Solubility of Crystalline Polymers. I. Polyethylene Fractions Crystallized in Bulk[1]

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ABSTRACT: The dissolution temperatures, or melting temperatures in very dilute solutions, of bulk crystallized molecular weight fractions of linear polyethylene have been investigated in a variety of solvents of differing thermodynamic interactions with the polymer. The samples studied, whose properties have previously been described in great detail, represent different morphologies and a range of crystallite sizes relative to the extended chain length. Analysis of the experimental data allows for the establishment of the equilibrium dissolution temperature for each solvent. This temperature represents the melting of the macroscopic perfect crystal of infinite molecular weight in the solvent. This quantity is extremely important in the analysis of the crystallization process from dilute solution. It is also shown that the interfacial free energy associated with the 001 basal plane increases with crystallite size as previously demonstrated for pure systems. The relative values are still maintained in the dissolution type experiment, irrespective of the nature of the solvent.

Recent studies of the thermodynamic,[2-4] morphological,[5] spectroscopic,[6] and mechanical properties of crystalline polymers,[5] particularly linear polyethylene, have demonstrated that there is a profound influence of molecular weight on the crystallization behavior and resulting properties. This difference in behavior has been observed in a diversity of properties[7-9] and is a reflection of the difference in the crystallite morphology that is developed. Although lamella-like crystallites are formed over the complete molecular weight range that has been studied up to now,[5,10] there are major differences in the relationship between the crystallite sizes in the chain direction and the extended chain lengths. For the lower molecular weight range the crystallite size is comparable to the extended chain length. As the molecular weight is increased beyond about 5×10^4, there is a decrease in the ratio of the crystallite size to extended chain length and this ratio becomes exceedingly small for molecular weights in the range of several hundred thousand and greater. Concomitantly, there is a significant increase in the interfacial free energy associated with the 001 basal plane,[5,11] reflecting the changing character of the molecular structure of the interfacial region. Interzonal regions, which connect crystallites, are also formed with the chain units being in random conformation. This is manifested by the decreasing level of crystallinity with increasing molecular weight.

To extend further the studies and understanding of the thermodynamic properties of crystalline polymers, it is of interest to examine their solubility temperatures or interactions with a large excess of a second monomeric component. In particular, it has been shown by Jackson, Flory, and Chiang[12] that the dissolution temperature, or melting temperature, of a very dilute solution yields interesting and useful results. When examined as a function of molecular weight, we not only have the usual variables of molecular weight and polymer–solvent interaction, but also the varying crystallite size and interfacial free energy. Furthermore, if the experiments and analysis can be carried out successfully, it is theoretically possible to arrive at the equilibrium melting temperature for a high molecular weight polymer in a dilute solution. This latter quantity, which has heretofore only been estimated, is of crucial importance in analyzing all aspects of the crystallization process from a dilute solution. In this report, therefore, we examine the dissolution temperature of molecular weight fractions of bulk crystallized polymers which encompass a wide range in crystallite size, morphology, and interfacial structure. A diversity of solvents are used which have a wide range in the intensity of their thermodynamic interactions.

Experimental Section

The crystalline samples of molecular weight fractions of linear polyethylene that were utilized in this work were for the most part identical with those previously described in great detail.[2,5] The viscosity average molecular weights, M_η, ranged from 1.6×10^3 to 5.7×10^5. The crystallization procedures that were used to prepare the crystalline specimens have also been described in detail.[2,5] In essence the crystallization was conducted isothermally *in vacuo* for periods of between 20 and 40 days. At the end of the predetermined crystallization time the samples were cooled to room temperature over a 24-hr period. The isothermal crystallizations from the melt were conducted at 130° except for molecular weights less than 12,500 where the crystallization kinetics necessitated the use of slightly lower temperatures.[2] Crystallization at these elevated temperatures for long periods of time is most conducive to producing the highest level of

(1) This work was supported by the Air Force Materials Laboratory for the Systems Engineering Group under Contract No. AF33(615)-3811.

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

(3) L. Mandelkern, J. G. Fatou, R. Denison, and J. Justin, *J. Polym. Sci., Part B*, **3**, 803 (1965).

(4) L. Mandelkern, A. L. Allou, Jr., and M. Gopalan, *J. Phys. Chem.*, **72**, 309 (1968).

(5) L. Mandelkern, J. M. Price, M. Gopalan, and J. G. Fatou, *J. Polym. Sci., Part A*, **2**, 4385 (1966).

(6) T. Okada and L. Mandelkern, *ibid., Part A*, **5**, 239 (1967).

