Thermodynamic Properties of Linear Polyethylene Crystals Formed from Dilute Solution[1a]

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ABSTRACT: The density and enthalpy of fusion of polyethylene crystals formed in dilute solutions from a variety of solvents has been determined. It was found that when compared at the same crystallite thickness, the results obtained were independent of the nature of the crystallizing solvents. Extrapolation of the data to crystallites of infinite size yield the proper thermodynamic values for the macroscopic crystals. By utilizing the general relation that has been established between crystallite thickness and the undercooling of the crystallization temperature, these data could be analyzed so as to establish the equilibrium dissolution temperature. The results are in good accord with those obtained by other methods.

Crystals formed from dilute solutions of homopolymers display a characteristic and well-established lamella-like habit whose thickness is of the order of 100 Å and whose lateral dimensions extend for several microns. Moreover, the chain axes are preferentially oriented normal to the wide faces of the lamella so that for high molecular weights a chain must traverse a crystallite many times. Quantitative kinetic studies[2,3] have demonstrated that the crystallization process in dilute solution is a nucleation controlled one. Furthermore, the crystallite thickness has also been shown to be controlled by the same nucleation process.[3,4] These deductions are made from the most general considerations of nucleation theory so that the details of the particular type of nucleus involved need not be assumed nor is it necessary to specify its molecular and interfacial structure. Conversely, unique conclusions in regard to nucleus structure are not made.

An analysis of the relation between the crystallite thickness and the crystallization temperature has shown that the interfacial free energy governing nucleation, σ_{en}, is independent of the solvent from which crystallization is occurring.[4,5] Similarly, solubility studies have shown that the interfacial energy characteristic of the mature crystallites, σ_{ec}, is also independent of the dissolution solvent.[4,5] In the present paper, we report and analyze the results of other properties of crystals formed from dilute solution. We focus particular attention on the density and enthalpy of fusion and examine how these quantities depend on the crystallization temperature and solvent medium.

Experimental Section

Two molecular weight fractions, having viscosity average molecular weights of 174,000 and 122,000, respectively, were utilized in this work. The method of fractionation and characterization has previously been described in detail.[6] The crystallite size–crystallization temperature relations have been shown to be independent of molecular weight in this range.[7,8]

The crystallizations were carried out from 0.08% solutions of toluene, *n*-octane, and *n*-hexadecane. The solvents were reagent grade and were degassed before being distilled under vacuum into a vessel containing the polymer. The vessel containing the polymer and solvent was sealed under vacuum in order to avoid contact with air during the dissolution and subsequent crystallization process. After dissolution, the sealed ampoules were immediately transferred to the crystallization thermostat which was set at a predetermined temperature. At the termination of the crystallization process, the crystals were separated from the mother liquor into the form of thin mats by slow filtration. The samples were then dried under vacuum at 50°. The crystallizations were conducted over as wide a temperature range as possible to ensure the development of a spectrum of crystallite sizes.[4]

The crystallite size, or thickness, at room temperature was determined from low-angle X-ray diffraction measurements utilizing a Rigaku-Kenki camera.[4] The well-defined maxima observed were converted to linear dimensions by means of Braggs' law. The uncertainty in the crystallite thickness is ±2 Å for sizes up to 155 Å and ±4 Å for larger sizes.

The enthalpies of fusion were determined with a Perkin-Elmer differential scanning calorimeter (DSCl-B) in a manner previously described.[7,9,10] The uncertainty in the results, based upon repetitive experiments on the same crystal preparation, was the order of ±1 cal/g. The densities were determined at 25° in a toluene–dioxane gradient column which had been calibrated with standard glass floats.[11] Five or six portions of each sample were added to the column and the density was determined after a 24-hr period. The uncertainty in the density, determined in this manner, is ±0.0005 g/cc. The absolute reliability of this method of

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[1] (a) This work was supported by a Grant from the Army Research Office (Durham); (b) to whom correspondence should be addressed.

[2] L. Mandelkern, *Polymer*, **5**, 637 (1964).

[3] C. Devoy, L. Mandelkern, and L. Bourland, *J. Polym. Sci., Part A-2*, **8**, 869 (1970).

[4] (a) J. F. Jackson and L. Mandelkern, *Macromolecules*, **1**, 546 (1968); (b) T. W. Huseby and H. E. Bair, *J. Appl. Phys.*, **39**, 4969 (1968).

[5] R. K. Sharma, J. F. Jackson, and L. Mandelkern, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **10** (2), 1327 (1969).

