temperature.[33] In view of these possibilities we note that the data can be given another representation. This is indicated by the dashed line of Figure 4. This new straight line is approximately parallel to the one from Figure 3 and would indicate that about the same interfacial free energy is involved. However, this line extrapolates to a much higher value of $T_m{}^0$. This latter representation would thus be in accord with theoretical expectations.[33] Hence for this particular set of data it could also be argued that the cross-linking process has altered the thermodynamic properties.

The new data that have been presented here, together with the data in the literature that have been cited, substantiate the premise that the annealing phenomenon and the attendant change in properties are a consequence of fusion. There is, therefore, a very natural explanation for the changes in properties observed upon annealing. It is thus not necessary that chain units within the interior of the crystals be endowed with any extraordinary mobility. The mobility and motion of the chain units that are involved are merely a consequence of the fusion process. The concept[2,7,9,10] that a regularly structured interface is maintained during annealing is clearly not acceptable.

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(31) H. E. Bair, T. W. Huseby, and R. Salovey in "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Ed., Plenum Publishing Corp., New York, N. Y. 1968, p 31.

(32) A. M. Rijke and L. Mandelkern, *J. Polym. Sci., Part B*, in press (1969).

(33) P. J. Flory, *J. Amer. Chem. Soc.*, **78**, 5222 (1956).

Dielectric Dispersion in Branched Polypropylene Oxides

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ABSTRACT: Liquid trifunctional star polymers of propylene oxide resemble the parent linear polymers in showing two distinct regions of dielectric dispersion. The principal peak occurs at the same frequency as in the linear polymer. The small secondary dispersion peak again corresponds to a parallel dipole moment component of 0.18 D per repeat unit, and its relaxation time can be predicted from the molecular weight and viscosity by means of the theoretical formulas of Ham or Zimm and Kilb.

Linear polymers of propylene oxide show two distinct regions of dielectric dispersion.[2] The principal relaxation peak is found in the same frequency region (at a given temperature and pressure) for all molecular weights;[2,3] it has been correlated[3] with mechanical[4a] and nmr[4b] relaxation data, and is due to local motions of the chain backbone. The small

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(2) M. E. Baur and W. H. Stockmayer, *J. Chem. Phys.*, **43**, 4319 (1965).

(3) G. Williams, *Trans. Faraday Soc.*, **61**, 1564 (1965).

(4) (a) B. E. Read, *Polymer*, **3**, 529 (1962); (b) T. M. Connor, D. J. Blears, and G. Allen, *Trans. Faraday Soc.*, **61**, 1097 (1965).