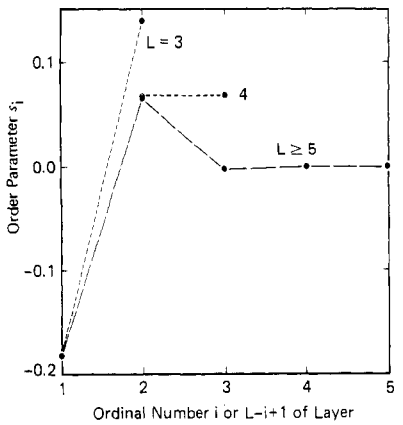

Figure 2. Order parameters for chain segments in successive layers of polymer melts between two hard walls, calculated for the layer thicknesses L indicated, with $\sigma = 0.6$ and $\eta = 0.01$.

Hence, their theory is not suitable for cases that involve significant changes in chain flux, or chain orientation, across the interphase. For polymer melts bounded by a hard wall, the degree of chain orientation in the interphase is not large and, hence, the difference between the predictions of the two theories is minor.

Polymer Melts in Thin Layers

For polymer melts in thin layers between two hard walls, or in thin films, the final layers as well as the initial layer has no vertical connections toward the exterior; that is, $p_{L+1} = 0$ and $u_{L+} = 0$ and, in addition, $p_1 = 0$ and $u_{1-} = 0$, as in the preceding section. The computational modifications required to include the former conditions in conjuction with eq 5 have been discussed above.

The results obtained with the lattice parameters $\sigma = 0.6$ and $\eta = 0.01$ are shown in Figure 2. Again, the interphase characteristics are symmetric with respect to the central layer. For $L \geq 4$ layers, the results are virtually unaffected by the inclusion of the second surface. For $L = 3$ layers, the only perturbation is a somewhat stronger preference of chain sequences in the second (central) layer for orientation normal to the surface. Hence, in practically all cases the interfacial characteristics of polymer melts in layers that are thin (but not monomolecular) are little dependent on the layer thickness.

References and Notes

(1) Flory, P. J.; Yoon, D. Y.; Dill, K. A. *Macromolecules*, preceding paper in this issue.
(2) Basset, D. C.; Hodge, A. M. *Proc. R. Soc. London, Ser. A* **1981**, *377*, 25.
(3) Voigt-Martin, I. G.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1769. Stack, G. M.; Mandelkern, L.; Voigt-Martin, I. G. *Macromolecules* **1984**, *17*, 321.
(4) Mandelkern, L. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 454; *Progr. Polym. Sci.* **1970**, *2*, 165.
(5) Sadler, D. M. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 106.
(6) Yoon, D. Y.; Flory, P. J. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 288.
(7) Weber, T.; Helfand, E. *Macromolecules* **1976**, *9*, 311. Helfand, E. *Ibid.* **1976**, *9*, 307.
(8) We have connected the points in Figure 1 by straight lines without attempting to fit them by smooth curves. The lattice model applies strictly to integral values of the abscissa only. The order parameter obviously is a continuous function of location in the interphase, and the results of the lattice theory may be presumed to approximate that function.

Equilibrium Melting Temperature of Long-Chain Molecules†

Leo Mandelkern* and Gary M. Stack

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306. *Received September 19, 1983*

ABSTRACT: Both the theoretical and experimental basis for determining the equilibrium melting temperature of chain molecules is discussed. Two distinctly different molecular situations need to be clearly distinguished in order to carry out the proper analysis. One of these is based on the melting of oligomers wherein molecular crystals are formed. For this situation the original Flory–Vrij analysis is shown to be correct. The modifications that have been proposed to this theory are critically reviewed. However, for real polymer chains of finite length, molecular crystals cannot be formed, no matter how well fractionated the system. In this case a different analysis is required. The difficulties involved here are discussed in terms of the available experimental data for linear polyethylene and poly(ethylene oxide) fractions.

Introduction

The equilibrium melting temperature T_m° of a crystalline polymer is the melting temperature of a perfect crystal formed by infinite molecular weight chains.[1] It is a very important molecular parameter. It not only reflects the molecular and conformational characteristics of a chain but is very important in analyzing crystallization kinetics. A difference of only several degrees makes major changes in the value of the nucleation interfacial free energy that is deduced from kinetic studies,[1] which, in turn, can be very significant in establishing basic crystallization mechanisms. By definition, this important quantity cannot be determined by direct experiment. Recourse is therefore made to theory and to extrapolative procedures involving the controlled crystallization and melting of a polymeric system of finite molecular weight. A more detailed analysis of the extrapolative experimental procedures and results has been given elsewhere.[2,3] We focus our primary attention here on the theoretical analysis of the dependence of melting temperature on molecular weight. The basic theories are due to Flory[4] and to Flory and Vrij,[5] with several additional modifications being proposed.[6-8] The results of the analysis, coupled with appropriate experimental data, can then be directly applied to the determination of the equilibrium melting temperature of linear polyethylene and poly(ethylene oxide).

Discussion and Results

As a basis for the ensuing discussion we first briefly review the theory given by Flory and Vrij.[5] In this basic

† Dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday.

0024-9297/84/2217-0871$01.50/0

paper they analyzed the fusion of the n-alkanes and were able to extrapolate the data to $T_m°$. It is important to recognize that for a given n-alkane all molecules have exactly the same length so that molecular crystals are formed. In the crystal lattice the chain ends from one layer are paired with that of the adjacent one. It is clear that this condition cannot be satisfied by polymers, no matter how well fractionated.[5,9] Hence there is a limitation that must be recognized in the application of this theory to polymers of finite length, although $T_m°$ for an infinite molecular weight chain can be determined. The application of this theory to the melting of chains of finite length is therefore incorrect. Flory and Vrij pointed out[5] that although the enthalpy of fusion could sensibly be taken to simply be a linear function of chain length, the entropy of fusion must have a more complicated behavior. This situation arises because upon melting, the end-pairing characteristic of the crystalline state is disrupted. Thus the terminal segments of a molecule can be paired with any of the cn segments of another molecule, where c is a constant. An additional contribution to the entropy of melting results, which is of the form $R \ln (cn)$.

