

Determination of Crystallinity by Gas Chromatography. Effect of Curvilinearity of Retention Diagrams

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ABSTRACT: Gas phase nonideality and changes in heat of vaporization of solute molecules with temperature cause a departure from linearity of gas chromatographic retention diagrams. The determination of the crystalline content of polymer stationary phases, involving a linear extrapolation of measured retention data, can thus lead to erroneous estimates of crystallinity. Studies of several polyolefin stationary phases reveal that the phenomenon is dependent on both experimental conditions and temperature. Computed crystallinities were found to vary by as much as 50%. It is shown that these discrepancies can be alleviated by proceeding to curvilinear extrapolations of retention data based on readily available solute vapor pressure data and second virial coefficients.

The field of applications of gas chromatography (GC) to the study of polymers extends beyond the measurement of polymer-probe interactions¹ to include properties of the pure polymer. Discontinuities in the temperature variation of the retention volume have been related to both glass transition temperatures² and melting³ of the stationary phases. Guillet and Stein⁴ showed that retention data through the melting transition could be analyzed quantitatively, yielding the crystalline content of the stationary phase. This method has been successfully applied to the determination of crystallinities and rates of crystallization of homo- and copolymers.^{5–7} Recently Courval and Gray⁸ have investigated polar polymer-solute systems for which analysis is complicated by concurrent adsorption at the polymer-solute interface, even at temperatures above the melting transition.

The GC route is particularly attractive for the determination of crystallinity since no calibration procedure is required. Its precision depends essentially on an extrapolation of retention data measured above the melting point to lower temperatures. The purpose of the present communication is to investigate the effects of the inexact linearity of retention diagrams on this extrapolation procedure and on the computed crystallinities.

Experimental Section

Instrumentation and experimental procedures were as described in previous publications.^{7,9} Specific retention volumes, V_g , were computed from the relation,¹⁰

$$V_g = (t_R F / w_L) J_2^3 (760 / P_o) \quad (1)$$

where t_R is the net retention time, F is the flow rate at 273.16 K (760), w_L is the mass of polymer, and J_2^3 is given by the relation¹¹

$$J_n^m = (m/n) \{ [(P_i/P_o)^n - 1] / [(P_i/P_o)^m - 1] \} \quad (2)$$

with $m = 3$ and $n = 2$, P_i and P_o being the inlet and outlet pressures. Details of column parameters are given in Table I.

Solute vapor pressures were computed from the Antoine equation

$$\log p_i^0 = A - B / (t + C) \quad (3)$$

where p_i^0 is the solute vapor pressure in mm Hg, t is the temperature (°C), and A , B , and C are constants taken from standard sources.¹² Densities were obtained from Orwoll and Flory's compilation.¹³ Second virial coefficients (B_{11}) were computed from the equation,¹⁴

$$B_{11} / \bar{V}_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (4)$$

where \bar{V}_c and T_c are critical volumes and temperatures, T is the temperature (°K), and n is the number of carbon atoms of the n -alkane. Following Cruikshank et al.¹¹ cross second virial coefficients (B_{13}) were derived from the same equation, ($n-1$) becoming ($n_1 +$

n_3)/2 with $n_3 = 1$ for nitrogen. \bar{V}_c and T_c are now pseudocritical volumes and temperatures, \bar{V}_{13} and T_{13} , given by the relations^{11,14,15}

$$\bar{V}_{13} = (1/8)(\bar{V}_{1c}^{1/3} + \bar{V}_{3c}^{1/3})^3 \quad (5)$$

$$T_{13} = (T_{1c} T_{3c})^{1/2} (\bar{V}_{1c} \bar{V}_{3c} / \bar{V}_{13}^2) \quad (6)$$

The constants used are given in Table II.

The polymers in the present work, all previously investigated,⁹ were Eastman Tenite 3310 high-density (0.96) polyethylene, poly(1-butene), X-6160-116A, and a 1 mil polypropylene (0.903) chill-roll film.