(7) L. Mandelkern, *ibid., Part C*, **15**, 129 (1966).

(8) L. Mandelkern, *ibid., Part C*, **18**, 51 (1967).

(9) L. Mandelkern, *Polym. Sci. Eng.*, **7**, 232 (1967).

(10) F. R. Anderson, *J. Appl. Phys.*, **35**, 64 (1964).

(11) J. M. Schultz, W. H. Robinson, and G. M. Pound, *J. Polym. Sci., Part A-2*, **5**, 511 (1967).

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

TABLE I
MELT DISSOLUTION TEMPERATURES OF WELL-CRYSTALLIZED POLYETHYLENE FRACTIONS IN VARIOUS SOLVENTS

M_η	Toluene	Decalin	Xylene	Tetralin	*n*-Octane	*n*-C_{16}	Bi-phenyl	Diphenyl ether	Dodeca-nol	Bulk[a]
1,600	92.0	94.3	92.6	98.6	99.2	106.7	...	...	...	126.0
2,500	98.6	95.7	98.6	107.2	111.1	114.0	...	...	...	131.3
3,200	...	...	101.8	106.9	114.2	120.6	118.2	122.4	126.9	133.0
5,600	...	...	106.5	108.0	...	120.9	...	...	...	134.5
6,000	105.2	105.2	106.7	110.2	116.0	121.5	...	...	...	135.1
7,000	109.2	106.2	108.0	116.0	120.5	122.1	...	...	...	136.0
12,500	107.8	107.3	109.3	111.8	117.1	123.0	121.5	124.2	129.2	136.2
38,000	...	...	108.9	110.7	117.5	123.0	121.5	124.2	...	137.0
47,000	107.8	108.4	108.7	110.7	117.1	122.5	121.5	124.2	129.2	137.2
56,000	108.9	108.4	109.5	112.2	117.9	123.5	120.0	125.2	129.8	137.2
200,000	108.9	109.2	110.4	114.0	118.8	124.6	123.5	125.2	129.8	137.5
301,000	108.9	109.2	110.0	113.1	118.8	124.4	123.5	125.8	129.8	138.0
570,000	108.9	109.2	110.4	112.2	120.4	124.4	123.5	125.2	129.8	139.0
High pressure–high temperature[b]	109.9	108.7	111.1	112.6	119.2	123.3		122.0		
High pressure–high temperature[c]	109.5 ± 0.5		110.9 ± 0.5	112.2 ± 0.5						138.7

[a] From ref 2, 5, and 14. [b] From ref 15. [c] From ref 16.

crystallinity attainable and the largest size crystals.[2,7,9] The range and average values of the crystallite sizes in the chain direction have been previously determined by electron microscope examination of replicas of fracture surfaces.[5] The solvents used in this study were 85–90% *p*-xylene distilled over sodium, and reagent grade toluene, tetralin, decalin, *n*-octane, *n*-hexadecane, biphenyl, diphenyl ether, and *n*-dodecanol, which were used as received.

In order to measure the dissolution temperature, T_s, appropriate amounts of diluent and polymer were placed in 25-ml tubes so that the final polymer concentration was less than 0.1%. N-Phenyl-β-naphthylamine was added as an antioxidant and the glass-stoppered tube was placed in a thermostated oil bath at a temperature below the expected dissolution temperature. The temperature was then raised at rates which varied between 0.5°/3 hr and 0.5°/day with intermittant shaking of the tubes. The dissolution temperature was taken as that temperature where the last remnants of polymer were observed to disappear visually. The dissolution temperature was sharply defined, allowing its determination for individual samples to within ±0.2°. Successive samples showed a somewhat wider deviation of about ±0.5°. For samples having $M_\eta < 10^4$ the error was somewhat greater. The dissolution temperature was found to be independent of heating rate, within the range specified, and the results with respect to heating rate were reproducible to within ±0.5°. Except for the very poor solvents, biphenyl, diphenyl ether, and *n*-dodecanol, the polymer samples dissolved completely at the dissolution temperature. For the latter three poor solvents a two-phase liquid system developed at a well-defined temperature characteristic of each solvent. This temperature was taken as T_s since it represents fusion and dissolution. Upon further heating one homogeneous liquid phase was formed. These solvents are known to yield liquid–liquid type of phase separation with linear polyethylene.[13]

The procedures utilized here, to determine the dissolution temperature, were found to give results identical with the experimental method described by Jackson, Flory, and Chiang.[12] In this latter method, small chips of well-crystallized polymer were placed in tubes of solvent at different temperatures near the expected dissolution temperature and left under these conditions for a period of about 1 day. Samples kept above a well-defined temperature dissolved completely (or formed two liquid phases) while samples below this temperature remained essentially unaltered in appearance. This temperature was taken as the melt dissolution temperature and agreed very well with the temperature determined by the method described above.