With the inclusion of this entropy term, the molar free energy of fusion of a chain of n repeating units, at a temperature T, can be expressed as

$$n\Delta G_n = n\Delta G_u(T) + \Delta G_e(T) - RT \ln n \quad (1)$$

In this equation, $\Delta G_u(T)$ represents the free energy of fusion of a repeating unit at the temperature T and $\Delta G_e(T)$ is the end-group contribution, which is assumed to be independent of n. The constant $R \ln c$ is incorporated into the ΔG_e term, which plays an analogous role to that of an interfacial free energy. The temperature dependence of the functions ΔG_u and ΔG_e is treated by expanding them in a Taylor series around the equilibrium melting temperature. The expression obtained for ΔG_u expanded to second order is

$$\Delta G_u(T) = \Delta G_u - \Delta S_u[T - T_m°] - \Delta C_p/(2T_m°)[T - T_m°]^2 \quad (2)$$

In this terminology the expressions ΔG_u and ΔS_u represent the values of these functions at $T_m°$. Defining $T = T_m° - T$ and noting that at $T_m°$, $\Delta G_u = 0$ and $\Delta S_u = \Delta H_u/T_m$, we find that eq 2 reduces to

$$\Delta G_u(T) = \Delta H_u \Delta T/T_m° - \Delta C_p(\Delta T)^2/2T_m° \quad (3)$$

Expanding ΔG_e to first order yields

$$\Delta G_e(T) = \Delta G_e - \Delta S_e[T - T_m]$$

$$\Delta G_e(T) = \Delta H_e - T\Delta S_e \quad (4)$$

These functions could obviously be expanded to as high an order as is desired and thus account for any extremes in temperature dependence. However, the first- and second-order expansions that are used here are adequate to account for any situations that have been encountered to date. Inserting these two expressions into eq 1 results in the following free energy expression:

$$n\Delta G_n = n[\Delta H_u \Delta T/T_m° - \Delta C_p(\Delta T)^2/2T_m°] + \Delta H_e - T\Delta S_e - RT \ln n \quad (5)$$

At the melting point of a given n-mer, $\Delta G_n = 0$ and T can be replaced with T_m. After these substitutions are made and eq 5 is rearranged, the relation describing the melting of a series of homologues of length n is given as[5]

$$n\Delta H_u \Delta T/R - n\Delta C_p(\Delta T)^2/2R - T_m T_m°(\ln n) = [T_m°/R](T_m \Delta S_e - \Delta H_e) \quad (6)$$

This is the equation that Flory and Vrij used to analyze the experimental melting point data that are available for the n-alkanes. The necessary parameters to perform the analysis were available. ΔH_u had been previously obtained by means of the melting point depression method,[10] and a value of 950 cal/mol was used. A good estimate of ΔC_p can be made from specific heat measurements of the n-alkanes.[11] The melting data for the n-alkanes were available in a compilation made by Broadhurst.[12] Using these parameters, one can calculate the value that the left-hand side of eq 6 has at the melting point of each n-alkane if a value of $T_m°$ is assumed. Since ΔH_u and ΔS_u are assumed to be independent of n, a plot of the left-hand side of this equation against $T_m°$ should be linear. Flory and Vrij performed these calculations using a range of $T_m°$ values. The best linearity was obtained with a $T_m°$ value of 145.5 °C. The linearity of the plot is quickly lost if the value assumed for $T_m°$ is changed only slightly. Therefore, this way of fitting the melting point data gives a very precise value for the equilibrium melting temperature. In their study, Flory and Vrij estimated the uncertainty in $T_m°$ to be ±1 °C. They also repeated these calculations by varying the values of ΔH_u and ΔC_p over ranges greater than the experimental uncertainties of these parameters. In every case, the best estimate obtained for $T_m°$ was within the reported tolerance range.

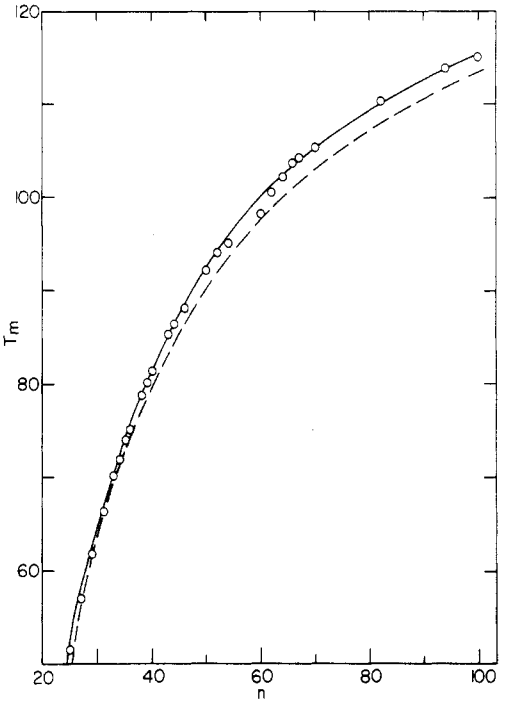

Figure 1. Melting temperatures of n-alkanes as a function of chain length. Experimental points taken from the Broadhurst compilation.[12] Solid curve calculated from the Flory–Vrij analysis.[5] Dashed curve calculated from polynomials derived by Atkinson and Richardson.[16]

In their original paper Flory and Vrij[5] did not use eq 6 and the best values for each parameter to recalculate the melting points of the individual n-alkanes. As will be seen subsequently, this procedure is an important issue in comparing their results with other works. In order to further assess the reliability of their analysis, we have performed this calculation. The results are represented by the solid line in Figure 1. The n-alkane melting temperatures from the compilation of Broadhurst are also plotted in this figure.[12] It is quite evident that the Flory–Vrij analysis gives an excellent representation of the accepted experimental melting temperatures of the n-alkanes.

Table I
Enthalpies of Fusion of *n*-Alkanes

		ΔH_n, cal/(mol of CH_2 units)					
n	ref	obsd	Flory–Vrij[a]	Flory–Vrij[b]	Δ	Richardson[c]	Δ
15	14	700	669	669	1	741	41
19	14	750	721	751	1	797	47
25	14	800	770	800	0	850	50
29	14	805	792	822	17	872	67
30	14a	795	796	826	31	879	84
43	14a	800	840	870	70	918	118
100	13	924	898	928	4	965	41

[a] Calculated assuming ΔH_u = 950 cal/mol. [b] Calculated assuming ΔH_u = 980 cal/mol. [c] Calculated from eq 9.