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

[7] L. Mandelkern, A. L. Allou, Jr., and M. R. Gopalan, *ibid.*, **72**, 309 (1968).

[8] H. E. Bair and R. Salovey, *J. Macromol. Sci., Part B*, **3**, 3 (1969).

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

[10] J. F. Jackson and L. Mandelkern in "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Ed., Plenum Publishing Co., New York, N. Y., 1968, p 1.

[11] R. K. Sharma and L. Mandelkern, *Macromolecules*, **2**, 266 (1969).

density determination has already been established.[11,12] In addition to the data obtained with the solvents listed above we also shall utilize data that we have previously reported in xylene,[4] as well as some unpublished results with this solvent, and pertinent data reported by other investigators.

Results and Discussion

Dependence on Crystallite Thickness. The density of the crystals, formed in the different solvents studied, are plotted against the reciprocal of the crystallite size (measured in terms of the number of CH_2 units) in Figure 1. The variation in the crystallite thickness is obtained by changing the isothermal crystallization temperature.[4a] For the larger crystallite sizes a single linear relation is obtained to which the data for the three different solvents adhere. For the smaller sizes, which are developed after crystallization at temperatures well removed from the equilibrium dissolution temperature (large undercoolings), deviations from the linear relation are observed. In this situation some variation in the density is obtained from the different solvents. Under these latter conditions, the crystallization rates are extremely rapid,[2,3] so that the crystallization is actually a nonisothermal process.[4a,13] Hence a distribution of crystallite sizes undoubtedly develops with the resulting uncertainty in assigning a unique size.

Restricting our considerations to the isothermal crystallization range, we note that the density is independent of the crystallizing solvents when comparison is made at the same crystallite thickness. Thus the only influence of the solvent is to relate the crystallization temperatures to a common undercooling. Hence for the same crystallite size, there is no direct solvent effect on the internal and interfacial structure. The straight line drawn through the experimental data of Figure 1 extrapolates to a density of 1.00 for $1/\zeta = 0$. This density value is in very good accord with that assigned to the unit cell.[14] We conclude, therefore, that the densities actually observed, which are less than that of the unit cell, are dependent only on the crystallite size. The postulated major contribution to the density, from defects and voids within the crystallite interior,[15,16] does not manifest itself.[17] If this type of defect were contributory then the observed extrapolation could not be made.

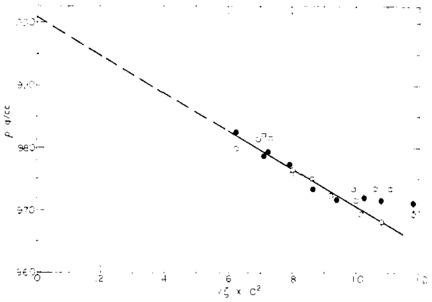

Figure 1. Plot of density as a function of the reciprocal crystallite thickness ζ, in CH_2 units, for samples crystallized from different solvents: from toluene ○; from *n*-octane, ●; from *n*-hexadecane, □; short vertical lines indicate nonisothermal crystallization.

A similar relation, for the crystallization of linear polyethylene from xylene, has been reported by Fischer and Schmidt,[19] Fischer and Hinrichsen,[20] and Blackadder and Roberts.[21] The latter investigators also determined the density as a function of the crystallization temperature in two other solvents, decalin and *n*-dodecane. They also concluded that the density was independent of the crystallizing medium. However, instead of comparing their measured densities with directly measured crystallite sizes the comparison was made through the temperature function $(T_s{}^0)^2/T_c(T_s{}^0 - T_c)$, developed from nucleation theory. Here $T_s{}^0$ is the equilibrium dissolution temperature and T_c is the crystallization temperature. To compare different solvents on this basis, the absolute value of $T_s{}^0$ is clearly a crucial quantity which must be independently established. The values that were actually chosen were much less than the acceptable values.[4a,5] Hence, although a correct conclusion was reached in this case with regard to the independence of density on the solvent, it was based on compensating errors in the assignment of $T_s{}^0$ for the different solvents.