Results and Discussion

The melt dissolution temperatures for the different molecular weight fractions in the various solvents are summarized in Table I. For the relatively good solvents T_s increases in the order toluene, decalin, xylene, tetralin, *n*-octane, and *n*-hexadecane, and for the highest molecular weight fraction studied ranges from 108.9 to 124.4°. The dissolution temperatures for the three poor solvents are generally higher. Jackson, Flory, and Chiang[12] found that a molecular weight fraction of 50,000, crystallized at 131° in a manner similar to that employed here, had a solubility temperature of 110° in tetralin. This stands in good agreement with the comparable samples listed in Table I. Also given in the table are the melting temperatures of the pure (undiluted) samples as determined by dilatometric techniques.[2,5,14] The dissolution temperature data reported by Nakajima, Hamada, Hayoshi, and Sumita[15] and by Wunderlich and Cormier[16] for crystals formed under conditions of extremely high pressure and high temperature[17] are also listed for subsequent discussion.

In order to analyze the dissolution temperature data, particularly its dependence on crystallite size, molecular weight, and thermodynamic nature of the solvent, we consider as a starting point the statistical thermodynamic analysis of fusion as formulated by Flory[18] since the dissolution temperature is the melting temperature

(13) A. Nakajima, H. Fujiwara, and F. Hamada, *J. Polym. Sci., Part A-2*, **4**, 507 (1966).

(14) M. R. Gopalan and L. Mandelkern, unpublished results.

(15) A. Nakajima, F. Hamada, S. Hayoshi, and T. Sumita, paper presented at IUPAC Meeting, Tokyo-Kyoto, Japan, 1966.

(16) B. Wunderlich and C. M. Cormier, *J. Phys. Chem.*, **70**, 1844 (1966); C. M. Cormier and B. Wunderlich, *J. Polym. Sci., Part A-2*, **4**, 666 (1966).

(17) B. Wunderlich and T. Arakawa, *ibid., Part A-2*, **2**, 3694 (1964).

(18) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

in a very dilute solution. Accordingly, the free energy of fusion of a crystallite ζ repeating units in length can be expressed as[18] eq 1. Here Δf_u is the free energy of

$$\frac{\Delta F}{xN(1-\lambda)} = \Delta f_u + RT\left\{\left[\left(\frac{1}{x_1}\right)\left(\frac{1-v_2}{v_2}\right)+\frac{1}{x}\right]\times \ln\left[1-v_2(1-\lambda)\right] + \frac{1}{\zeta}\left[\ln v_2 + \frac{2\sigma_{ec}}{RT} + \ln\left(\frac{x-\zeta+1}{x}\right)\right] + \frac{\chi_1}{x_1}\frac{(1-v_2)^2}{(1-v_2+v_2\lambda)}\right\} \quad (1)$$

fusion per repeating unit in a pure crystal of infinite size, x_1 is the ratio of the molar volume of the solvent to that of the repeating unit, λ is the fraction of the polymer that is noncrystalline, x is the degree of polymerization, N is the number of polymer molecules in the system, and χ_1 is the thermodynamic interaction parameter for the polymer–solvent system and σ_{ec} is the excess free energy or interfacial free energy per crystalline sequence at the junction of the crystalline and noncrystalline regions for the actual crystallite that is present. The physical interpretation of the quantities appearing in eq 1 have already been given.[18] This equation represents both the fusion of the crystalline polymer and its ultimate dissolution or mixing with the monomeric solvent. Equation 1 is predicated on the assumption that the melt is composed of one liquid phase with a uniform distribution of polymer segments. Hence in the form given it would not be applicable to the situations described above where two immiscible liquid phases are formed upon melting.

