Extrapolation of n-Alkane Melting Temperatures

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ABSTRACT: Romankevich and Frenkel[6] have suggested that the equilibrium melting point of polyethylene derived by the method of Flory and Vrij[1] should be altered by omitting calculated n-alkane melting points from the data base. Analysis shows such omission is not justified and would not give agreement with other empirical methods as claimed. Other extensions or restrictions of the data base appear to be important when the original fitting procedure of Flory and Vrij is used, but when a curve-fitting procedure is used that gives equal weight to all data, changing the data base becomes relatively unimportant.

Introduction

The equilibrium melting point of infinite perfect crystals of linear polyethylene, T_0, is an important fixed point in polymer crystallization theory, and significant disagreements about its value exist in the literature.[1-8] It has been obtained by extrapolation of the equilibrium melting points of finite crystals, T_m, and both n-alkane crystals[1,8] and polyethylene (PE) crystals[2,7] have been used. The extrapolation of the melting of n-alkanes to infinite n and thus infinite thickness is well-founded thermodynamically,[1,8] but the extrapolation is over a large size range, as the thickest n-alkane crystals available are about 15 nm thick.

PE crystals can be grown 100 times thicker than n-alkane crystals,[2] but there is no theory of their equilibrium melting that allows extrapolation without other assumptions. It is usually assumed that the end surface free energy, σ_e, is a constant because the observation of straight lines on simple plots of polymer crystal melting is most easily interpreted in this way. A constant σ_e allows extrapolation to a different, lower value of T_0 than that obtained from n-alkanes. If the n-alkane value is taken as correct, then the PE melting temperatures can be used to derive the effective end surface free energies at the melting point, which then rise rapidly with crystal thickness.[9]

This longstanding disagreement over the equilibrium melting point of polyethylene makes the reliability of the n-alkane extrapolation particularly important. Mandelkern and Stack[8] recently gave a detailed review of other published analyses of the melting temperature of n-alkanes.[3-5] They show that the Flory–Vrij equation[1] is correct and should only be applied to n-alkanes. Choice of the correct equation is the first part of an extrapolation procedure; the other is the choice of a data base and its weighting.

Romankevich and Frenkel[6] are concerned with the correct choice of extrapolation procedures for obtaining the equilibrium melting point of PE. They attempt extrapolations both from n-alkanes and from PE, using the Flory–Vrij equation and Flory's theory of the equilibrium melting of finite polymer crystals.[10] (Unfortunately they use eq 31″ of ref 10 where eq 28 with $\upsilon_2 = 1$ would be more correct.) Romankevich and Frenkel claim that the increase of T_0 from 414.3 K in Broadhurst[11] to 418.5 K in Flory and Vrij[1] was due to the change in the data base and not to the different equation used. Thus they claim that it is correct to use only the experimental results for the melting of orthorhombic n-alkanes (omitting the melting temperatures calculated for orthorhombic n-alkanes of $n < 44$, which transform to the hexagonal phase before melting) and that the Flory–Vrij extrapolation then produces the same result as extrapolations of PE crystal melting points.

Even if the calculated melting temperatures of $n < 44$ n-alkanes are found to be reliable and correct, a large change in the extrapolated value when they are omitted would be a cause for concern. It would mean that the accepted equilibrium melting point could well change significantly when new reliable data are obtained. Systematic errors of this sort are implied by the graphical plots in the paper of Flory and Vrij,[1] but it has been assumed that they are less important than random errors.

n-Alkane Melting Point Data

Broadhurst compiled and correlated melting temperatures and transition temperatures, heats of fusion and heats of transition, and X-ray data for n-alkanes from $n = 1$ to $n = 100$ in 1962.[11] He used the experimental melting temperatures of the orthorhombic n-alkanes (which can be obtained only for $n > 43$) for his linear extrapolation, which gave $T_0 = 414.3$ K.[12] Flory and Vrij[1] used these data plus calculated melting temperatures for the orthorhombic n-alkanes with n odd and between 11 and 43. The calculated values are simply derived from the temperatures and enthalpies associated with the orthorhombic-to-hexagonal transition and the melting of the hexagonal phase. In a later paper,[13] Broadhurst refined the calculations and found the calculated melting temperatures of alkanes with n between 11 and 19 to be reduced by 0.1–0.3 K by consideration of second-order terms.[14]