Results and Discussion

Retention volumes on semicrystalline polymer stationary phases exhibit drastic increases as temperature is increased through the glass (T_g) and melting (T_m) transitions, as depicted in Figure 1. At T_g the retention mechanism changes from surface adsorption below T_g to bulk sorption. At temperatures below melting, polymer-solute interactions are restricted to the amorphous domains owing to a difference in solubility of the solute in crystalline and amorphous phases. Upon melting of the stationary phase the amorphous content becomes larger, leading to an increase in retention volumes. Since no change in retention mechanism takes place, the crystalline fraction of the stationary phase can be determined, at all temperatures, by the relation⁴

$$X_c = 1 - (V_g / V_g') \quad (7)$$

where X_c is the crystalline weight fraction, V_g is the measured retention volume, and V_g' is the retention volume corresponding to the totally amorphous polymer. In previous work V_g' was obtained⁴ by a linear extrapolation of retention volumes measured above T_m , i.e., for the amorphous polymer, as indicated in Figure 1. In the event of concurrent surface adsorption, both V_g and V_g' must be determined by extrapolation to infinite thickness of the stationary phase.⁸

The accuracy of the method is dependent on the quality of the retention data obtained above T_m and also on the approximations involved. The specific retention volume is related to the polymer-solute properties by the expression^{16,17}

$$\ln V_g = \ln [273.16R / (a_1/w_1)^{\infty} p_i^0 M_1] - (p_i^0 / RT)(B_{11} - \bar{V}_1) + (P_o J_3^3 / RT)(2B_{13} - \bar{V}_1) \quad (8)$$

where $(a_1/w_1)^{\infty}$ is the infinite dilution weight fraction activity coefficient, p_i^0 , \bar{V}_1 , and M_1 are the vapor pressure, molar volume, and molecular weight of the solute, B_{11} and B_{13} are the second virial coefficients, R is the gas constant, T is the temperature, and J_3^3 is given by eq 2. For a retention diagram to be linear, the value of the derivative, $\partial \ln V_g / \partial (1/T)$, must be constant at all temperatures. Since the heat of vaporization of the solute is known to vary with temperature, it is to be

Table I
Column Parameters

Polymer	Solvent	Packing and column			
		Inert support	Loading, % (w/w)	Mass, g	Solute
Polypropylene	Xylene	Chromosorb G, AW DMCS, 70-80	8.16	0.2160	<i>n</i> -Decane
Poly(1-butene)	Xylene	Chromosorb G, AW DMCS, 70-80	8.10	0.4341	<i>n</i> -Octane
Polyethylene	Xylene	Chromosorb G, AW DMCS, 70-80	5.23	0.0367 ^a	<i>n</i> -Tetradecane

^a 1/8 in. o.d. column.

Table II
Physical Constants for Solutes and Carrier Gas

Compd	No. of carbon atoms	Antoine equation				\bar{V}_c , ^a cm ³	T_c , ^b K	\bar{V}_{13} , ^c cm ³	T_{13} , ^d K
		Constants			Temp range				
		A	B	C					
<i>n</i> -Octane	8	6.923 77	1355.126	209.517	40 < <i>t</i> < 155	486.02	569.4	235.17	212.1
<i>n</i> -Decane	10	7.307 12	1648.0	246.9	155 < <i>t</i> < 296	601.97	619.2	269.97	207.9
		7.338 83	1719.86	213.8	25 < <i>t</i> < 80				
<i>n</i> -Dodecane	12	6.953 67	1501.268	194.480	75 < <i>t</i> < 210	717.93	659.2	303.25	202.7
		7.315 7	1830.0	198.3	25 < <i>t</i> < 150				
<i>n</i> -Tetradecane	14	6.980 59	1625.928	180.311	150 < <i>t</i> < 280	830.02	695.2	334.29	198.1
		7.314 3	1930.4	183.8	25 < <i>t</i> < 147				
<i>n</i> -Hexadecane	16	6.995 7	1725.46	165.75	147 < <i>t</i> < 325	949.88	725.2	366.50	192.6
		7.333 09	2036.4	172.5	70 < <i>t</i> < 175				
Nitrogen	“1”	7.030 44	1831.317	154.528	175 < <i>t</i> < 358	90.071	126.1		

^a Critical molar volume. ^b Critical temperature. ^c Pseudocritical volume. ^d Pseudocritical temperature.