We require the melting temperature of a nonequilibrium crystallite of size ζ characterized by the interfacial free energy σ_{ec}. This quantity is obtained[18,19] by setting $(\partial\Delta F_f/\partial\lambda)_\zeta = 0$ and letting $\lambda \rightarrow 1$ in the resulting expression. It is then found that

$$T_m^\circ - T_s = \Delta T_s = \frac{RT_m^\circ T_s}{\Delta H_u}\times \left\{\frac{2\sigma_{ec}}{RT_s\zeta} - \frac{1}{\zeta}\ln\left(\frac{x-\zeta+1}{x}\right) + \frac{v_2}{x} - \frac{1}{\zeta}\ln v_2 + \frac{1}{x_1}(v_1 - \chi_1 v_1^2)\right\} \quad (2)$$

where T_m° is the equilibrium melting temperature of a pure infinite size crystal, T_s the dissolution temperature for the system described. The usual approximation of $\Delta f_u(T_s) = [\Delta H_u(T_m^\circ - T_s)]/T_m^\circ$ has been made, where ΔH_u is the enthalpy of fusion per repeating unit of the infinite chain crystal. In the absence of diluent, when $v_2 \rightarrow 1$, eq 2 becomes

$$T_m^\circ - T_m = \Delta T_m = \frac{RT_m^\circ T_m}{\Delta H_u}\times \left\{\frac{2\sigma_{ec}}{RT_m\zeta} - \frac{1}{\zeta}\ln\left(\frac{x-\zeta+1}{x}\right) + \frac{1}{x}\right\} \quad (3)$$

which is the equation utilized previously[5,7] in the analysis of the melting temperature–crystallite size relations. For the crystallites under consideration, T_m°, the undiluted equilibrium melting temperature, can be eliminated from eq 2 and 3 with the result that

$$T_m - T_s = \Delta T_{ms} = \left(\frac{R\zeta T_m T_s}{\zeta\Delta H_u - 2\sigma_{ec}}\right)\times \left\{\frac{1}{x_1}(v_1 - \chi_1 v_1^2) + \frac{(v_2-1)}{x} - \frac{1}{\zeta}\ln v_2\right\} \quad (4)$$

Equation 4 is based on the inherent assumption that in the dissolution experiments the interfacial free energy of the crystal is independent of the concentration and nature of the solvent species.

For the pure polymer σ_{ec} is known to vary from about 2000 to 8000 cal/mol of sequences depending on molecular weight and crystallite size.[5,11] Correspondingly ζ varies from 10^2 to 10^3 repeating units. Since for polyethylene ΔH_u is approximately 10^3 cal/mol of units the term $2\sigma_{ec}$ will be very much less than $\zeta\Delta H_u$ in eq 4. Therefore, when $v_1 \rightarrow 1$, eq 4 can be written to a very good approximation as

$$\frac{\Delta T_{ms}}{T_m T_s} = \frac{T_m - T_s}{T_m T_s} \approxeq \frac{R}{\Delta H_u}\times \left\{\frac{1}{x_1}(1-\chi_1) - \frac{1}{x} - \frac{1}{\zeta}\ln v_2\right\} \quad (5)$$

Equation 5 thus allows for a direct analysis of the effect of diluent on the dissolution temperature, without requiring the equilibrium melting point of the pure crystal, provided that the interfacial energies are the same.

The experimental results are plotted according to the suggestion of eq 5 in Figure 1. The melting points are taken from Table I and the average crystallite sizes from the work previously cited. The size of the very low molecular weights is taken to be near that of the extended chain length.[5,10] The data can be well represented by a series of straight lines. The line drawn for each of the diluents represents a least-squares analysis. According to eq 5 the intercept of each straight line for the systems which form one liquid phase is equal to $(R/\Delta H_u)(1/x_1)(1-\chi_1)$ and the slope can be identified with $(R/\Delta H_u)\ln v_2$. In Table II the values thus obtained for the quantity $(1/x_1)(1-\chi_1)$ for each of the diluents are given. These values are to be compared with those listed in the second column of the table which were

TABLE II
VALUES OF T_s° AND $(1/x_1)(1-\chi_1)$ DEDUCED FROM DISSOLUTION TEMPERATURE

Solvent	$(1/x_1)\times(1-\chi_1)^a$	$(1/x_1)\times(1-\chi_1)^b$	T_s°, °C[c]
Decalin	8.59×10^{-2}	9.72×10^{-2}	116.5
Toluene	8.40	8.44	117.2
Xylene	8.03	8.08	118.6
Tetralin	7.47	7.84	120.1
n-Octane	5.63	6.34	126.1
n-Hexadecane	4.17	4.93	130.9
Biphenyl	4.25	5.67, 4.85	129.8
Diphenyl ether	3.07	4.28, 4.24	132.1
Dodecanol	1.56	3.69	137.6

[a] Calculated from plot of Figure 1 and eq 5. [b] From ref 13, 15, and 20. [c] Calculated from eq 6 and 7 with T_m° = 145.5 ± 1°.