By expanding ΔH_u as a function of temperature, one can also obtain an expression for the enthalpies of fusion of the *n*-alkanes. Thus

$$n\Delta H_n = n\Delta H_u - \Delta C_p \Delta T + \Delta H_e \quad (7)$$

This expression was used by Flory and Vrij to calculate the enthalpies of fusion of those systems whose values had been determined experimentally. Their original results, using a value of 950 cal/mol, are listed in column four of Table I along with the corresponding experimental values. Subsequently, the enthalpy of fusion for $C_{100}H_{202}$ was measured by Hay.[13] The theoretical value for this sample has also been calculated with eq 7 and is included in Table I. In these calculations the values for each of the parameters are the same as those in the original Flory–Vrij analysis. The very good agreement that was obtained serves as a good confirmation of the choice of parameters that were made.[5] In addition, the adequacy of a temperature expansion to represent the enthalpy of fusion gives support for the use of such an expansion to represent the free energy of fusion. The temperature dependence that was used is clearly more than adequate. A value of 950 cal/mol was used by Flory and Vrij for ΔH_u. Since the initial analysis, subsequent experiments have indicated that 980 cal/mol is a better estimate of ΔH_u.[15] Therefore the enthalpies of the *n*-alkanes have been recalculated by using this value. However, this procedure will not change the equilibrium melting temperature deduced previously. These enthalpies are given in column five of Table I. They agree even closer with the experimental values, except for the hydrocarbons $C_{30}H_{62}$ and $C_{43}H_{88}$. The experimental results for these two alkanes (which are from a different study than the lower alkanes[14a]) seem questionable. They deviate from the continuous increase with chain length that is observed with the other members of the series. We conclude, therefore, that the analysis of Flory and Vrij[5] gives a quantitative explanation for the fusion of the *n*-alkane and consequently a reliable value for $T_m°$.

The first alternative extrapolation to the Flory–Vrij procedure was recently given by Wunderlich and Czornyj.[6] In this work a value of 141.5 °C was obtained for the equilibrium melting temperature of polyethylene. Since this value for $T_m°$ is significantly different from that previously deduced, we need to examine this analysis in more detail. The basic data in this analysis come from a previous calorimetic study performed by Atkinson and Richardson.[16] In this work, specific heat measurements were made on three *n*-alkanes: $C_{19}H_{40}$, $C_{23}H_{48}$, and $C_{42}H_{86}$. In these experiments, the initially crystalline *n*-alkane was heated to a temperature above its melting point. The enthalpy and entropy changes occurring during this process were calculated from the specific heat data with standard thermodynamic relations. In addition, a previously derived heat capacity equation applicable to liquid alkanes was used to calculate the enthalpy and entropy changes associated with cooling the liquid *n*-alkane from the final temperature to a supercooled liquid at the initial temperature. Combining these values, the enthalpy, entropy, and free energy changes associated with the isothermal transformation from solid to supercooled liquid at the initial temperature were calculated. Each *n*-alkane was heated from various initial temperatures below its melting point. After each experiment the free energy change associated with transforming the *n*-alkane from solid to supercooled liquid at this initial temperature was calculated. This procedure yielded the free energy changes associated with the melting of each *n*-alkane at different temperatures. For the highest molecular weight hydrocarbon studied, the experimental data extended to 70 °C. It is quite appropriate to apply Flory and Vrij's most general equation describing the free energy of melting of molecular crystals to these data. Atkinson and Richardson[16] actually fit their data to this equation. They represented ΔG_u by a third-order polynomial in temperature and ΔG_e by a second-order polynomial. The best values for their coefficients were determined by means of a multiple regression analysis. The equilibrium melting point can then be determined by calculating the temperature which makes the ΔG_u polynomial equal to zero. This method gave a value for $T_m°$ of 141.5 °C, which clearly is in disagreement with that determined by Flory and Vrij. This analysis is logically correct. It differs from that of Flory and Vrij only in the type and method of fitting of the thermodynamic data used. Therefore, to determine which of these two values of $T_m°$ is more accurate, it is necessary to compare these two analyses on the basis of how well they can reproduce the available experimental thermodynamic data for all the *n*-alkanes.

Such a comparison was made by Wunderlich and Czornyj.[6] It was concluded that the extrapolation method of Atkinson and Richardson yields a more reliable value for $T_m°$. We have found it necessary to reexamine this comparison. Substitution of Richardson's two polynomials[16] into Flory and Vrij's most general expression (eq 1) yields the following relation for the free energy of melting:

$$n\Delta G_n = n(5.2 \times 10^{-5}T^3 - 1.7 \times 10^{-2}T^2 - 8.3T + 1369) + (0.11T^2 - 17.4T - 13480) - RT \ln n \quad (8)$$

The melting point for each *n*-alkane can be calculated from this expression by determining the temperature at which the free energy becomes zero for each value of *n*. Wunderlich performed these calculations and plotted the deviation of this calculated value from the experimental melting points as a function of chain length. The deviation of the melting points predicted by the Flory–Vrij analysis was also plotted. From an examination of this plot, it would appear that for large chain lengths, greater than n = 250, Richardson's analysis does a better job of reproducing the experimental melting points. This result is the

Table II
Melting Points of n-Alkanes (°C)

n	Broadhurst	ref 17[a]	present results
50	92.2	95.0	91.7
70	105.4	108.5	105.0
94	113.9		114.3

[a] Used by Wunderlich and Czornyj[6] in their analysis.