Mandelkern and Stack[8] also used the Broadhurst data.[11] A few more recent results for high-n n-alkanes have been obtained by Heitz et al.,[15] Mandelkern and Stack,[8] and Takamizawa et al.[16] Wunderlich and Czornyj[5] included the results of Heitz in their work on T_0, but Mandelkern and Stack[8] have repeated the melting temperature determination on some samples of $n < 100$ used in ref 15 and obtain results much closer to those in ref 11. They therefore discard the results of Heitz et al.[15] Takamizawa et al.[16] have obtained melting temperatures for $n = 60$, 80, 100, 120, and 160 by dilatometry and by DTA. Their results for $n < 100$ are quite close to the results of Broadhurst.[11]

As the preparation of pure n-alkanes becomes more difficult at high n, we should expect a decline in the reliability of melting point determination as n increases. There is no way of knowing the correct weighting to use, so the best one can do is to give each value of T_m that has been obtained equal weight (unless specific results are thought to be in error, and they can be given a low or zero weight) and to explore the effects of weighting to see if the arbitrary choices affect the results significantly.

Theoretical Expressions for n-Alkane Melting Points

Flory and Vrij took the fundamental equation that they derived (eq 7[1]) and approximated by dropping higher order

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terms. Their result (eq 8[1]) is here multiplied throughout by $R/\delta H_u$, to make comparison with other expressions easier, giving

$$n\delta T - n\delta C_p(\delta T)^2/2\delta H_u - RT_mT_0 \ln(n)/\delta H_u = (T_0\delta S_e/\delta H_u)T_m - (\delta H_e/\delta H_u)T_0 \quad (1)$$

Here δT is $(T_0 - T_m)$, δH_u is the enthalpy of fusion per repeat unit at T_0, and δS_e and δH_e are the end-group contributions to entropy and enthalpy changes at the melting point.

The left-hand side of this equation should be a linear function of T_m. To perform the extrapolation Flory and Vrij calculated the left-hand side for each experimental point with a given value of T_0, and the left-hand side was plotted against T_m. The value of T_0 that gave the best straight line on this plot was taken as the extrapolated equilibrium melting point. A plot of the actual deviations between data and fit is then a helpful check on the procedure.

Data sets have also been fitted to the linear equation of Broadhurst,[12] although it is not correct, to investigate the claims of Romankevich and Frenkel that the data base is the important factor. Broadhurst[12] fitted the data to

$$T_m = T_0(n + a)/(n + b) \quad (2)$$

This equation can be simply transformed to give a right-hand side that is a linear function of T_m as in eq 1.

$$n\delta T = bT_m - aT_0 \quad (3)$$

It was pointed out[17] that fitting data to eq 3 may give a different result from that obtained by fitting to eq 2, because in the left-hand side of eq 3 the experimental result T_m appears as nT_m. Thus high-n melting point data are given higher statistical weighting. This is particularly undesirable as these high-n n-alkanes are less likely to be pure.

In eq 1 the first (and largest) term on the left-hand side is $n\delta T$. Thus the extrapolation procedure used by Flory and Vrij[1] also gives too much weight to high-n results. It was to avoid such problems that a more complicated method of fitting was used by Broadhurst in his later paper.[13,17] There an almost explicit expression for T_m was obtained, and an iterative procedure was used to fit the data. To get an explicit expression for T_m from eq 1, it is here solved as a quadratic in δT, giving

$$T_m = T_0 - (T_0/n\delta C_p)[n\delta H_u/T_0 + n\delta S_e + R\ln(n) - \{(n\delta H_u/T_0 + n\delta S_e + R\ln(n))^2 - 2n\delta C_p(\delta S_e + R\ln(n) - \delta H_e/T_0)\}^{1/2}] \quad (4)$$

The right-hand side of eq 4 has been fitted to the data sets with a nonlinear least-squares fitting procedure derived from the Fortran IMSL library. δH_e is set to a series of values and the procedure finds the best values of T_0 and δS_e for each. The deviation parameter χ^2 is then plotted against T_0.

Results of Extrapolations

To investigate the effects of changes in data base independently of changes of the equation and fitting procedure used, all four of the above equations have been applied to the data of Broadhurst[11] and to those of Flory and Vrij[1] using δC_p = 1 cal mol^{-1} K^{-1} and δH_u = 980 cal mol^{-1},[8] and the results are summarized in Table I.