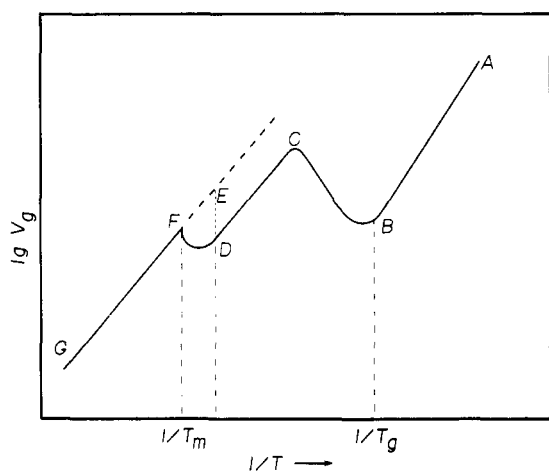


Figure 1. Generalized retention diagram for semicrystalline polymer.

expected that retention diagrams can only be considered linear, in first approximation, over a very limited range of temperature. As a result the crystallinity computed through eq 7 may become significantly different from its actual value whenever a wider range of temperature is studied.

To assess the magnitude of the deviation from linearity and its effect on computed crystallinities, retention data were measured for a semicrystalline polypropylene over the range 50 to 210 °C. The corresponding retention diagram with an *n*-decane solute is given in Figure 2. The melting curve computed from these data by a linear extrapolation of the data above T_m (165 to 210 °C) is included in Figure 2. It is seen that the crystalline content passes through a maximum and de-

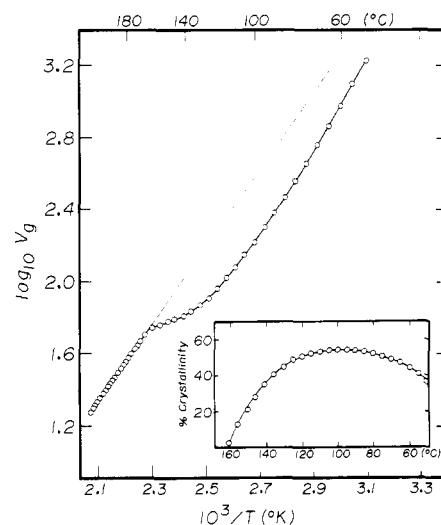


Figure 2. Retention diagram and melting curve for *n*-decane on polypropylene.

creases at the lower temperatures, failing to reach a constant value. The value at 50 °C, 36%, is hardly commensurate with the crystallinity computed from the density of the material (0.903), 64%. Considering the variation of retention volumes with temperature, as expressed in eq 8, and the increase in heats of vaporization of solutes with decreasing temperature, one would expect the retention volume of a 100% amorphous polypropylene to be larger than computed by a linear extrapolation of high-temperature data. As a result the apparent crystallinity is lowered. From the computed melting curve it is readily seen that the linear approximation becomes in-

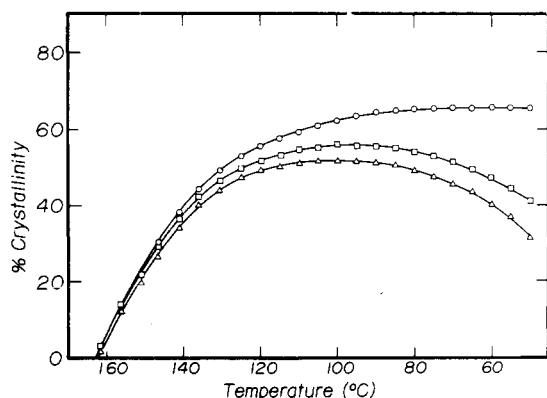


Figure 3. Melting curves of polypropylene. Extrapolation of high-temperature retention data for *n*-decane: linear (Δ) 180–210 °C, (\square) 165–195 °C, and (\circ) curvilinear.

creasingly inappropriate as the temperature range is increased.