main evidence upon which Wunderlich bases his conclusion that Richardson's analysis yields a more reliable estimate of $T_m°$. However, a careful examination of this comparison shows that for the large values of n, which serves as the basis for the conclusion, the melting temperatures of polyethylene fractions are being used. These are fractions that were isothermally crystallized and then etched by nitric acid treatment. The chain length assigned to each sample corresponds to the average crystallite thickness after etching. It is clearly invalid to include these data in an assessment of the two extrapolation procedures since they are clearly not n-alkanes. Even after etching the molecules will not be of uniform chain length. Therefore, molecular crystals, which are mandatory requirements for the analysis, are not present. The only melting data which can be legitimately used in this comparison are for the n-alkanes. In Wunderlich's comparison these consisted mainly of the melting points up to $C_{100}H_{202}$, originally compiled by Broadhurst,[12] and are the data also used by Flory and Vrij. In addition, Wunderlich included the melting temperatures for $C_{120}H_{242}$ and $C_{140}H_{282}$, which have been recently determined[17] by differential calorimetry. However, in the work where the melting points of these latter two samples were reported those for n-alkanes of shorter chain length differed from their values in Broadhurst's compilation. Thus, there is concern with respect to the absolute values of these new melting points. To help decide if the melting points of these latter two larger n-alkanes were reliable, we determined the melting temperatures of some of the n-alkanes studied in ref 17 by differential scanning calorimetry.[25] The melting points that we determined for two samples ($C_{94}H_{190}$ and $C_{70}H_{142}$) are given in Table II along with that for $C_{94}H_{190}$, which had been studied previously in this laboratory. Also included in this table are the melting points of the three samples given in the Broadhurst compilation and the corresponding values reported in ref 17. The melting temperature measured here for $C_{94}H_{190}$ is close to the original value listed in the Broadhurst compilation. This confirms that reliable melting points can be obtained for pure compounds by means of differential scanning calorimetry. The melting points obtained here for $C_{50}H_{102}$ are close to those in the Broadhurst compilation. However, the values reported by Heitz et al.[17] differ by as much as 3 °C from the values in the Broadhurst compilation. Since the melting points reported for these samples are inaccurate, we must therefore be concerned with the absolute values given for $C_{120}H_{242}$ and $C_{140}H_{282}$. These values were the ones used by Wunderlich.[6] It would appear that the only reliable melting points which can be used in evaluating n-alkane extrapolation procedures are those given in the original Broadhurst compilation.[12]

We have used Richardson's polynomial expressions to recalculate the melting points of the n-alkanes up to $C_{100}H_{202}$. This is the highest molecular weight n-alkane listed in the compilation of Broadhurst.[12] The results of this calculation are represented in Figure 1 by the dotted line. It is obvious from this figure that the Flory–Vrij analysis does a much better job of reproducing the experimental data of the n-alkanes whose melting temperatures are well established. Furthermore, the melting points predicted by Atkinson and Richardson are consistently and systematically too low. Therefore, it is not surprising that the value of $T_m°$ deduced by them will also be low.

In a further comparison between the two methods, we have calculated ΔH values for the n-alkanes from Richardsons's polynomials using the Gibbs–Helmholtz relationship

$$\Delta H_n = -T^2 \partial(\Delta G_n/T)/\partial T \tag{9}$$

The values calculated by this procedure for the n-alkanes whose enthalpies of fusion have been experimentally measured are also given in Table I. Examination of this compilation makes quite evident that the Flory–Vrij analysis also reproduces the experimental enthalpies of fusion in a much more satisfactory manner. The values calculated from Richardson's analysis are consistently higher than the experimental values. They differ by amounts significantly greater than any uncertainty in the experimental data.

It should also be pointed out that the claim[6] that the Flory–Vrij analysis does not properly take into account the temperature dependence of ΔH_u is not even pertinent to the Flory–Vrij analysis. The erroneous conclusion was based on a plot of the temperature dependence of ΔH_u calculated from Richardson's polynomial for ΔG_u. In this plot ΔH_u goes through a maximum at about 127 °C, a temperature which is well outside Richardson's experimental range. This maximum is most likely an artifact of these polynomials since at the higher temperatures, the higher power terms predominate.

The comparison given above demonstrates that the Flory–Vrij analysis is a much more quantitative representation of the fusion of the n-alkanes. Therefore, their extrapolated value of $T_m°$ must be considered to be more reliable. The problem with Richardson's analysis may be due to an inherently greater experimental error in measuring specific heat as opposed to melting temperatures. In addition, serious errors may arise from the use of polynomials in the fitting of the data. While such polynomials are known to give a good representation of calorimetric data over the actual experimental temperature range, the validity of using these polynomials at higher temperatures well beyond the experimental range is questionable. The extrapolation to obtain $T_m°$ involves extending Richardson's polynomial more than 70 °C beyond the temperature range of the data actually used in its determination.

More recently, Hay[8] has derived another equation describing the melting of molecular crystals of chain molecules. His result differs from the equation given by Flory and Vrij.[5] In order to determine the reason for these differences, it is necessary to undertake the laborious task of examining in detail each step in his analysis. Instead of the $R \ln (cn)$ term for the additional entropy of mixing of the terminal groups, Hay derived the expression

$$\Delta S_{mix} = R \ln [n(n-1)] - R \ln 2 \simeq 2R \ln n - R \ln 2 \tag{10}$$

This equation was obtained by assuming a model in which the end groups are excluded from the crystalline regions. This increase in entropy which occurs upon melting is attributed to the fact that the terminal groups can now penetrate the region previously occupied by the crystalline segments. This treatment actually is an oversimplification of the entropy changes that occur during the melting of chain molecules whose ends are excluded from the crystal lattice. The proper theoretical analysis for this model has already been given previously by Flory[4] and will be dis-

cussed in detail in a subsequent section of this work. Hay fits the melting data of the *n*-alkanes to the final equation that is derived (cf. seq). This procedure is clearly a contradiction in logic. The analysis is developed by assuming a model in which the chain ends are excluded from the crystallite. The *n*-alkanes form molecular crystals within which the chain ends are paired and clearly do not satisfy the basic requirement of the model.

Along with the conceptual error pointed out above, analytical errors are also made in the derivation. These also contribute to the differences between the final equation and that of Flory and Vrij. The quantities ΔH_u and ΔS_u are expressed as separate Taylor series expansions in temperature rather than expanding ΔG_u.[8] As will be shown below in another context, these separate expansions do not give the correct temperature dependence of the free energy of fusion. Despite this, by performing these individual expansions to first order and including the end-group contribution of eq 10, one obtains the following expressions for the enthalpy and entropy of fusion of an *n*-mer.

$$\Delta H_n = n\Delta H_u + n\Delta C_p \Delta T + 2\Delta H_e \quad (11)$$

$$\Delta S_n = n\Delta S_u + n\Delta C_p \ln (T_m°/T) + \Delta S_e + 2R \ln n \quad (12)$$

The $R \ln 2$ term is incorporated into ΔS_u, and $\ln (T_m°/T)$ is used as an approximation for $(T_m° - T)/T_m°$.

