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Pressure Dependence of Secondary Transitions. 6. T_{α_c} and T_{α_a} in Polyethylenes

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ABSTRACT: Isotherms of branched and linear polyethylenes from 20 to 200 °C at P = 1–2000 bars have been examined by a linear form of the Tait equation, $Y = P/b$, where Y is an exponential function of volume and b is the normalizing constant in the Tait equation. Isothermal V–P data from ca. 175 to 200 °C follow the linear Tait equation exactly with a single value of b. Lower temperature isotherms in the region of the secondary α_a (intercrystalline) and the α_c (intracrystalline) relaxations ($T_{\alpha_c} > T_{\alpha_a}$ at constant P) do not follow a single $Y = P/b$ line because of pressure-induced α_a and α_c relaxations. Instead, $n + 1$ $Y = P/b$ lines per isotherm are required with n intersections at pressures P_1^{i}, $P_2^{\mathrm{i}} - P_n^{\mathrm{i}}$, where $1 < n \leq 3$ for $P_{\max}$ of 2 kbars. A computerized intersection search method based on minimizing the standard error has been employed to locate these intersection pressures and to calculate the intercepts and slopes of the $n + 1$ lines needed to define each isotherm. The step increase in b at each pressure-induced transition is readily calculated. Results of the intersection search method were verified by linear regression analysis with residuals. Past practice in the literature with Tait analysis of isothermal V–P data tended to obscure the existence of secondary relaxations. Use of the linear form $Y = P/b$ with the statistical procedures used herein greatly extends the utility of the Tait equation in search for weak secondary transitions. Hence we judge the empirical Tait equation to be remarkably useful for representing isothermal V–P data when properly used. Values of T_{α_c} and T_{α_a} obtained by the above procedures and independently from isobaric V–T data are linear in P with pressure coefficients of 48–56 K/kbar for α_c and 50–60 K/kbar for α_a. The linear Tait method was applied to isothermal V–P data on two n-alkanes with P up to ca. 5 kbars. Exact linearity obtains with no evidence of transitions. Residuals, while small, are nonrandom.

Introduction

Previous papers in this series have employed variations of and approximations to the Tait equation to determine the pressure dependence of the T_{ll} transition in amorphous polymers,[1–3] the temperature dependence of the Tait parameter, b, above T_g,[4] the change in coefficient of expansion at $T_{\mathrm{ll'}}$ and $\mathrm{d}T_{\mathrm{ll}}/\mathrm{d}P$ from isobaric V–T data.[5] Isotactic PMMA has been studied to locate $T_{\mathrm{ll'}}$ using a linear form of the Tait equation.[6]

Here we employ this same linear variation of the Tait equation to analyze the P–V–T behavior of branched and linear polyethylenes (PE) with several objectives in mind: (1) to provide a rigorous test of the Tait equation using isothermal V–P data in the melt of PE where we anticipated no pressure-induced transitions other than T_m, (2) to study the premelting or intracrystalline process, designated as the α_c transition, lying at about $(0.85–0.90)T_m$; as well as the amorphous intercrystalline or α_a process lying just below the α_c event, and (3) to search the lower temperature isotherms from room temperature to T_m for amorphous-phase transitions, in particular for T_{ll}. In addition, we examine isobaric V–T data for confirmatory and/or supplementary information, especially in regard to the α_a and α_c processes.

A note on nomenclature: While melting at temperature T_m is a thermodynamic first-order transition, the glass-to-liquid transition, designated T_g, has relaxational character or frequency dependence. Still it has been designated as a transition by Fox and Flory.[7] Likewise the α_a and α_c processes have a relaxational aspect but are clearly revealed herein by P–V–T data. Various designations have been used in the literature for these two processes, e.g., α', α'', mechanism 1, mechanism 2, $\alpha_c(1)$, and $\alpha_c(2)$. We prefer α_a to symbolize an amorphous-phase event and α_c to symbolize the crystalline-phase event, especially since the molecular mechanisms are now well-known, as will be shown later. In treating isothermal V–P data we use the symbol P_n^{i} to indicate an intersection pressure corresponding to a transition or relaxation. n is a small integer denoting the number of the intersection along any isotherm going from low to high pressure. n seldom exceeds 3 for any polymer and in this study does not exceed 2. The corresponding symbol for isobaric V–T data is T_n^{i}, again with n not exceeding 2 for P not greater than 2 kbars.