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

obtained by Nakajima, *et al.*[13,15,20] In this latter work the quantity $(1/x_1)(1 - \chi_1)$ was determined from the conventional analysis[21] of the melting point depression of the polymer as a function of diluent concentration. In this latter analysis major attention is given to the more concentrated polymer-diluent mixtures.[21] The agreement for the two sets of values of $(1 - \chi_1)$ obtained by the different type of experiment and mode of analysis is very good. This consistency lends support to the assumption made above that the interfacial free energy of crystallites initially formed in the bulk is independent of the nature and the concentration of the solvent.

With the establishment of the values of $(1/x_1)(1 - \chi_1)$ the equilibrium dissolution temperature for a high molecular weight perfect crystal can be calculated from the relation[18]

$$\frac{1}{T_m^\circ} - \frac{1}{T_s^\circ} = -\left(\frac{R}{\Delta H_u}\right)\left(\frac{1}{x_1}\right)(v_1 - \chi_1 v_1^2) \quad (6)$$

which for a very dilute solution, $v_1 \to 1$, reduces to

$$\frac{1}{T_m^\circ} - \frac{1}{T_s^\circ} = -\left(\frac{R}{\Delta H_u}\right)\left(\frac{1}{x_1}\right)(1 - \chi_1) \quad (7)$$

In order to calculate T_s° the appropriate value for T_m° must be known. Based on the theoretical analyses of the fusion of monomeric normal hydrocarbons[22] and the experimental results for the dependence of the melting temperature of linear polyethylene on the crystallization and molecular weight,[19] we have taken T_m° to be 145.5 ± 1°. The values of T_s°, calculated from eq 7, are also listed in Table II. The uncertainty of the extrapolated values for T_s° lies within the same range as the uncertainty in the theoretical value for T_m°.

From the slopes of the straight lines in Figure 1, the average value of v_2 is 0.025 for the good solvents. This quantity would not be expected to be identical with the nominal concentration in very dilute solution because of the nonuniformity of the polymer segment-solvent distribution. A very similar value for this effective volume fraction has been deduced from crystallization kinetic studies of dilute polyethylene solutions.[23] In addition, this value is the same order of magnitude as the limiting volume fraction of polymer for forming infinite networks in poly(vinyl alcohol)–water networks.[24]

For those binary systems which form two immiscible liquid phases upon melting, the analysis has to be slightly modified. According to the phase rule, the melting temperature must become invariant with concentration under these circumstances. Several examples of this phenomenon have already been reported in the literature.[13,25–27] Thus, above some critical

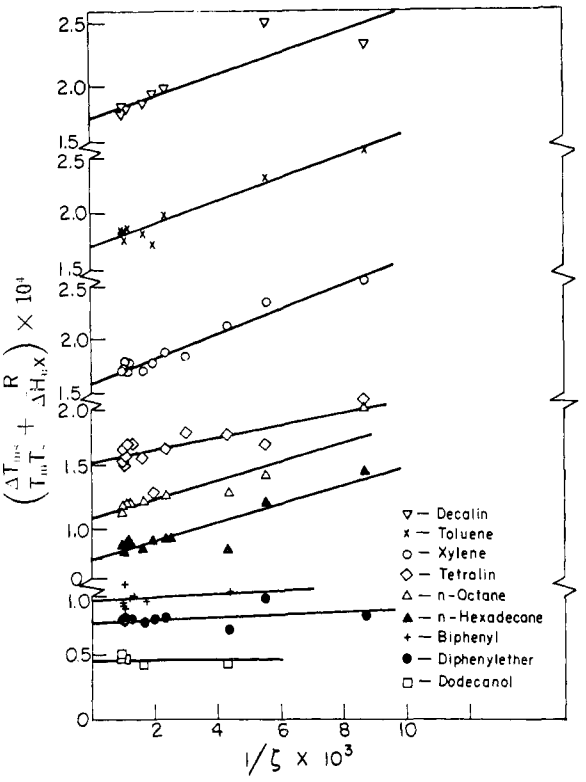

Figure 1. Plot of quantity $(\Delta T_{ms}/T_m T_s) + (R/\Delta H_u x)$ against $1/\zeta$ for indicated solvents.

concentration v_2^*, the melt is homogeneous and eq 2–5 apply. Below this concentration the melting temperature is invariant and characterized by the value at v_2^*. Therefore, at all concentrations below v_2^*, the melting temperature or dissolution temperature is given by eq 2 with $v_2 = v_2^*$. Accordingly, eq 4 with $2\sigma_{ec} \ll \zeta \Delta H_u$ can be rewritten as

$$\frac{\Delta T_{ms}}{T_m T_s} = \frac{T_m - T_s}{T_m T_s} \cong \frac{R}{\Delta H_u} \times \left\{\frac{1}{x_1}[v_1^* - \chi_1 (v_1^*)^2] + \frac{(v_2^* - 1)}{x} - \frac{1}{\zeta} \ln v_2^*\right\} \quad (8)$$