Romankevich and Frenkel claimed that when the original Broadhurst data base ($n > 43$) is used, the addition of the logarithmic term in the Flory–Vrij equation makes little difference to the value of T_0. Table I shows that this is true when fits to eq 1 and 2 are compared. However, this is not a valid comparison; similar weighting must be used for both expressions. With equal weighting and the Broadhurst data base, T_0 rises from 414.1 to 416.8 K when the logarithmic term is added to give the correct Flory–Vrij expression. Adding to the data base causes a further increase in T_0 to 419.0 K, only 0.5 K over that obtained from eq 1.[19] Table I thus shows that the equation used, the data base, and its weighting can have significant effects.

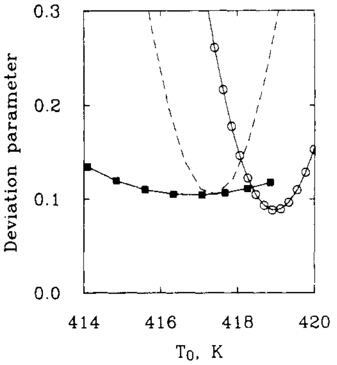

Figure 1. χ^2 deviation parameter from a fit of the right-hand side of eq 4 to the melting point data for n-alkanes plotted as a function of the value chosen for T_0 with various data sets: (○) melting point data from ref 1 and 13 ($11 < n < 100$); (■) melting point data from ref 11 ($44 < n < 100$); (---) melting point data ($44 < n < 100$) and hexagonal-phase melting points from ref 11 ($11 < n < 43$).

Table I

	T_0, K			
	Broadhurst		Flory–Vrij	
data source	eq 3	eq 2[11]	eq 1[1]	eq 4
ref 11	412.5	414.1	415.0	416.8
ref 1, 13	414.2	413.6	418.5 418.5,[2] 419.3[8]	419.0

The possible effects of errors in the calculated orthorhombic melting points can be investigated in a pragmatic manner by replacing them with their upper and lower bounds and seeing the effect of this on the extrapolation. The bounds are the hexagonal-phase melting temperatures[11] and the orthorhombic–hexagonal transition temperatures,[11] as the correct melting temperature cannot lie outside these limits. When the original Flory–Vrij method (eq 1) is used, it is found that the effect of these substitutions on T_0 is no more than ±1 K, the original quoted deviation for T_0.[1] This demonstrates the low weighting given to low-n results by eq 1. When eq 4 is used, there are significant differences, but even use of the upper limiting values does not reduce T_0 as much as omitting the data, as shown in Figure 1. The lower limits are up to 10 K different from the calculated values and produce a very poor fit.

Figure 1 is a plot of the deviation parameter obtained from fits to eq 4 against the derived value of T_0. It shows a well-defined minimum at 419.0 K for the data used by Flory and Vrij and an equally sharp minimum at 417.4 K when hexagonal-phase melting points are used in place of the calculated orthorhombic melting points. If no data are used for $n < 44$, the minimum at 416.8 K is very broad. The figure in Romankevich and Frenkel[6] seems to show a sharp minimum for the reduced data set, but this is only because they do not include zero deviation in their plot. The apparent agreement of their result for n-alkane extrapolation with other procedures of various sorts was the main reason why Romankevich and Frenkel[6] chose not to use the calculated melting points of $n < 44$ n-alkanes. Not only does this agreement not occur in the case they describe when equal weighting schemes are used to fit the

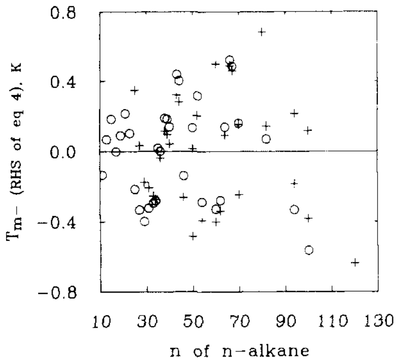

Figure 2. Difference between experimental data and fitted curve derived from eq 4 for two data sets: (○) melting point data from ref 1 and 13 ($11 < n < 100$); (+) melting point data from ref 1 and 13 ($25 < n < 100$) and from ref 8 and 16.

data, but no possible values of the low-*n* melting points can make it occur.

Figure 2 is a plot of the deviation of the data of Flory and Vrij from the best fit derived from eq 4 vs. *n*, and it shows no particular trend below $n = 44$. If there is nothing special about the data for $n < 44$ and if systematic errors are small, removal of data should increase the standard deviation of the equilibrium melting point and alter its value randomly. If there are large systematic effects, then one may infer that addition of new reliable values for the melting point of high-*n* *n*-alkanes would continue to alter T_0.