After inserting the above expressions for an *n*-mer into that for the melting temperature, defined by the relation

$$\Delta H_n - T_m \Delta S_n = 0 \quad (13)$$

one finds that[8]

$$T_m = T_m°[1 - (2RT_m° \ln n)/n\Delta H_u] + f(n) \quad (14)$$

Here, $f(n)$ is defined as

$$f(n) = (T_m°/n\Delta H_u) \times [n\Delta C_p \Delta T + 2\Delta H_e - T_m(2\Delta S_e + n\Delta C_p) \ln (T_m°/T)] \quad (15)$$

For subsequent calculations eq 14 can be recast into the form

$$1 - T_m/T_m° = (2RT_m° \ln n)/n\Delta H_u + f'(n) \quad (16)$$

where $f'(n)$ is now defined as

$$f'(n) = f(n)/T_m° \quad (17)$$

Unfortunately, eq 14 still contains an additional algebraic error. This error is best demonstrated by deriving the melting relation under the assumption, for the sake of the argument, that the entropy and enthalpy expressions of eq 11 and 12 are correct. Inserting eq 11 and 12 into eq 13 yields the expression

$$(n\Delta H_u + n\Delta C_p \Delta T + 2\Delta H_e) - T_m(n\Delta S_u + 2\Delta S_e + 2R \ln n + n\Delta C_p \ln (T_m°/T)) = 0 \quad (18)$$

Defining

$$f''(n) = n\Delta C_p \Delta T + 2\Delta H_e - T_m(2\Delta S_e + n\Delta C_p \ln (T_m°/T)) \quad (19)$$

simplifies eq 18 to

$$n\Delta H_u - T_m n\Delta S_u - 2RT_m \ln n + f''(n) = 0 \quad (20)$$

Inserting $\Delta S_u = \Delta H_u/T_m°$ results in

$$n\Delta H_u - (n\Delta H_u/T_m°)T_m - 2RT_m \ln n + f''(n) = 0 \quad (21)$$

Multiplying by $T_m°/n\Delta H_u$ and solving this equation for $T_m°$ give the melting relation

$$T_m = T_m°[1 - (2RT_m \ln n)/n\Delta H_u] + f(n) \quad (22)$$

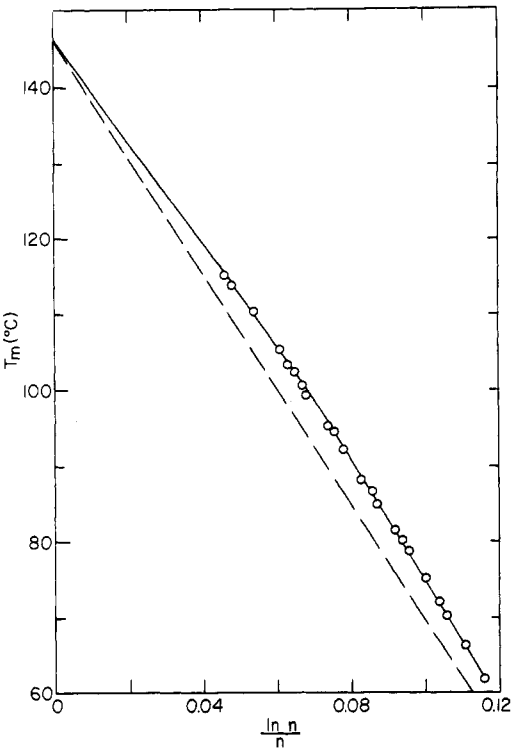

Figure 2. Melting temperatures of *n*-alkanes as a function of $(\ln n)/n$. Experimental points taken from compilation of Broadhurst.[12] Solid curve calculated from the Flory–Vrij analysis.[5] Dashed line calculated from Hay's analysis.[8]

Here, $f(n)$ has the same value as in eq 15. Comparing eq 22 and 14 makes it clear that the $(2RT_m° \ln n)/n\Delta H_u$ term in Hay's final equation should contain a factor of T_m instead of $T_m°$. It was concluded from the erroneous equation that a plot of the *n*-alkane melting points vs. $(\ln n)/n$ should be linear, and $T_m°$ can be calculated from its intercept. Clearly, replacing $T_m°$ with T_m removes and remaining theoretical basis for predicting such a plot to be linear.

We are, however, now faced with a serious dilemma for the following reason. A plot of melting temperatures against $(\ln n)/n$, which is linear, is presented for the *n*-alkanes.[8] Furthermore, from an analysis of the slope and intercept of this line by means of eq 14, values for $T_m°$ and ΔH_u of 146 °C and 940 cal/mol, respectively, are obtained.[8] Despite the errors in the derivation, the accuracy of these deduced parameters, together with the observed linearity of the plot, requires further examination. In Figure 2 the *n*-alkane melting points have been plotted as a function of $(\ln n)/n$ along with Hay's fitted line (the dashed line), which has been reproduced from his reported slope and intercept. Contrary to assertions,[8] it is clear that the straight line presented does not properly or adequately describe the melting of the *n*-alkanes. The *n*-alkane melting points could be fitted to a straight line of a similar slope, which is not shown and which has an intercept corresponding to a $T_m°$ value of about 151 °C. It is therefore clear that this analysis lacks a sound theoretical basis, has serious analytical errors, and also yields an erroneous value for $T_m°$.

The experimental *n*-alkane melting points in Figure 2 do show a linear functionality despite the fact that there is no theoretical basis to predict such behavior. To investigate this question further, the melting point curve calculated by Flory and Vrij is also plotted in this figure. Although this curve is very close to linear over the range of available experimental data, it displays significant curvature for the larger *n* values, for which no experimental

Table III
Factors Contributing to the Melting of the *n*-Alkanes

n	T_m,[a] K	$1 - T_m/T_m^\circ$[c]	term 1[b]	term 2[c]	$(2RT_m^\circ \ln n)/n\Delta H_u$[d]
11	245.6	0.4131	0.1124	0.2638	0.3816
15	280.6	0.3295	0.1064	0.1995	0.3161
19	303.1	0.2757	0.0986	0.1606	0.2713
25	325.1	0.2232	0.0879	0.1243	0.2254
31	339.7	0.1883	0.0790	0.1015	0.1939
43	357.9	0.1448	0.0657	0.0743	0.1531
60	372.3	0.1104	0.0534	0.0539	0.1195
82	382.9	0.0851	0.0432	0.0397	0.0941
94	386.7	0.0760	0.0392	0.0348	0.0846
100	388.4	0.0719	0.0376	0.0327	0.0806