To derive an adequate value of the crystalline content of the stationary phase at all temperatures, the curvature of retention diagrams must be included in extrapolation procedures. Equation 8, which expresses the magnitude and temperature variation of the retention volume, can be evaluated at any temperature from readily available literature data (p_1^0 , M_1 , \bar{V}_1 , ...) with the exception of activity coefficients. However, for the totally amorphous polymer ($T > T_m$) the activity coefficients and their temperature dependence can be computed from the measured retention volumes

$$\Delta h_1^{\infty}/R = [\partial \ln(a_1/w_1)^{\infty}]/[\partial (1/T)] \quad (9)$$

where Δh_1^{∞} is the partial molar enthalpy of mixing. This, in turn, allows for the computation of the retention volume of totally amorphous polymer at any temperature. Assuming the partial molar enthalpy of mixing to be constant, one may write

$$\ln(a_1/w_1)^{\infty} = \Delta h_1^{\infty}/RT + \ln b \quad (10)$$

where the constants $\Delta h_1^{\infty}/R$ and $\ln b$ are determined by linear least-squares analysis of activity coefficients above T_m . The retention volume of a totally amorphous polymer at any temperature is thus written

$$\ln V_g = \ln \frac{273.2R}{p_1^0 M_1 b \exp(\Delta h_1^{\infty}/RT)} - (p_1^0/RT)(B_{11} - \bar{V}_1) + (P_o J_3^4/RT)(2B_{13} - \bar{V}_1) \quad (11)$$

Although the partial molar enthalpy of mixing might not be constant over the temperature range of interest (50 to 210 °C), its variation with temperature is at least one order of magnitude smaller than other factors. This procedure, herein called curvilinear extrapolation, was applied to the retention data of Figure 2. The last term of eq 11, containing the cross virial coefficient, was, however, omitted. Its magnitude (usually quite small) and importance in the present context will be discussed later. Crystallinities computed through curvilinear extrapolation of high-temperature data (165 to 210 °C) are shown in Figure 3 as a melting curve. As expected, the computed crystallinities are larger, levelling off to a constant value of about 66%, in good agreement with density estimates. In contrast to linear extrapolations, the computed crystallinities were found insensitive to the set of high-temperature data chosen (165 to 195 °C, 165 to 210 °C, 180 to 210 °C). The corresponding melting curves obtained from linear extrapolations (165 to 195 °C and 180 to 210 °C), showing the large variations in computed crystallinities, are included in Figure

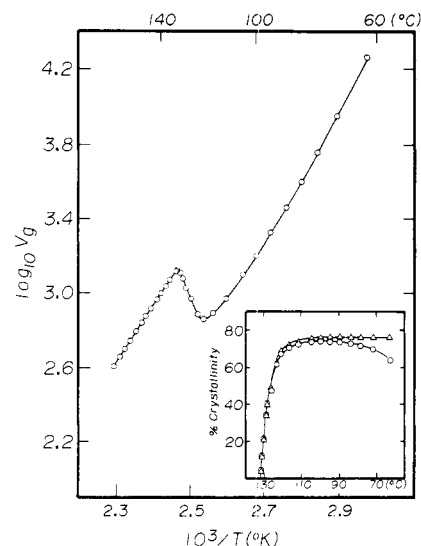


Figure 4. Retention diagram and melting curves for *n*-tetradecane on polyethylene: (\circ) linear and (Δ) curvilinear extrapolations.

3. Depending on the set of data chosen, the actual temperature range investigated differs, 50 to 195 °C vs. 50 to 210 °C, resulting in variations of the computed crystallinities.

It should be mentioned, however, that other factors could give rise to a maximum in the melting curve as recorded in Figure 2. As already pointed out, eq 7 is only valid for bulk retention volumes. If concurrent surface adsorption occurs, retention volumes will be larger than they should be, resulting in an apparent decrease in computed crystallinity. Since the surface contribution increases with decreasing temperature, particularly at temperatures close to T_g , a melting curve such as earlier reported could be observed. Such an effect can, however, be discounted in the present study. The retention characteristics of these polymers in the vicinity of T_g , studied under identical conditions of surface to volume ratio with *n*-alkane solutes,⁹ indicated no such surface contribution in the temperature range chosen for the present study.