From very general considerations, the measured enthalpy of fusion per repeating unit can be expressed as[7]

$$\frac{\Delta H^*}{1 - \lambda} = \Delta H_u - \frac{2\Delta H_e}{\zeta} + \alpha \Delta H_d \qquad (1)$$

Here, $1 - \lambda$ is the degree of crystallinity, ΔH_u is the theoretical enthalpy of fusion per repeating unit for the completely crystalline macroscopic crystal, ΔH_e is the enthalpy deficiency per sequence at the terminus of each crystalline sequence (the enthalpic contribution to the interfacial free energy), α is the fraction of units per sequence, within the interior of the crystal, which is defected, and ΔH_d is the enthalpic contribution from this effect. If the solution formed crystals possessed a regularly structured interface, exemplified by regularly folded chains, then $1 - \lambda$ must be unity. For this case a plot of ΔH^* against $1/\zeta$ should be linear. However, if the interface is amorphous, with the chain units in nonordered conformations, then $\Delta H^*/(1 - \lambda)$ should be a linear function of $1/\zeta$. Here $1 - \lambda$ could be determined from density or infrared measurements in the conventional manner.[22,23]

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(12) D. A. Blackadder and P. A. Lewell, *Polymer*, **9**, 249 (1968).

(13) H. Nagai and N. Kajikawa, *ibid.*, **9**, 177 (1968).

(14) C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

(15) P. H. Lindenmeyer, *Science*, **147**, 1256 (1965).

(16) D. A. Blackadder, *J. Macromol. Sci., Rev. Macromol. Chem.*, **1**, 297 (1967).

(17) Small changes in the lattice parameters, and unit cell densities, which are a function of the crystallization temperature, have now been reported.[18] These results, however, do not sensibly affect the conclusions drawn above.

(18) (a) G. T. Davis, R. K. Eby, and G. M. Martin, *J. Appl. Phys.*, **39**, 4973 (1968); (b) R. Kitamaru and L. Mandelkern, *J. Polym. Sci.*, in press.

(19) E. W. Fischer and G. F. Schmidt, *Angew. Chem.*, **74**, 551 (1962).

(20) E. W. Fischer and G. Hinrichsen, *Kolloid-Z. Z. Polym.*, **219**, 93 (1966).

(21) D. A. Blackadder and T. L. Roberts, *Makromol. Chem.*, **126**, 116 (1969).

(22) L. Mandelkern, *Polym. Eng. Sci.*, **1**, 232 (1967).

(23) T. Okada and L. Mandelkern, *J. Polym. Sci., Part A-2*, **5**, 239 (1967).

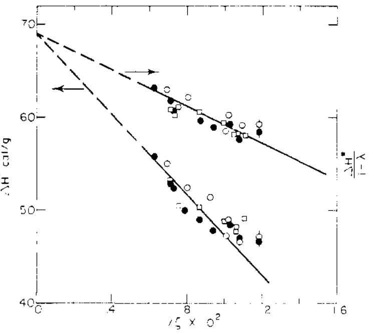

Figure 2. Plot of enthalpy of fusion ΔH^* or enthalpy of fusion divided by the degree of crystallinity as a function of the reciprocal crystallite thickness ζ for samples crystallized from different solvents: from toluene, ○; from *n*-octane, ●; from *n*-hexadecane, □; short vertical lines indicate nonisothermal crystallization.

The enthalpy of fusion data that has been obtained is plotted for both interfacial models in Figure 2 according to the suggestion of eq 1. Linear relations result for either case. As was previously reported for the crystallization from xylene,[7] from a much more restricted set of data, the functional form for either model of interfacial structure is obeyed. Hence a discrimination can not be made on this basis alone. More important, in the present context, is the fact that the enthalpy of fusion of samples crystallized from the different solvents delineate the same straight line. Hence when comparison is made at the same crystallite thickness, the enthalpy of fusion is also independent of the crystallizing solvent. For either of the models, the straight line extrapolates to $\Delta H^* = 69 \pm 1$ cal/g when $1/\zeta = 0$. This is in excellent accord with the theoretical value for ΔH_u[24] and the value deduced from studies of the melting temperature by monomeric diluents.[25] Thus no contributions from internal defects to the measured enthalpy of fusion can be detected. These contributions would manifest themselves in the term $\alpha \Delta H_d$ of eq 1.

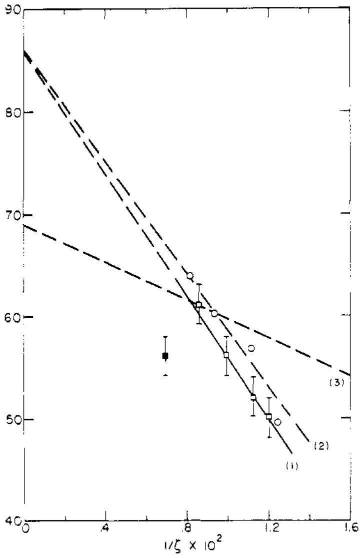

Figure 3. Plot of enthalpy of fusion ΔH^* as a function of reciprocal crystallite thickness ζ for crystallization from xylene: curve 1 (□) from ref 27a, solid rectangle for seeded sample; curve 2 (○) from ref 27b; curve 3 described in text.