[a] Calculated from the Flory–Vrij analysis. [b] First term on the right-hand side of eq 23. [c] Second term on the right-hand side of eq 23. [d] From eq 16.

melting temperatures exist. To help understand this behavior, we have rearranged Flory and Vrij's melting relation, eq 6, into a form similar to that of eq 16. This rearrangement yields the expression

$$1 - T_m/T_m^\circ = (RT_m \ln n/n\Delta H_u) + \left[\frac{T_m\Delta S_e - \Delta H_e}{n\Delta H_u}\right] + n\Delta C_p(\Delta T)^2/2\Delta H_u T_m^\circ \quad (23)$$

The values for each of the three terms on the right-hand side of eq 23 have been calculated for *n*-alkanes. The values of the first two terms, which are significantly larger than the third term, are listed in Table III for each of the *n*-alkanes. These two terms have approximately equal values over the range within which experimental data are available. The claim was made that the *n*-alkane melting data could be described by the first term on the right-hand side of eq 16.[8] This one term, which is also listed in Table III, is approximately a factor of 2 greater than either of the two terms in the Flory–Vrij equation. It is clear that this one term can approximate the observed melting points over the range of available data where the first two terms of eq 23 are approximately equal. At higher values of n, beyond the range of available data for the *n*-alkanes, Flory and Vrij's two terms are no longer equal. The observed curvature of their predicted melting points, leading to the correct value of T_m°, thus results. The apparent reliability of the parameters deduced by Hay[8] is thus a consequence of compounded errors in analysis and of coincidence.

A compilation of the experimentally extrapolated values for T_m°, derived from the melting of finite chain systems, has recently been given.[2] These values range from 138 to 146 °C. Since directly observed values of 139 °C have been obtained for an atmospherically crystallized fraction of polyethylenes,[18] the reported T_m° values of 138 °C[19,20] are clearly erroneous. The remaining reports fall into two groups, one about 141 °C and the other about 146 °C. The foregoing analysis of the fusion of the *n*-alkanes clearly favors the latter set of results.

Extrapolations have also been attempted to determine the equilibrium melting point of poly(ethylene oxide).[7,8] Buckley and Kovacs[17] performed on analysis similar to that of Flory and Vrij on low molecular weight fractions of this polymer and obtained a value for T_m° of 68.9 °C. Although extended-chain crystals are formed in this molecular weight range, these fractions are not composed of molecules having identical chain length. Thus, the cannot form molecular crystals.[5,9] Therefore, use of the Flory–Vrij analysis is clearly inappropriate and the extrapolation is incorrect. This conclusion is supported by reports of directly observed temperatures which are equal to or greater than this deduced equilibrium value. These melting points were for higher molecular weight fractions of poly(ethylene oxide) which were crystallized under isothermal conditions. They include a value of 69 °C measured dilatometrically and 72 °C obtained by differential scanning calorimetry.[22] The directly observed melting temperatures will always be less than the equilibrium value.[1]

The melting relation derived by Buckley and Kovacs is of the form[7]

$$n\Delta G_n = n(\Delta H_u + \Delta C_p\Delta T) - nT(\Delta S_u + \Delta C_p \ln (T/T_m^\circ)) - (\Delta H_e - T\Delta S_e) \quad (24)$$

This equation is algebraically quite different from that of Flory and Vrij[5] even though the same basic premises are involved. This apparent dilemma is easily resolved by noting the error made by Buckley and Kovacs[7] in their derivation. This mistake arises from the independent temperature expansion of ΔH_u and ΔS_u rather than the direct expansion of ΔG_u. Performing these independent expansions to first order yields

$$\Delta H_u(T) = \Delta H_u + \Delta C_p[T - T_m^\circ] \quad (25)$$

$$\Delta S_u(T) = \Delta S_u + \frac{\Delta C_p}{T_m^\circ}[T - T_m^\circ] \quad (26)$$

These equations were then combined by the relation

$$\Delta G_u(T) = \Delta H_u(T) - T\Delta S_u(T) \quad (27)$$

so that

$$\Delta G_u(T) = \Delta H_u(1 - (T/T_m^\circ)) + \Delta C_p(T - T_m^\circ)(1 - (T/T_m^\circ)) \quad (28)$$

to first order. Expansion of ΔG_u directly to first order, the correct procedure, yields the equation

$$\Delta G_u(T) = \Delta S_u[T_m^\circ - T] = (\Delta H_u/T_m^\circ)(T_m^\circ - T) \quad (29)$$

which is clearly different from the above result. It is clearly incorrect to perform separate expansions and then combine the results. The differences obviously come about because ΔS_u was incorrectly expanded rather than $T\Delta S_u$. If this latter term is expanded and combined with the expansion for ΔH_u, then the same result as expanding ΔG_u directly is obtained, giving the Flory–Vrij expression.[5] As we have previously noted, a similar error was made by Hay.[8]

These errors are, in turn, reflected in the value deduced for T_m°. The best estimate for the equilibrium melting temperature of poly(ethylene oxide) is obtained by the extrapolation of melting temperature–crystallization temperature plots of high molecular weight fractions. Values in the range 75–80 °C have been reported.[21-23] These are significantly greater than the deduced value.[17]

Hay has also fitted the melting point data of the low molecular weight poly(ethylene oxide) fractions to the theoretical expression that he derived (eq 14). He found that the observed melting temperatures were a linear

function of $(\ln n)/n$. Values of 76 °C for $T_m°$ and 1.88 kcal/mol for the enthalpy of fusion were obtained from analysis of the slope and intercept of this line. The result for the enthalpy of fusion is in good agreement with the accepted value of 1.98 kcal/mol. The observed linearity and the accuracy with which Hay's equation reproduces the thermodynamic parameters are noteworthy. However, because of the compounding of errors, previously noted, there is the strong suggestion that this agreement is again fortuitous. The linearity is likely due to the compensation, similar to that pointed out for the *n*-alkanes. As has been recently shown,[24] the melting point data of low molecular weight polymer fractions, where extended-chain crystals are formed, can be properly treated by using the relations derived by Flory.[4] A similar analysis will be given for the low molecular weight poly(ethylene oxide) fractions in the following section.