Similarly Guillet and Stein,⁴ in early studies of inverse gas chromatography, detected in some experiments similar variations in computed crystallinities with temperature outside the melting range observed by differential scanning calorimetry. Unpublished results of Guillet and Stein on high-density polyethylene with *n*-tetradecane are reproduced in Figure 4 as a retention diagram and melting curve (linear extrapolation). The decrease in computed crystallinity is quite noticeable at temperatures below $T_m - 40$. To account for these observations, Stein and Guillet investigated the time dependency of their computed crystallinities. They found, however, that the measured retention volumes, and hence crystallinities, at temperatures below $T_m - 40$ were constant for periods of several days. Their data were then reexamined with the procedure outlined herein, namely curvilinear extrapolation of the high-temperature retention data (135 to 165 °C). The results of these computations, included in Figure 4 as melting curve, show that a constant value is obtained for the computed crystallinity at temperatures below $T_m - 40$. While the difference between both extrapolation procedures is not nearly as large as in the case of polypropylene, it should be noted that the temperature range investigated is smaller (63 to 165 °C).

The applicability of the GC technique was further investigated with poly(1-butene). It is indeed well known^{18,19} that poly(1-butene), when cooled from the melt, forms into an unstable crystalline form, modification II (mp 120 °C), which, upon standing, turns into the stable modification I (mp 130

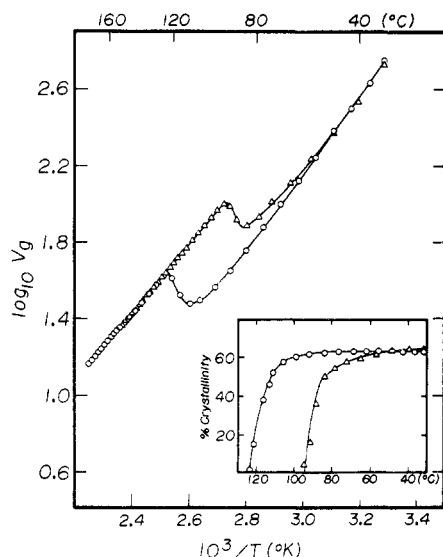


Figure 5. Retention diagrams and melting curves for *n*-octane on poly(1-butene), curvilinear extrapolation: (O) increasing and (Δ) decreasing temperature scans.

°C). Due to a large difference in crystal densities, 0.96 and 0.886 for I and II, it has been found that the density of the material increases upon standing without change in crystallinity as observed by x rays.¹⁸ The GC technique should be particularly well suited to provide an insight into the crystalline content of the stationary phase in each case. To that effect the packed poly(1-butene) column was ballistically annealed from above the melting point and kept several weeks at room temperature. Its melting curve was then determined from retention data collected between 30 and 175 °C, while increasing the temperature. Upon standing overnight at 180 °C, retention data were obtained while progressively cooling down the column to 30 °C. The results of these experiments are given in Figure 5 as retention diagrams with the corresponding melting curves. In the present case crystallinities were computed by curvilinear extrapolations of the high-temperature retention data. Linear extrapolations yielded a maximum in both melting curves, with a crystallinity of about 42% at the lowest temperature (30 °C).

While the melting curves were found quite different, as would be expected, the crystallinities achieved in both cases were nearly identical, somewhat larger for modification II. In good agreement with reported thermal measurements,¹⁹ crystallization of modification II occurred at lower temperature than melting (~90 vs. 120 °C). Of particular interest to the GC process is the detection of crystallinity in the case of modification II. Unlike most semicrystalline polymers investigated,⁴⁻⁸ which are characterized by differences of at least 0.1 density points between crystalline and amorphous phases, poly(1-butene) exhibits a very slight difference, 0.886 vs. 0.866, in crystalline and amorphous densities. Figure 5 clearly indicates that the difference in permeability of the two phases is, however, maintained.

During the course of this study it was found that the solute molecule used had a definite effect on the resulting crystallinities if the data were subjected to linear extrapolations. Fortunately the effect of the solute on curvilinearity of retention diagrams, hence crystallinity, can be apprehended directly from eq 11. If one assumes the polymer-solute system to be athermal (i.e., $\Delta h_1^\circ = 0$), eq 11 becomes

$$\ln V_g = \ln c - \ln p_1^0 - (p_1^0/RT)(B_{11} - \bar{V}_1) + (P_o J_3^4/RT)(2B_{13} - \bar{V}_1) \quad (12)$$