From the slopes of the straight lines in Figure 2 the interfacial enthalpy is found to be 14,860 ± 400 and 6730 ± 400 cal/mol for the regularly folded and disordered interface models, respectively. These values agree favorably with those previously reported from a more limited set of data.[7] From dissolution studies, the interfacial free energy characteristic of the mature crystallites was found to be independent of solvent and equal to 3400 cal/mol.[4a,5] Thus, in the vicinity of 400°K, the interfacial entropy, ΔS_e, is 29.0 and 8.5 eu for the regularly folded and disordered interface model, respectively. From purely thermodynamic reasons, therefore, there is a finite contribution to the temperature coefficient of the interfacial free energy, σ_{ec}. Although we are dealing with a thermodynamic quantity, the interfacial enthalpy and consequently the interfacial entropy that is deduced must depend on the model chosen. A similar restriction must also hold for the analyses of specific heat measurements. Utilizing the regularly folded model, Richardson[26] has deduced a slightly lower value than is reported here for the interfacial entropy. In this analysis[26] contributions to the specific heat were assumed to come only from the ordered regions since a completely crystalline sample was tacitly assumed.

Other investigators[27] have reported substantially higher values for the measured enthalpy of fusion, determined by the same technique for similar crystallization conditions. Their results are summarized in Figure 3 as plots of ΔH^* as a function of $1/\zeta$. The data of Bair, Huseby, and Salovey[27a] is for an unfractionated linear polyethylene (Marlex 6000, type 50) crystallized from xylene. The data of Hamada, *et al.*,[27b] is for a molecular weight fraction $M = 42{,}000$.[28a] These data also follow a linear relation. However, extrapolation to $1/\zeta = 0$ leads to the inordinately high value of 86 cal/g for ΔH_u.[29] Any theoretical basis for such a high value evades explanation. It clearly cannot be attributed to defected structures, which would require an enthalpy less than that assigned to a repeating unit in the crystalline state. Further analyses of these data and a discussion of curve 3 in this figure will be given subsequently.

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

(25) F. A. Quinn, Jr., and L. Mandelkern, *ibid.*, **80**, 3178 (1958); **81**, 6355 (1959).

(26) M. J. Richardson, *Trans. Faraday Soc.*, **61**, 1876 (1965).

(27) (a) H. E. Bair, T. W. Huseby, and R. Salovey in "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Ed., Plenum Publishing Co., New York, N. Y., 1968, p 31; (b) F. Hamada, B. Wunderlich, T. Sumida, S. Hayashi, and A. Nakajima, *J. Phys. Chem.*, **72**, 178 (1968).

(28) (a) Although the crystallite thickness is not explicitly given in this work,[27b] the appropriate sizes can be obtained from the crystallization temperatures. For xylene there is virtually unanimous agreement in the published work of many investigators as to the relationship between crystallite size and crystallization temperature;[4a,27a,28b] (b) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964.

(29) Hamada, *et al.*,[27b] extrapolate their data by plotting against the specific volume of the sample. By this method, they obtain $\Delta H_u = 70$ cal/g. However, it has since been shown that their measured densities are inordinately high and incorrect.[11,12] The extrapolation presented by Bair, Huseby, and Salovey[27a] of their data, which leads to $\Delta H_u = 68 \pm 2$ cal/g, will be discussed below.