Up to this point, the analysis has been limited to the case where molecular crystals are formed. Although an extrapolation to within ±1 °C can be made to the melting temperature of infinite molecular weight chains, the equilibrium melting temperatures of crystals formed by chains of finite molecular weight are not accessible. This situation can be alleviated when extended-chain crystals are formed, so that a molecule can only participate in a single crystallite. Such structures have been formed by low molecular weight fractions of linear polyethylene[24] and poly(ethylene oxide).[7,8] For these cases the required experimental data for a proper analysis are in hand.

When the crystallite thickness formed are comparable to the extended-chain length, for finite-size chains, it can be assumed that the crystallites have attained their equilibrium sizes. Under the assumption that the chain ends are excluded from the crystal lattice it has been shown that[4]

$$1/T_{m,e} - 1/T_m° = R/\Delta H_u[1/x + 1/(x - \zeta_e + 1)] \quad (30)$$

$$2\sigma_e = RT_{m,e}[\zeta_e/(x - \zeta_e + 1) + \ln (x - \zeta_e + 1)/x] \quad (31)$$

Here, $T_{m,e}$ is the equilibrium melting temperature of the finite chain of x repeat units, characterized by the equilibrium length ζ_e. ΔH_u is the enthalpy of fusion per repeat unit and σ_e is the effective interfacial free energy associated with the basal plane of the equilibrium crystallite. If $T_m°$ is known independently, ζ_e and σ_e can be calculated by using the measured melting points of the fractions. However, if only $T_{m,e}$ and x are available, the usually accessible experimental quantities, then eq 30 and 31 make clear that $T_m°$ cannot be determined without some arbitrary assumptions being made with respect to either σ_e or ζ_e.

An analysis of the melting of low molecular weight polyethlene fractions, $M_n = 1.5 \times 10^3$ to 5.6×10^3, based on the above equations has already been given,[24] taking 145 ± 1 °C as the equilibrium melting temperature.[26] It was found that both ζ_e and σ_e increase with molecular weight. The increase in σ_e is caused by the first term on the right of eq 31. It arises from consideration of the number of ways the equilibrium sequence of crystalline units, ζ_e, can be chosen from among the x units of the chain if the ends are excluded. It can be expected that both ζ_e/x and σ_e would eventually reach limiting values at some higher molecular weight. The difference between x and ζ_e is also found to increase with molecular weight. A continuing increase in this difference would be expected with increasing chain length. These results point out the inherent difficulty that exists in treating melting point data of low molecular weight polymer fractions. The fact that σ_e is very likely to be a function of molecular weight makes it impossible to describe the melting relations as any simple function of chain length. Furthermore, there seems to be no obvious way that such melting point data can be used to perform an extrapolation to an undetermined equilibrium melting temperature of a given polymer. This problem is made further apparent when one analyzes the melting temperature of low molecular weight fractions of poly(ethylene oxide). Here also, the crystallite thicknesses are comparable to their extended-chain length.

Table IV[a,b]
Parameters Governing Fusion of Poly(ethylene oxide)

M_n	x	T_m, °C	ζ_e	ζ_e/x	σ_e, cal/mol	$x - \zeta_e$
1110	25	43.3	23	0.90	1413	2
1350	31	46.0	28	0.91	1734	3
1890	43	52.7	39	0.91	1995	4
2780	63	57.6	58	0.93	2567	5
3900	89	60.4	84	0.94	3410	5
5970	136	63.3	129	0.95	4776	7
7760	176	64.3	169	0.96	6080	7

[a] Melting data of ref 7. [b] Calculations performed assuming $T_m°$ = 80 °C.

Table V[a,b]
Parameters Governing Fusion of Poly(ethylene oxide)

M_n	x	T_m, °C	ζ_e	ζ_e/x	σ_e, cal/mol	$x - \zeta_e$
1110	25	43.3	22	0.88	1186	3
1350	31	46.0	28	0.90	1447	3
1890	43	52.7	38	0.89	1588	5
2780	63	57.6	57	0.90	1954	6
3900	89	60.4	82	0.92	2523	7
5970	136	63.3	127	0.93	3389	9
7760	176	64.3	166	0.94	4261	10

[a] Melting data of ref 7. [b] Calculations performed assuming $T_m°$ = 76 °C.

Table VI[a,b]
Parameters Governing Fusion of Poly(ethylene oxide)

M_n	x	T_m, °C	ζ_e	ζ_e/x	σ_e, cal/mol	$x - \zeta_e$
1110	25	43.3	21	0.84	791	4
1350	31	46.0	26	0.85	944	5
1890	43	52.7	36	0.83	882	7
2780	63	57.6	52	0.83	899	11
3900	89	60.4	74	0.84	997	15
5970	136	63.3	113	0.83	1006	23
7760	176	64.3	148	0.84	1126	28

[a] Melting data of ref 7. [b] Calculations performed assuming $T_m°$ = 69 °C.

The melting temperatures reported by Kovacs and Buckley[7] can be treated by the equilibrium analysis outlined above. For poly(ethylene oxide) the problem is complicated by the fact that the correct value of $T_m°$ is not as well established as it is for polyethlene. Values of 76 and 80 °C have been obtained from extrapolations of high molecular weight poly(ethylene oxide) fractions.[22,23] The equilibrium analysis will therefore be performed by using these two values for $T_m°$ as well as the lower value of 69 °C given by Kovacs and Buckley.[7] The results of these calculations are given in Tables IV–VI for each of these melting temperatures. For the two higher $T_m°$'s the quantities σ_e and ζ_e/x are of the same order of magnitude. They show the same trend with increasing chain length as does polyethylene (see ref 24). Lower values for σ_e and

ζ_e/x are obtained for T_m° = 69 °C, the latter being invariant with molecular weight. Although this type of analysis cannot be used to directly determine a value for T_m°, an erroneous choice of T_m° leads to clearly suspect results.

In summary, we have reemphasized the need to distinguish between two situations in analyzing the equilibrium melting of chain molecules. One is based on the melting of oligomers, as, for example, *n*-alkanes, which require that molecular crystals be formed. This analysis can lead to the equilibrium melting temperature, T_m°, of an infinitely long chain. The Flory–Vrij result has been shown to be the correct one for this case. On the other hand, real polymer chains of finite length, no matter how well fractionated, cannot form molecular crystals. Hence, although they have the same value for T_m°, they must be analyzed differently. A quite different melting temperature–molecular weight relation results. Because the parameters involved here are also molecular weight dependent, it is not possible to correctly extrapolate to T_m° using solely the melting temperatures of equilibrium crystallites formed by chains of finite length.