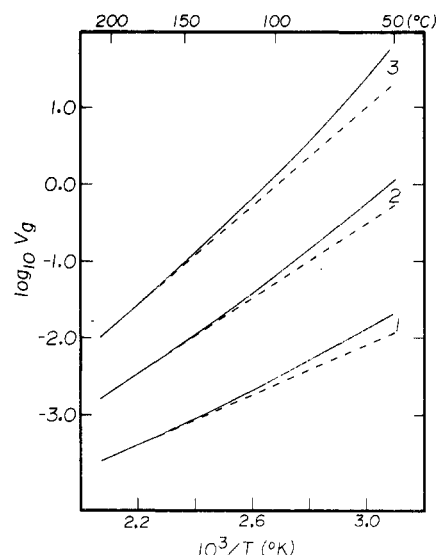


Figure 6. Computed retention diagrams (eq 13) for (1) *n*-octane, (2) *n*-dodecane, and (3) *n*-hexadecane. Dashed lines are linear extrapolations.

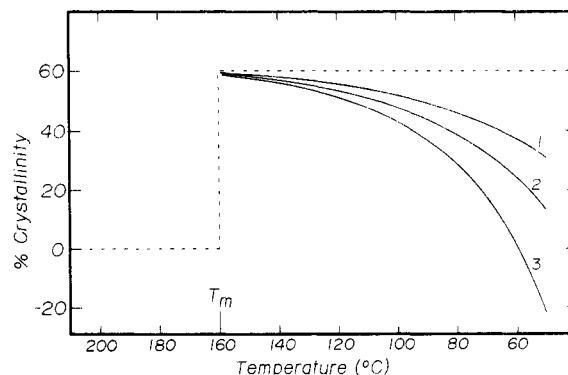


Figure 7. Computed melting curves for (1) *n*-octane, (2) *n*-dodecane, and (3) *n*-hexadecane using a linear extrapolation (180–210 °C). Dashed line is actual melting curve.

and since crystallinity is computed through a ratio of retention volumes (eq 7) one may set for the present purpose the constant c equal to 1, so that

$$\ln V_g = -\ln p_1^0 - (p_1^0/RT)(B_{11} - \bar{V}_1) + (P_o J_3^4/RT)(2B_{13} - \bar{V}_1) \quad (13)$$

Quite clearly the retention volume as given by eq 13 can be evaluated directly from literature data. Figure 6 shows retention diagrams computed from this equation over the range 50 to 210 °C for *n*-octane, *n*-dodecane, and *n*-hexadecane. The dashed lines correspond to linear extrapolations of the retention data in the temperature range 180–210 °C. The computations were carried out for nitrogen as carrier gas (B_{13}) with $P_o J_3^4$ equal to 1 atm ($P_o = P_i = 1$ atm). It is seen that as the temperature range is increased the linear approximation becomes less satisfactory. Furthermore, the difference between both methods of computation increases with the boiling point of the alkane probe. In the case of hexadecane at 50 °C the retention volume computed by eq 13 is about three times larger than the value obtained from a linear extrapolation. It is to be noted, however, that over a 30 °C range the retention diagrams are very nearly linear.

The effects of nonlinearity of retention diagrams on the resulting crystallinities are illustrated in Figure 7 for several probes. For simplicity it was assumed that the stationary

Table III
Heats of Solution for Selected Solutes in Different Temperature Ranges Computed from eq 13 (see Text)

Solute	Heat of solution, kcal/mol					
	180–210 °C			50–80 °C		
	1	2 ^c	3 ^{a,d}	1	2 ^c	3 ^{a,d}
<i>n</i> -Octane	8.519 ± 0.02	7.535 ± 0.015	7.526 ± 0.015	9.479 ± 0.020	9.385 ± 0.025	9.364 ± 0.025
<i>n</i> -Decane	9.993 ± 0.010	9.370 ± 0.018	9.359 ± 0.018	11.662 ± 0.024	11.628 ± 0.026	11.604 ± 0.026
<i>n</i> -Dodecane	11.656 ± 0.013	11.255 ± 0.020	11.242 ± 0.020	13.917 ± 0.038	13.906 ± 0.039	13.880 ± 0.039
<i>n</i> -Tetradecane	13.390 ± 0.018	13.136 ± 0.023	13.121 ± 0.023	16.448 ± 0.057	16.444 ± 0.057	16.416 ± 0.057
<i>n</i> -Hexadecane	15.140 ± 0.023	14.982 ± 0.026	14.966 ± 0.026	18.562 ± 0.036 ^b	18.560 ± 0.036 ^b	18.531 ± 0.036 ^b