Dependence on Undercooling. Since the density and enthalpy of fusion are found to be proportional to $1/\zeta$ and since ζ is nucleation controlled[8,4a] and thus dependent on the undercooling at which the crystallization is conducted, these data can be used to delineate T_s^0. When plotted against the undercooling, ΔT, the experimental data should, therefore, extrapolate linearly to the proper limiting values of $\rho = 1.00$, or $\Delta H_u = 69 \pm 1$ cal/g for $\Delta T = 0$. Thus, by analyzing the data for a given solvent, with arbitrarily assigned value for T_s^0, the correct value can be obtained. The value for T_s^0 determined by this method can then be compared with the corresponding quantity obtained by other techniques. The results of adopting this procedure are illustrated in Figures 4, 5, and 6 for some typical density data. Figure 4 is for the crystallization from toluene. The data are analyzed for the three indicated values of T_s^0 which cover a wide range of assignments. For a given crystallization temperature, ΔT will of course be dependent on T_s^0. At the large undercoolings the densities are clearly seen to be independent of the undercooling irrespective of the assigned values of T_s^0. This is a consequence of the nonisothermal character of the crystallization in this temperature range that was previously cited. Hence there is no need for any detailed theoretical explanation for this aspect of the data.[30] However, at the lower undercoolings, within the experimentally accessible range where data can be obtained a separate linear relation is obeyed for each of the assigned values of T_s^0. Linearity alone does not, therefore, establish the correct value for T_s^0. A discrimination can only be made on the basis of the proper value for the limiting densities. A density of 1.00 is obtained for $T_s^0 = 116.9°$, agreeing with previous extrapolations of other type of data.[4,5] If T_s^0 is reduced to 114.0° the limiting density is 0.995. For T_s^0 of 110°, the limiting density of 0.992 is clearly not acceptable. A similar analysis for *n*-octane crystallization is shown in Figure 5. The nonisothermal temperature region manifests itself quite clearly again. From the value of the limiting density obtained T_s^0 can be assigned a value of 127° for this solvent.

Figure 6 represents an analysis for the crystallization from xylene. The data in this instance are taken from the recent careful work of Blackadder and Roberts.[21] In this figure, it is clear that the limiting density of 1.00 is achieved for a T_s^0 of 118.6°. The other values of T_s^0 that were examined in this figure yield values for the limiting density which are too low and unacceptable. In their original analysis, Blackadder and Roberts[21] assumed that T_s^0 in xylene was 105°. This value is clearly much too low. A T_s^0 value of 110° has been used in a very detailed analysis of a limited set of experimental data.[30] This melting temperature yields the unacceptable limiting density of 0.994 so that a reexamination of this analysis is indicated. A T_s^0 of 113.7 has also been popular for this solvent.[4b,27a] It also yields a low value for the limiting density.

The acceptable values for T_s^0, delineated in the manner described, are listed in the first column of Table I for the various solvents studied. They will be compared subsequently with the corresponding quantities determined by other methods.

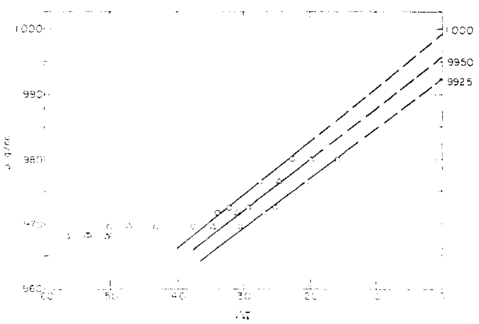

Figure 4. Plot of density as a function of undercooling, ΔT, for different values of T_s^0 for samples crystallized from toluene: $T_s^0 = 116.9°$, ○; $T_s^0 = 114°$, △; $T_s^0 = 110°$, □.

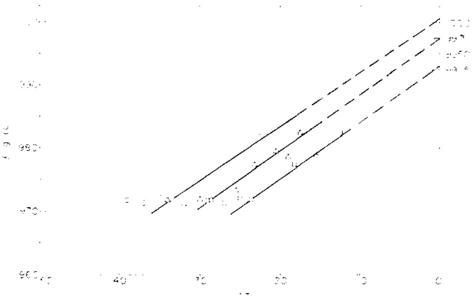

Figure 5. Plot of density as a function of undercooling, ΔT, for different values of T_s^0 for samples crystallized from *n*-octane: $T_s^0 = 127,^0$ ○; $T_s^0 = 122,°$ △; $T_s^0 = 117°$, □.

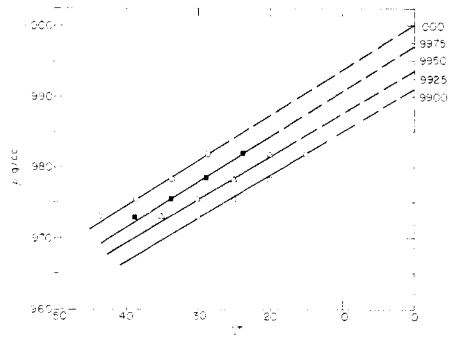

Figure 6. Plot of density as a function of undercooling, ΔT, for different values of T_s^0 for samples crystallized from xylene: $T_s^0 = 118.6°$, ○; $T_s^0 = 113.7°$, ■; $T_s^0 = 110°$, △; $T_s^0 = 105°$, □; data from ref 21.