Acknowledgment. Support of this work by Exxon Chemical Corp. is gratefully acknowledged.

Registry No. Polyethylene (homopolymer), 9002-88-4; poly(ethylene glycol) (SRU), 25322-68-3.

References and Notes

(1) Mandelkern, L. "Crystallization of Polymers"; McGraw-Hill: New York, 1964.
(2) Mandelkern, L.; Stack, G. M.; Mathieu, M. In *Anal. Calorim.*, in press.
(3) Stack, G. M. Ph.D. Dissertion, Florida State University, 1983.
(4) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 223.
(5) Flory, P. J.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(6) Wunderlich, B.; Czornyj, G. *Macromolecules* **1977**, *10*, 960.
(7) Buckley, C. P.; Kovacs, A. J. *Prog. Colloid Polym. Sci.* **1975**, *58*, 44.
(8) Hay, J. N. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2845.
(9) Fatou, J. G.; Mandelkern, L. *J. Phys. Chem.* **1965**, *69*, 417.
(10) Quinn, F. A. Jr.; Mandelkern, L. *J. Am. Chem. Soc.* **1958**, *80*, 3178.
(11) Finke, H. L.; Gross, M. E.; Waddington, G.; Huffman, H. M. *J. Chem. Soc.* **1954**, *76*, 33.
(12) Broadhurst, N. G. *J. Chem. Phys.* **1962**, *36*, 2578.
(13) Hay, J. N. *J. Polym. Sci., Polym. Lett. Ed.* **1970**, *8*, 395.
(14) Schaerer, A. A.; Busso, C. J.; Smith, A. F.; Skinner, L. *J. Am. Chem. Soc.* **1955**, *77*, 2017. (a) Mazee, W. M. *Recl. Trav. Chim. Pays-Bas* **1948**, *67*, 197.
(15) Mandelkern, L. In "Progress in Polymer Science"; Jenkins, A. D., Ed.; Pergamon Press: New York, 1970.
(16) Atkinson, C. M. L.; Richardson, M. J. *Trans. Faraday Soc.* **1969**, *65*, 749.
(17) Heitz, W.; Wirth, T.; Peters, R.; Strobl, G.; Fischer, E. W. *Makromol. Chem.* **1972**, *162*, 63.
(18) Mandelkern, L.; Price, J. M.; Gopalan, M.; Fatou, J. G. *J. Polym. Sci., Part A-2* **1966**, *4*, 385.
(19) Varnell, W. D.; Harrison, J. R.; Wang, J. I. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *19*, 1577.
(20) Runt, J.; Harrison, I. R.; Dobson, S. *J. Macromol. Sci., Phys.* **1980**, *B17*, 99.
(21) Beech, D. R.; Booth, C. *J. Polym. Sci., Part B* **1970**, *8*, 731.
(22) Allen, R. C. M.S. Thesis, Florida State University, 1980.
(23) Hay, J. N. *J. Chem. Soc., Faraday Trans.* **1972**, *68*, 656.
(24) Stack, G. M.; Voigt-Martin, I. G.; Mandelkern, L. *Macromolecules*, in press.
(25) We thank Professor G. Strobl for furnishing us with these samples. We also note that in their work the study of the thermodynamics of fusion was not of primary concern.
(26) It must be recognized that the molecular weight range over which extended-chain crystals are formed is severely limited.[24]

Regime III Crystallization in Polypropylene[†,‡]

Elizabeth J. Clark

Center for Building Technology, National Bureau of Standards, Washington, D.C. 20234

John D. Hoffman*

Engineering Materials Program, Department of Chemical and Nuclear Engineering, University of Maryland, College Park, Maryland 20742. *Received November 15, 1983*

ABSTRACT: The recently developed theory for regime III crystallization from the melt is applied to isotactic polypropylene (i-PP) spherulite growth rate data. As the temperature decreases, a marked *upward* change in the slope of the published growth rate vs. temperature curves is observed, which is interpreted as a regime II → regime III transition. (A regime I → regime II transition would have exhibited a *downward* change in slope with decreasing temperature.) The regime II → regime III transition occurs near 137 °C, which corresponds to an undercooling of $\Delta T \sim 48$ °C. The experimentally observed change of slope in plots of $\ln G + U^*/R(T - T_\infty)$ vs. $1/T(\Delta T)$ at the II → III transition is 2.087, which is close to the theoretically predicted value of 2. Also, the ratio of the preexponential factors for regimes III and II, $G_{0(III)}/G_{0(II)}$, is reasonably close to the theoretical estimate. Nucleation constants for i-PP are determined, and the surface free energies $\sigma \simeq 11.5$ erg cm^{-2} and $\sigma_e \simeq 65$–70 erg cm^{-2} are estimated. The latter leads to a work of chain folding of $q \simeq 6.4$–6.8 kcal mol^{-1}, applicable to both regimes II and III. The q values are physically reasonable and fit into a more general picture for hydrocarbon polymers with –C–C– backbones. A method of obtaining q directly from the observed growth rate data without knowing the enthalpy of fusion is illustrated. Growth rate data on syndiotactic polypropylene are discussed briefly. The significance of regime III crystallization is discussed in a general way.

Introduction

At a moderately large undercooling, isotactic polypropylene (i-PP) exhibits a distinct and rather abrupt upward trend in its spherulite growth rate vs. temperature curve as the crystallization temperature is lowered. This phenomenon leads to a considerable departure from a straight-line fit in the conventional plots of $\log G + U^*/2.303R(T - T_\infty)$ against $1/T(\Delta T)$ suggested by nucleation theory. (Here, G is the growth rate, U^* a "universal" constant characteristic of the activation energy of chain motion (reptation) in the melt, R the gas constant, T the crystallization temperature, T_∞ the theoretical temperature at which all motion associated with viscous flow or reptation ceases, $\Delta T = T_m^\circ - T$ the undercooling, and

[†] Dedicated with respect and appreciation to Professor Walter Stockmayer.

[‡] From a dissertation to be submitted to the graduate school, University of Maryland, by E.J.C. in partial fulfillment of the requirements for the Ph.D. degree in Chemical Engineering.

0024-9297/84/2217-0878$01.50/0