Thus in order to interpret the intercept and slope of the plots in Figure 1 for the three liquids in question, the values for v_2^* need to be independently known. These data are available from the phase diagram studies of Nakajima, Fujiwara, and Hamada.[13] The appropriate volume fractions found by direct experimental determination are 0.095, 0.25, and 0.21 for biphenyl, diphenyl ether, and dodecanol, respectively. The values for $(1/x_1)(1 - \chi_1)$ calculated in this manner for the immiscible systems are also given in Table II. The agreement with the results of Nakajima, *et al.*,[13,15,20] is not quite as good as with the other solvents and can be attributed to a much greater experimental uncertainty in both types of experiments for the immiscible systems. The dissolution temperatures listed in the table for these three liquids represent the invariant melting temperature and are calculated from eq 6 with $v_1 = v_1^*$. The values for v_2, calculated from the slopes of the straight line in Figure 1, range from 0.46 to 0.61. These higher apparent volume fractions are to be expected for the

(20) A. Nakajima and F. Hamada, paper presented at the 14th Symposium of Polymer Science in Kyoto, Japan, Oct 5–7, 1965.
(21) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.
(22) P. J. Flory and A. Vrij, *J. Amer. Chem. Soc.*, **85**, 3548 (1963).
(23) L. Mandelkern, *Polymer*, **5**, 637 (1964).
(24) J. F. Jackson and S. J. Gill, *J. Polym. Sci., Part A-2*, **4**, 663 (1967).
(25) A. M. Bueche, *J. Amer. Chem. Soc.*, **74**, 65 (1952).
(26) P. J. Flory, L. Mandelkern, and H. K. Hall, *ibid.*, 73, 2532 (1951).
(27) R. B. Richards, *Trans. Faraday Soc.*, **42**, 10 (1946).

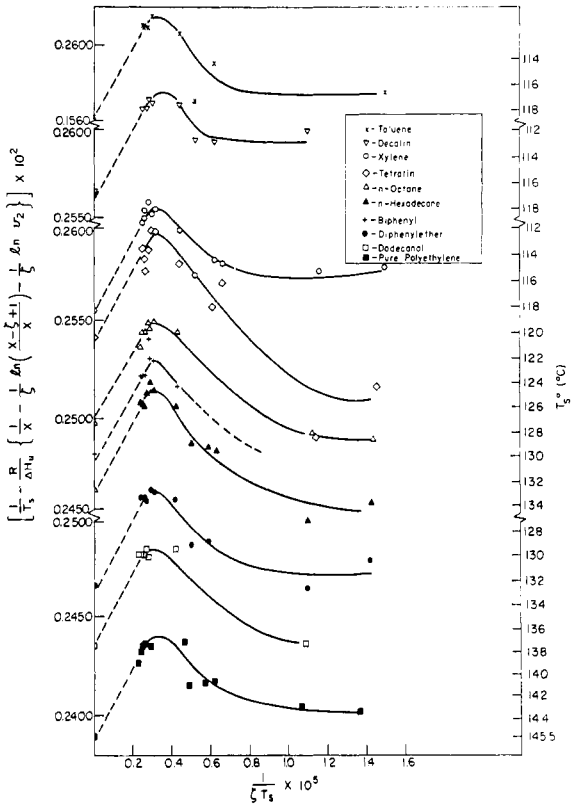

Figure 2. Plot of quantity $(1/T_s) - (R/\Delta H_u)\{(1/x) - (1/\zeta)\ln[(x - \zeta + 1)/x] - (1/\zeta)\ln v_2\}$ against $(1/\zeta T_s)$. The right-hand ordinate gives values of T_s° corresponding to the values extrapolated to the point where the abscissa is zero.

thermodynamically poorer solvents with the greater interpenetrations of solute molecules.