The enthalpy of fusion data can be analyzed in a similar manner. Typical examples are shown in Figures 7 and 8 for crystallization from *n*-octane and xylene,[7] respectively. In both these plots the nonisothermal crystallization region is again easily discerned. For *n*-octane, an acceptable limiting value, $\Delta H^* = 69$ cal/g, is attained with $T_s^0 = 127°$. A T_s^0 of 122° yields 66 cal/g. For $T_s^0 = 117°$ the limiting value of 62 cal/g is very low and rules out its usage. In xylene, ΔH^* equals 70 cal/g with $T_s^0 = 118.6$; T_s^0 of 110° yields the low value of 65 cal/g. Very similar results for T_s^0 are obtained when the function $\Delta H^*/(1 - \lambda)$ is used in the analysis. The values of T_s^0, determined from the analysis of ΔH^* and $\Delta H^*/$

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(30) J. D. Hoffman, J. J. Lauritzen, Jr., E. Passaglia, G. S. Ross, L. J. Frolen, and J. J. Weeks, *Kolloid-Z. Z. Polym.*, **231**, 564 (1969).

TABLE I
THE VALUES OF T_s^0 FOR LINEAR POLYETHYLENE

Solvent	(1) Density − ΔT	(2) ΔH^* − ΔT (regular fold model)	(3) ΔH^* − ΔT disordered interface	(4) Nucleation theory[a]	(5) Nucleation theory[b]	(6) Dissolution of solution crystals[b]	(7) Dissolution of bulk crystals[c]
Decalin	114.6 ± 1[d]			113.0 ± 1.5	114.5 ± 1	116.0 ± 1	116.5 ± 2
Toluene	116.9 ± 1	116.9 ± 1	116.9 ± 1	118.6 ± 2	116.9 ± 1	116.9 ± 1	117.2 ± 2
p-Xylene	118.6 ± 1[d]	118.6 ± 1	118.6 ± 2	118.6 ± 2	118.6 ± 2	118.6 ± 2	118.6 ± 2
n-Octane	127.0 ± 1	125.6 ± 1	124.0 ± 2	127.7 ± 2	127.0 ± 1	125.6 ± 1	126.1 ± 2
n-Hexadecane	134.0 ± 2	134.0 ± 1	134.0 ± 1	133.1 ± 2	134.0 ± 1	134.6 ± 1	130.9 ± 2

[a] From ref 4. [b] From ref 5. [c] From J. F. Jackson, L. Mandelkern, and O. C. Long, *Macromolecules*, **1**, 218 (1968). [d] Data from Blackadder and Roberts.[21]

(1 − λ), are listed in the second and third columns of Table I.

This method of extrapolation, utilizing ΔT as a variable, can be examined more quantitatively since it is possible to calculate the expected slope which corresponds to the proper limiting density or enthalpy of fusion. The data presented in Figure 1 can be represented by the relation[19]

$$\rho = \rho_c - (k/\zeta) \tag{2}$$

where ρ_c, the intercept at $1/\zeta = 0$, represents the density of the macroscopic crystal. If ζ is identified with ζ^*, the critical nucleus size, then[4a, 28b]

$$\zeta = \zeta^* = KT_s^0/\Delta H_u \Delta T \tag{3}$$

Equation 3 is a very general expression which is independent of the specifics of the nucleation act. As has been demonstrated, the functional form of eq 3 is obeyed for a variety of solvents when the crystallization is conducted isothermally.[4,5] The details of the nucleation process are embodied in the interpretation of the parameter K. For the purposes at hand, however, only the magnitude of this parameter is pertinent. From the experimentally observed relation of ζ as a function of T, K can be determined for selected values of T_s^0.[4a,5] Substitution of eq 3 in eq 2 yields

$$\rho = \rho_c - \frac{k\Delta H_u \Delta T}{KT_s^0} \tag{4}$$

Hence, for a plot of ρ against ΔT the value of the slope can be predicted. Thus, a set of linear relations can be calculated and the fit of the experimental data examined.