^a N₂ carrier gas (*B*₁₃). ^b Temperature range 70 to 80 °C. ^c $P_o J_3^4 = 0$. ^d $P_o J_3^4 = 1$ atm.

phase melted sharply at 160 °C and had a crystallinity of 60%. The crystallinities were computed using a linear extrapolation of data in the range 180 to 210 °C. As observed experimentally, it was found that the computed crystallinities decreased steadily with increasing temperature range, even becoming negative. A negative crystallinity, while physically meaningless, is brought about when the experimental retention volumes become larger than the (linearly) extrapolated amorphous retention volume. It is to be noted that even at temperatures close to *T*_m the error introduced by linear extrapolation procedures is quite significant. Furthermore, this error is seen to increase regularly from octane to dodecane to hexadecane, i.e., with the boiling point of the solute (at least for *n*-alkanes).

To assess the magnitude and contribution of each term of eq 13 to the curvature of the log *V*_g vs. 1/*T* plot, heats of solution were computed over the two extreme temperature ranges, 180 to 210 °C and 50 to 80 °C. The heat of solution, $-\Delta H_s$, is derived from the slope of the retention diagram by the relation

$$-\Delta H_s = R[\partial \ln V_g / \partial (1/T)] \quad (14)$$

The results of these computations are given in Table III in kcal/mol, for the even-numbered alkanes from octane to hexadecane. In column 1 only the first term of eq 13 is considered, in column 2 the first two terms ($P_o J_3^4 = 0$), and column 3 corresponds to eq 13 with $P_o J_3^4 = 1$ atm. It is seen that the degree of curvature, related to the change in heat of solution between low- and high-temperature data, introduced by vapor pressure data (column 1) increases drastically with the boiling point of the probe. However, upon inclusion of the second term (column 2) the difference between low- and high-boiling solutes is very much reduced. Indeed the magnitude of this second term increases both with temperature and solute vapor pressure, amounting to nearly 1 kcal/mol for *n*-octane at high temperature, and consequently increasing the curvature of the low-boiling solutes. In comparison the magnitude of the last term, increasing with decreasing temperature, is almost negligible (10 to 30 cal/mol). It is worth noting that this term acts against the other two, reducing the degree of curvature, though only very slightly. The overall effect is to impart an increasing degree of curvature with increasing boiling point, consistent with the results of Figures 6 and 7.

Owing to the scarcity of experimental and computed cross virial coefficients together with the lesser magnitude of the third term of eq 13, this correction factor is most often omitted in GC data treatment, except for GC determinations of *B*₁₃.^{11,20,21} It was included in the present work to gauge its importance in the computation of crystallinities. It was found that its omission from eq 8 and 13 yielded essentially identical crystallinities for the results of Figures 3 and 7. In the case of

decane on polypropylene the difference in the computed crystallinity at 50 °C was less than 0.1%, smaller in effect than the magnitude of the correction term itself (0.7%). This was brought about through cancellation of errors incurred in both high- and low-temperature ranges. Quite clearly for absolute determinations of *V*_g and partial molar heats, particularly for nearly athermal systems, this correction ought to be included. It is felt, however, that a suitable set of experimental conditions would, in most cases, alleviate the need for correction. Unlike the second term of eq 13, *B*₁₃ is dependent on both the nature of the carrier gas and pressure in the column.^{11,16} By minimizing the latter and choosing a carrier gas, usually helium or hydrogen, where *B*₁₃ is nearly equal to $\bar{V}_1/2$, the magnitude of this term should become extremely small.

Needless to say, the results of the present study can also be instrumental in designing experimental conditions which would minimize errors in crystallinities computed from a linear extrapolation of high-temperature data. Considering the results of Figure 7 and Table III it is seen that it is desirable to use a volatile solute. Due to practical considerations, however, the latitude of choice is restricted by rapidly decreasing retention volumes with increasing solute volatility. Similarly it has been shown that the larger the temperature range investigated, the larger the discrepancy. While at temperatures below *T*_m polymer properties (melting range) preclude any gain, the temperature range above *T*_m can be reduced to the required minimum. Owing to the importance of high-temperature data, a sufficient number of retention data must be collected to ensure proper extrapolation, be it linear or curvilinear. Whenever possible, however, the curvilinear extrapolation should be used.