By eliminating T_m° between eq 6 and 2 there is obtained

$$\frac{1}{T_s} - \frac{1}{T_s^\circ} = \frac{2\sigma_{ec}}{\Delta H_u}\left(\frac{1}{\zeta T_s}\right) - \frac{R}{\Delta H_u \zeta}\ln\left(\frac{x - \zeta + 1}{x}\right) + \frac{R v_2}{x \Delta H_u} - \frac{R}{\zeta \Delta H_u}\ln v_2 \quad (9)$$

which for x of the order 3×10^4 and greater reduces to

$$\frac{1}{T_s} - \frac{1}{T_s^\circ} = \frac{2\sigma_{ec}}{\Delta H_u}\left(\frac{1}{\zeta T_s}\right) - \frac{R}{\zeta \Delta H_u}\ln v_2 \quad (10)$$

Accordingly, the quantity

$$\frac{1}{T_s} - \frac{R}{\Delta H_u}\left\{\frac{v_2}{x} - \frac{1}{\zeta}\ln\left(\frac{x - \zeta + 1}{x}\right) - \frac{1}{\zeta}\ln v_2\right\}$$

is plotted against $1/\zeta T_s$ in Figure 2. The average value of $\ln v_2$ previously obtained is used to construct the plots for the good and the poor solvents, respectively. Also given in this figure are the data for the melting of the pure system, with T_s being replaced by T_m in this instance. If we first examine the data for the high molecular weights ($M \geq 56{,}000$) for the bulk system, it becomes very clear that because of the limited range of the crystallite sizes that are presently available a legitimate *a priori* extrapolation to T_m° cannot be made. However, as the dashed straight line in the figure indicates, the data are consistent with a value for T_m° of 145.5, but clearly cannot be used as an experimental verification of this quantity. The plot for the melting of the pure system does demonstrate rather succinctly the essential constancy of σ_{ec} for the high molecular weight samples, irrespective of the exact value assigned to T_m°. For $T_m^\circ = 145.5$ the value of σ_{ec} is found to be 8730 cal/mol of chains from the slope of the straight line drawn through the data. As the molecular weight decreases below 38,000, however, the interfacial free energy decreases with decreasing molecular weight as is manifest in the nature of the curve delineated. For a molecular weight, $M = 3200$, the interfacial free energy has been reduced to 2300 cal/mol of chains. These values for the interfacial free energy are virtually identical with those previously deduced from a point by point analysis.[5,7] As can be seen from the plot, the general character of the dependence of the interfacial energy on molecular weight is not dependent on the exact value assigned to T_m°.

The character of plots for the dissolution temperatures in the various solvents is very similar to that for the pure system. The dashed straight lines that are drawn through the high molecular weight samples are parallel to one another and to the line representing the pure samples. This is again a reflection of the fact that the interfacial free energy of the crystallites is essentially independent of the nature of the solvents for samples precrystallized in the bulk. As is also indicated in the figure, the dashed line for each solvent extrapolates to a value for T_s° which is virtually identical with that listed in Table II. This is shown by including the calculated values of T_s° from Table II on the left ordinate of the figure. The determination of T_s° from Figure 2 does not involve the assignment of a value to T_m°, as do the solubility temperatures given in Table II. Values of T_s° are included on the right-hand ordinate for convenience in comparing the extrapolations. The character of the curves for the lower molecular weight samples is very similar for the dissolution-type experiments and the pure systems. Thus the solubility temperature–crystallite size relations indicate that σ_{ec} is decreasing in a similar manner independent of the nature of the diluent. We can thus conclude that the interfacial free energy for the mature crystallites is unaffected, within the experimental error of measuring solubility temperatures, by the presence of diluent for the different morphologies and relative crystallite sizes that have been developed. Thus the major effect of dilution is in altering the free energy of the liquid state. There are no interactions with the crystalline portions or any detectable unique interactions with the interfacial regions.

It is of interest to examine at this point the solubility temperatures of crystals formed in the bulk under conditions of high pressure and temperature.[17] The claim has been made[28] that the crystals formed under high pressure are extended chain crystals, with crystallite sizes of the order of 2–3 μ.[28,29] It was pointed out previously,[30] with the somewhat limited solubility data

(28) P. H. Geil, F. R. Anderson, B. Wunderlich, and T. Arakawa, *J. Polym. Sci., Part A*, **2**, 3707 (1964).
(29) J. L. Kardos, E. Baer, P. H. Geil, and J. L. Koenig, *Kolloid-Z.*, **204**, 1 (1965).
(30) L. Mandelkern, M. R. Gopalan, and J. F. Jackson, *J. Polym. Sci., Part B*, **5**, 1 (1967).

then available, that the dissolution temperatures of these high-pressure crystals were essentially the same as those of higher molecular weight samples crystallized in the conventional manner. As is indicated in Table I, this observation is given further substantiation by the dissolution data for the diversity of solvents that has now been studied. Examination of the pertinent data in the table indicates no difference, within the experimental error, for the dissolution temperatures of the two types of crystalline systems. Similar agreement is obtained when the solubility temperatures for crystalline unfractionated Marlex-50 are compared.[30]