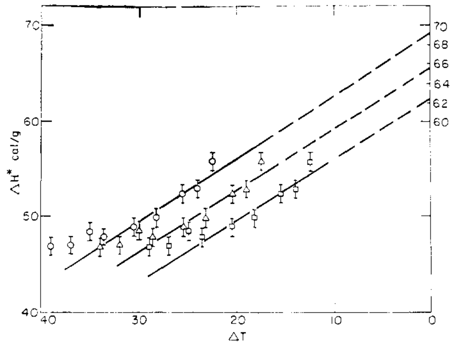

Figure 7. Plot of enthalpy of fusion, ΔH^*, as a function of undercooling, ΔT, for different values of T_s^0 for samples crystallized from *n*-octane: T_s^0 = 127°, ○; T_s^0 = 122°, △; T_s^0 = 117°, □.

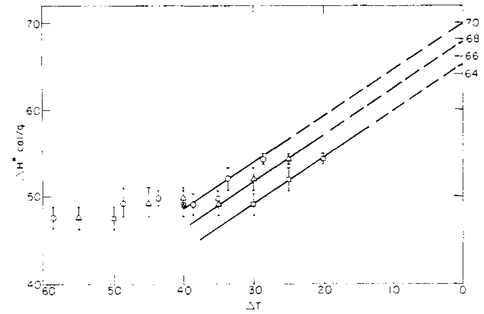

Figure 8. Plot of enthalpy of fusion ΔH^* as a function of undercooling, ΔT, for different values of T_s^0 for samples crystallized from xylene: T_s^0 = 118.6°, ○; T_s^0 = 115°, △; T_s^0 = 110°, □.

The necessary ζ-T_c data for xylene have already appeared in the literature.[4a] The necessary data for the other solvents have also been reported[5] and a detailed analysis will be given elsewhere.[31] It is important to note that for the restricted range of crystallite sizes that can be developed there is always a set of values for T_s^0 which satisfies the functional form of eq 3.

In Figure 9 the solid straight lines represent the theoretical expectation for the dependence of the density on ΔT for crystallization from toluene. Each of the lines represents a different value of T_s^0 and each extrapolates to $\rho = \rho_c = 1.00$. The plotted points represent the experimental data and the best fit is obtained for T_s^0 = 116.9°. The data do not fit as well

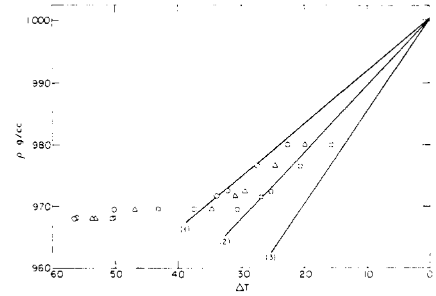

Figure 9. Plot of density as a function of undercooling, ΔT, for samples crystallized from toluene: T_s^0 = 116.9°, ○; T_s^0 = 114°, △; T_s^0 = 110°, □. Straight lines represent theoretical expectation calculated according to text. Curve 1 for T_s^0 = 116.9°; curve 2 for T_s = 114°; curve 3 for T_s^0 = 110°.

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(31) R. K. Sharma and L. Mandelkern, to be published.

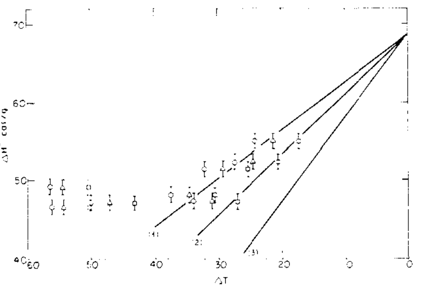

Figure 10. Plot of enthalpy of fusion ΔH^* as a function of undercooling, ΔT, for samples crystallized from toluene: $T_s^0 = 116.9°$, ○; $T_s^0 = 114°$, △, $T_s^0 = 110°$, ⊏. Straight lines represent theoretical expectation calculated according to text. Curve 1 for $T_s^0 = 116.9°$; curve 2 for $T_s^0 = 114°$; curve 3 for $T_s^0 = 110°$.

for $T_s^0 = 114$ and $T_s^0 = 110$ must be ruled out altogether. Similar results are obtained with all the solvents studied. The best value for T_s^0 in each case is the same as is listed in the first column of Table I.

The enthalpy of fusion data can be analyzed in a similar fashion. By substituting the expression for ζ from eq 3 into eq 1 there is obtained

$$\frac{\Delta H^*}{1 - \lambda} = \Delta H_u - \frac{2\Delta H_e \Delta H_u \Delta T}{K T_s^0} + \alpha \Delta H_d \qquad (5)$$

The basis for the linear extrapolation with ΔT is established by eq 5 and the slope defined by data from other experiments. A typical set of results is given in Figure 10 where ΔH^* is plotted against ΔT for crystallization from toluene. The lower values for T_s^0 are clearly ruled out and the best fit with the theoretical line is again found for $T_s^0 = 116.9°$. A similar conclusion with regard to T_s^0 is reached when $\Delta H^*/(1 - \lambda)$ is plotted against ΔT.