Conclusions

The effects of nonlinearity of gas chromatographic retention diagrams were investigated by collecting retention data over a large temperature range encompassing the polymer melting transition. It is found that the crystallinity computed from linear extrapolations of high-temperature data is reduced from its actual value because of the normal curvature of retention diagrams. The magnitude of the discrepancy increases with the temperature range investigated and the boiling point of the *n*-alkane solute. By including the proper correction terms in the treatment of high-temperature data, it is shown that physically meaningful crystallinities are derived. To obtain reliable crystallinities for polymers from retention data, both solute vapor pressures and second virial coefficients are required, particularly if the data are collected over a large temperature range. Since the necessary data are readily available for most hydrocarbon probes, it is suggested that this correction be applied generally whenever it is desired to obtain accurate crystallinity values by this method.

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Copolymer Chain Statistics. The Pseudo-Stereochemical Equilibrium Approach within the Continuum of Rotational States. The Unperturbed Dimensions of Atactic Polypropylene

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ABSTRACT: The double Fourier expansion method (asr scheme) to calculate the configurational integral of a polymer chain with energy interactions between first-neighboring skeletal rotations is adapted to the pseudo-stereochemical equilibrium statistical treatment of linear copolymers. The unperturbed dimensions of atactic polypropylene in the range 125–175 °C are obtained, after assuming the methyl group as a spherical body with a van der Waals radius of 1.85 Å, in agreement with previous calculations. Two different statistical models of d and l unit sequences are assumed; in either case the chains upon which our calculations are based obey very closely the (first-order) Markoffian rules for unit succession. The results are in good agreement with experimental results. It is confirmed that the convergence limit is achieved by pushing the Fourier expansion up to terms of about order 10, at the temperatures under consideration.

The statistical treatments of macromolecular chains in the unperturbed state, subject to energy interactions between rotational states around neighboring chain bonds, have aroused considerable interest in recent years. They enable the calculation of several averages correlated with experimental properties of polymer solutions, such as the average square dimensions of the molecular coil in the unperturbed theta state, their higher moments, the mean-squared optical anisotropy, the stress-optical parameter $\Delta\alpha$, etc.¹

Matrix methods based on the assumption that a suitable set of discrete rotations give a sufficiently adequate statistical description of the chain (rotational isomeric state, or ris scheme) have been proposed and successfully employed for homopolymers. Two distinct approaches may be recognized, namely the one proposed by Volkenstein,² Birshtein and Ptitsyn,³ Lifson,⁴ Hoeve,⁵ Nagai,^{6,7} and Corradini and Allegra,⁸ where attention is mainly focused on infinitely long chains, and that given by Flory,^{1,9} who proposes a generalized treatment for chains of any polymerization degree. Within the first approach the chain statistics are fully described by a convenient square matrix containing the statistical weights relative to the pairs of adjacent rotations on the general monomer unit by its largest eigenvalue and corresponding eigenvectors. Instead, Flory employs a larger matrix containing the statistical weights involving the terminal monomer units as well (generating matrix), obtaining all the relevant infor-

mation after a suitable process of matrix self-multiplication.⁹

If the chains contain different types of comonomer units, distributed according to some statistical law (copolymer chains), the above method of statistical-mechanical description cannot be applied. In fact, the problem is now complicated to a considerable extent by the existence of two interlocking statistics, the first of which is related with the specification of the comonomer unit sequence, while the other reduces to the usual statistics in the configurational space of the rotation angles and depends in turn on the unit sequence itself. Lehman and McTague^{10,11} have given an exact solution to this problem in terms of functional equations by assuming either a Bernoullian or a first-order Markoffian law for the comonomer unit distribution. In particular they have computed the temperature breadth of the helix-coil transition for DNA macromolecules characterized by different sequential statistics of the G-C and A-T base pairs.¹¹ Their model allows for two states on either type of units (i.e., base pairs), and it may also be applied directly, e.g., to a linear Ising ferromagnet containing two different types of spins. In the case that more than two states were to exist, it is likely that the Lehman-McTague approach would be more and more difficult to apply, since it should involve the numerical solution of functional equations in at least $(n - 1)$ variables (n = the number of states accessible to either unit).