The crystallite thickness of the higher molecular weight conventionally crystallized material is the order of 1000 CH_2 units.[5] If these facts are accepted then the only way that the identical dissolution temperatures (melting temperatures) can be explained is for σ_{ec} of the extended chain, high pressure crystals to be twenty times greater than the conventionally crystallized specimens. This conclusion is reached without the necessity of assigning a value to T_m°.[28] Such an extraordinarily high interfacial free energy for extended chain crystals is physically incomprehensible. The problem can be looked upon in another way in that the difference between T_s° as calculated and listed in Table II, and the dissolution temperature for the high-pressure crystals is about 7.5° for all the solvents studied. If it is supposed that the high-pressure crystals represent the equilibrium crystallite and that its solubility temperature can be identified with T_s°, as has been assumed,[15,16] then from eq 7 T_m° is found to be 137.2° utilizing the χ_1 value for xylene. This value of T_m° is about 8° below the theoretically calculated values[22] and that experimentally extrapolated.[19] This melting temperature corresponds to that which is conventionally observed experimentally[2,5] so that one would have to conclude that the directly measured melting temperature of a bulk polymer crystallized at atmospheric pressure represents T_m°. This conclusion is contrary to a wide array of experimental observation and theoretical analysis.[21] It becomes clear, therefore, that the concept that crystals formed under high pressure are very extended in the chain direction is in need of reexamination.

Conformations of Polyacetaldehyde Model Compounds *via* Dipole Moment Studies and Minimum Potential Energy Calculations[1]

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ABSTRACT: The monomer, dimer (*meso* and racemic) and trimer (isotactic, syndiotactic, and heterotactic) model compounds of polyacetaldehyde were prepared. Their high-resolution nmr spectra were determined and assigned. Dipole moment measurements and minimum potential energy calculations for these compounds (along with calculated dipole moments corresponding to most stable conformations) were carried out. The isotactic trimer model compound was found to have similar internal rotation angles (σ_3^t 125°, σ_4^t 315°) at the potential energy minimum to crystalline isotactic polyacetaldehyde (97.5°, 315°) where the internal rotation angles were deduced from X-ray crystallographic data. The internal rotation angles of syndiotactic (σ_3^t 230°, σ_4^t 25°) and heterotactic (σ_3^t 130°, σ_4^t 340°) trimer model compounds at their potential energy minima cannot be compared to polymeric species since high polymer structural analogs have not been prepared to date.

Since Bovey and his associates[3–5] applied nuclear magnetic resonance to the study of the stereochemistry of polymers, many polymeric systems have had their tacticity analyzed and interpreted by this technique. Model compounds of various polymers have also been examined.[6–9] Their nmr peaks have been related to peaks for respective polymeric analogs. These model compounds generally have known configurations and nmr data can provide conformational information which in turn can be related to the structure of corresponding polymer system.[6–8]

In addition to vinyl polymers, polyaldehydes have also been studied by high-resolution nmr spectros-

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(2) Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.
(3) F. A. Bovey, G. V. D. Tiers, and G. Filipovich, *J. Polym. Sci.*, **38**, 73 (1959).
(4) F. A. Bovey and G. V. D. Tiers, *ibid.*, **44**, 173 (1960).
(5) F. A. Bovey and G. V. D. Tiers, *Fortschr. Hochpolym. Forsch.*, **3**, 139 (1963).
(6) S. Fujiwara, Y. Fujiwara, K. Fujii, and T. Fukuroi, *J. Mol. Spectrosc.*, **19**, 294 (1966).
(7) (a) T. Shimanouchi, M. Tasumi, and Y. Abe, *Makromol. Chem.*, **86**, 43 (1965); (b) Y. Abe, M. Tasumi, T. Shimanouchi, S, Satoh, and R. Chujo, *J. Polym. Sci., Part A-1*, **4**, 1413 (1966); (c) D. Doskocilova, *ibid., Part B-2*, 421 (1964).
(8) (a) F. A. Bovey, F. P. Hood, III, E. W. Anderson, and L. C. Snyder, *J. Amer. Chem. Soc.*, **42**, 3900 (1965); (b) D. Doskocilova and B. Schneider, *J. Polym. Sci., Part B-3*, 209 (1965).
(9) M. Murano and R. Yamadera, *ibid.*, **5**, 483 (1967).