We have previously noted, as is illustrated in Figure 3, the reports of much larger values of ΔH^* than are reported here, for the same crystallite sizes. Bair, Huseby, and Salovey[27a] have reported that when their values of ΔH^* are plotted against ΔT, the limiting value, at $\Delta T = 0$, is 68 ± 2 cal/g. The plot in Figure 11 has been made from their tabulated data. The solid line drawn is taken from the original paper.[27a,32] We note that if the seeded sample is ignored a reasonable linear representation of the data is obtained for $T_s^0 = 110°$. From the slope of this straight line, the value of ΔH_e can be calculated from eq 5.[32b] With this value of ΔH_e and the extrapolated value of ΔH_u the expected relationship between ΔH^* and $1/\zeta$ can be reconstructed. This result is represented by the dashed line in Figure 3. It is quite obvious that this line bears no resemblance to the actual corresponding experimental data. There is, therefore, a major internal inconsistency between the extrapolated value of $\Delta H_u = 68 \pm 2$ cal/g and the observed ΔH^*-ζ relation. The reason for this is the low value for T_s^0 that was arbitrarily selected. Although this allows for an acceptable extrapolated value for ΔH_u, the shortcomings in the original data were not recognized. It is clear that the establishment of a linear relation with ΔT does not by itself offer a satisfactory and sufficient explanation of the data.

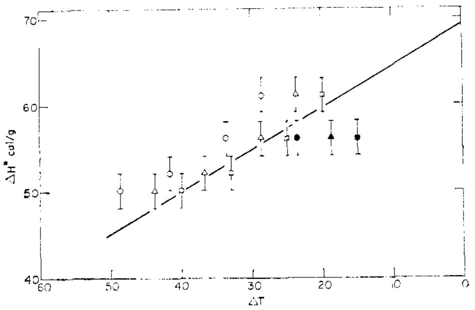

Figure 11. Plot of enthalpy of fusion ΔH^* a a function of undercooling, ΔT, for sample crystallized from xylene. Data taken from ref 27a: $T_s^0 = 118.6$, ○; $T_s^0 = 113.7$ △; $T_s^0 = 110.0$, ⊏. Solid line taken from ref 27a.

The values for T_s^0 that we have obtained in the different solvents, by the methods described above, are summarized in the first three columns of Table I. It is clear that concordant results are obtained for each solvent by the different methods. The results are also in accord with values formerly reported which were obtained by still other methods. Column 4 is a summary of T_s^0 which resulted from an analysis, according to nucleation theory, of the crystallite size–crystallization temperature data existing in the literature.[4a] Column 5 summarizes the results of a similar analysis of additional data which were obtained more recently.[5] The last two columns represent the results of the analysis of measured dissolution temperature–size relations for solution crystallized and bulk crystallized samples, respectively.[5,33] From the results for the very different types of analysis presented in Table I it becomes evident that a concordant set of values for T_s^0 has emerged. The values listed for *p*-xylene, decalin, and *n*-hexadecane have also been substantiated by quantitative studies of crystallizations kinetics from dilute solution.[3] We also note that the values for the equilibrium dissolution temperatures listed in Table I are much greater than the observed dissolution temperatures for samples crystallized in the bulk under conditions of high temperature and pressure. The reasons for these differences have already been previously discussed in great detail.[33,34]

The analysis that has been given above is a relatively simple one. It is based on the now widespread experimental base that the thermodynamic quantities are proportional to $1/\zeta$ and that ζ is proportional to the reciprocal of the undercooling. It becomes readily apparent that as long as the analysis is restricted to samples prepared under isothermal crystallization conditions and the applicability of the general aspects of nucleation theory is recognized, the introductions of further complicating features serves to no advantage at present.

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(32) (a) Although in the text of the paper[27a] it is stated that T_s^0 was taken to be 113.7°, careful comparison between their tabulated and plotted data indicates that the T_s^0 actually taken was 110°; (b) the crystallite size–crystallization temperature data that are given[27a] are the same as reported by other investigators so that the same values for K that were used sbove still apply.

(33) See Table I, footnote *c*.

(34) L. Mandelkern, M. R. Gopalan, and J. F. Jackson, *J. Polym. Sci., Part B*, **5**, 1 (1967).