If we add the new data in ref 8 and 16, the result is a fit with a low T_0 and a very high minimum error. Half of the total error is caused by a single point, that of $n = 160$,[16] and this may be sufficient reason for rejecting it. The remaining data when added to those of Flory and Vrij reduce T_0 to 416.5 K when their fitting procedure is used but only slightly to 418.8 K when the weighting is even. (Duplicated measurements are simply put into the data twice.) If low-*n* data are removed to give 33 data points as before, the effect is naturally less when using eq 1 and more when using eq 4, the result being then an equilibrium melting point of 417.9 K and a minimum deviation parameter 20% greater than that obtained for the original data base. The differences between this fit and the data again show no trends as long as consideration is limited to the fitted points (Figure 2). The excluded data points have deviations of several degrees, as is implied by the well-defined minima in Figure 1.

Figure 3 summarizes results obtained from several subsets of the data. *It is a plot of T_0 obtained as a function of the mean value of n in the data set used.* The data sets ranged from $11 < n < 43$ (only the calculated melting temperatures) to $44 < n < 140$ (the data used by Broadhurst[12] plus new results). The mean value of *n* in the data of Flory and Vrij is 43.6. The circles are from fits made to the original Flory–Vrij equation, eq 1, and the dotted line is their trend. The solid triangles are obtained from fits to eq 4, and the solid line is their trend. Thus on the basis of the original equation, a very clear correlation exists between the mean value of *n* in the data base and the resulting extrapolated value. The changes in T_0 with mean *n* are larger than the statistical uncertainty even of reduced data sets. This remains true if fits at higher mean *n* values (<60) are rejected from consideration because of the unreasonable values of thermodynamic parameters such as the surface contribution to the entropy and enthalpy of fusion that they imply.[1,13] It is not intended to suggest that the extreme values of T_0 shown in Figure 3 are reasonable. Indeed unreasonable values obtained from reliable results were a reason for studying the matter in detail.

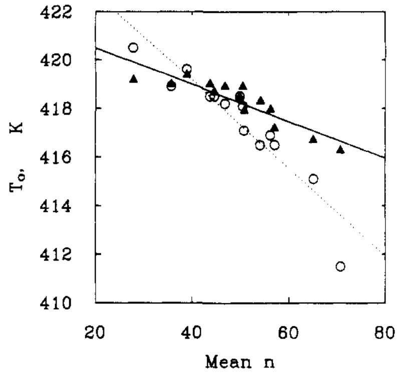

Figure 3. Plots of the value of the equilibrium melting point T_0 derived from the Flory–Vrij equation for *n*-alkane melting points vs. the mean value of *n* in the data used with straight-line fits to the data: (···, ○) fitted with eq 1; (—, ▲) fitted with eq 4.

When the low-*n* melting points are properly weighted by use of eq 4, the results are quite different. There is still a downward trend, but now a majority of the results fall within 1 K of 418.5 K. The problem of systematic dependence of T_0 on *n* is still present in principle, for if the data and the expression were exactly correct, it would not matter what statistical weighting was used, and it is not clear why the change in fitting procedure reduces the slope of the line in Figure 3 so much. But in practice the problem is no longer a serious concern because random errors are likely to remain more important for some time. For example, addition of the "unreliable" data previously rejected produces points that still lie on the solid line in Figure 3. The lines in Figure 3 intersect at about $n = 40$, *near to the mean value of n in the current data base.* This coincidence makes the current best value of T_0 depend little on the fitting procedure used, and a lot more data will be needed before this is not the case.

As the systematic effects are small, it is easy to find sources for them. The theoretical expression used is an approximation.[1] It implicitly assumes perfect order in the crystal phase and complete disorder in the liquid phase. If either of these conditions is not fulfilled, by the presence of order in liquid alkanes or by the increase in crystal defects as melting approaches, the melting point will change.[18] The experimental melting points may be slightly too low to a degree that increases with increasing *n*, as impurities cause the melting point to fall and higher *n* materials are more difficult to obtain in a pure state.

Summary

The suggestion of Romankevich and Frenkel[6] that the true equilibrium melting temperature of polyethylene will be obtained by extrapolation of orthorhombic *n*-alkane melting temperatures for $n > 44$ only, omitting calculated melting points, is not supported by the evidence. When the fitting procedure of Flory and Vrij[1] is used, omitting data or adding new data can alter T_0 substantially. However, a better fitting procedure (similar to that of Broadhurst[13]) that does not contain hidden weighting factors substantially reduces the systematic effect of choice of data. It is not clear why this is so, but the result is that the current best extrapolated value of the orthorhombic *n*-alkanes is not an accident of the data currently available.

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Mechanical Measurements in the Reaction Bath during the Polycondensation Reaction, near the Gelation Threshold

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ABSTRACT: The evolution of the mechanical properties, as a function of time t, during the gelation process was studied by means of the sphere magnetorheometer near the gel point t_g. For the set of samples studied, the weight fraction of solvent and the mean molecular weight between two successive junctions points of the branched polymer were modified. As a function of the reduced time $1 - t/t_g$, the viscosity η and the shear elastic modulus G can be described by simple power laws only for samples that have the smallest mean molecular weight between two successive junction points. We find $\eta \sim (1 - t/t_g)^{-0.8\pm0.1}$ and $G \sim (t/t_g - 1)^{3.2\pm0.5}$. The exponent values are independent of the weight fraction of the solvent. Those results are in agreement with percolation theory and recent theoretical predictions.

Introduction

The evolution of the reaction during the gelation process is characterized by the conversion factor,[1] p; this parameter is equal to 0 and 1 at the beginning and at the end of the reaction, respectively. The mechanical properties are typical of the sol–gel transition; at the gel point, p_c, the reaction bath goes from a liquid medium to an elastic medium.[2] For $p < p_c$, there is a sol that is an assembly of polydisperse finite clusters. For $p > p_c$, there is a sol embedded in a gel that is an infinite cluster (i.e., it has the size of the vessel). Our aim is to study the mechanical properties near p_c because, according to percolation or classical theories, they must be universal whatever the structure of the gel in its final state ($p = 1$).

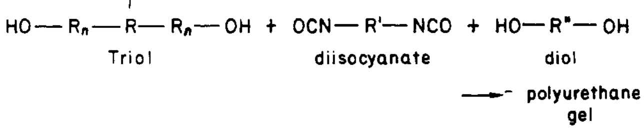
Previous[3,4] mechanical measurements were performed on radical copolymerization with solvent (polystyrene/divinylbenzene/benzene) and polycondensation without solvent (diisocyanate/triol). In both systems it was found that the viscosity η diverges at the gel point as $\eta \sim (p_c - p)^{-S}$ with $S = 0.78 \pm 0.05$. The increase of the elastic modulus was different in the two systems: we obtained $G \sim (p - p_c)^T$ with $T = 2.1 \pm 0.3$ for copolymerization and $T = 3.2 \pm 0.6$ for polycondensation. These measurements were done with a new apparatus, the sphere magnetorheometer, and the strong difference observed between the T exponent values could be assigned to experimental difficulties.[3] In order to validate the preliminary results we have performed experiments on several polycondensation samples, in which the hydroxyl groups and isocyanate groups have equal reactivities[5] and which present the following advantages: the gel time is a controllable quantity and can be chosen to be very long (132–500 h); well-defined "quenched samples" can be prepared.

In this way, it is possible to perform measurements at low shear rates and low shear deformations very near the gel point and to determine quantitatively the perturbation induced by mechanical measurements.

We have also changed the proportion of solvent and the mean molecular weight between two successive junction points in order to observe their influence on the mechanical properties. We already know that those parameters have a strong influence on the absolute value of p_c.[6,7]

Experimental Conditions

Samples and Materials. The polycondensation reaction studied is



$$\underset{\text{Triol}}{\mathrm{HO{-}R_{\mathit{n}}{-}\overset{\overset{\displaystyle OH}{|}}{\overset{R_{\mathit{n}}}{\overset{|}{R}}}{-}R_{\mathit{n}}{-}OH}} + \underset{\text{diisocyanate}}{\mathrm{OCN{-}R'{-}NCO}} + \underset{\text{diol}}{\mathrm{HO{-}R''{-}OH}} \longrightarrow \begin{matrix}\text{polyurethane}\\ \text{gel}\end{matrix}$$

The condensation occurs between the OH groups of the polyols and the NCO groups of the diisocyanate. The polycondensation was studied on four types of samples (I–IV) that differ by the weight fraction of diol, the weight fraction of solvent (toluene), and the molecular weight of the triol. The composition and the characteristics of the four types of polycondensation are given

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