Motivation for this study arose from the fact that we have been questioned on several occasions about the reliability of the Tait equation for locating weak secondary events, in part because of its empirical nature and in part because of a paucity of isobars. Even though it has been widely employed with polymers, major emphasis has always been on T_g and T_m, which are strong primary transitions. We concede however that a rigorous test of the Tait equation is desirable. One possibility is to locate a polymer that is completely free of secondary transitions in some region of P–V–T space. The melt of PE seemed, a priori, to meet this requirement, and indeed it does.

It apparently had been considered by some authors[8–12] that the seeming constancy of b across an isotherm constituted a verification of the Tait equation although Quach and Simha did find departure from Tait in the β region

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of PS and PoMS.[9] We have located similar deviations in the glassy state of other polymers, as well as in the T_{ll} region.[1-3,6] Our experience, other than for the high-temperature isotherms of PE to be reported now, is that b is almost never constant across an isotherm. The seeming constancy of b arises in part by calculating it from the origin, as will be more evident later from Figures 9 and 10.

General Comments on the Tait Equation

Following Simha and his collaborators,[9-12] the Tait equation is written in the isothermal form as

$$1 - V/V_0 = C' \ln (1 + P/b)_T \qquad (1)$$

where V is the specific volume in cm^3 g^{-1} at pressure P, V_0 is the corresponding quantity at a reference pressure, usually $P = 0$ bar, and C' is assigned a universal value of 0.0894. b is a constant across any isotherm that is free from a pressure-induced transition.

For computerized linear regression analysis, eq 1 is written in its linear form:[6]

$$Y_T = \exp[(1/C')(1 - V/V_0)] - 1 = P/b \qquad (2)$$

where the subscript on Y signifies an isotherm and where all of the symbols have the same meaning as before. Our experience with most amorphous polymers studied thus far is that Y_T is not linear in P over an entire isotherm either above or below T_g, presumably because of a pressure-induced secondary transition(s). Instead, plots of P/b against P consist of two or three linear segments whose intersection pressures, $P_n{}^{\mathrm{i}}$, are considered to denote transition or relaxation pressures for a specific isotherm (see Figure 1 of ref 6 and Figures 4 and 6 of this report). Strictly speaking, the right-hand side of eq 2 should read $(P - P_0)/b$,[6] where P_0 is the reference pressure, which is 1 bar in the present case. We have assumed $P = 1 \equiv P = 0$.

While visual inspection of P/b plots locates transition pressures approximately, more rigorous criteria are desirable to cope with subjective judgment, scatter in the data, and an insufficient number of isobars along an isotherm, especially if there are several transitions and/or if any P^{i} value is close to either extreme of pressure. Two methods have been devised and tested in ref 6.

1. An automatic computer search method is used to locate the intersection(s) between two, three, or four straight lines which will minimize the standard error for the two-, three-, or four-line fit. This method, developed by K. Šolc of our Institute is described in detail in ref 6.

2. A residuals method employing computer calculation of RES/SE as a function of P is used, where RES represents a residual and SE is the standard error in Y(calcd). The computer fits the linear least-squares regression line to the Y values with the line constrained to pass through $P = 1$ and $P/b = 0$. RES then is defined as Y(obsd) − Y(calcd). (For details consult our recent review article[13] or any standard text on statistics, for example ref 14 or 15.)

Experimental Section

While this study consists of statistical analysis of published P–V–T data, the procedure by which the data were obtained is relevant. Olabisi and Simha[12] used the experimental procedure developed by Quach and Simha[9] as follows. Pressure was increased in increments of 100 bars to 400 bars and then of 200 bars, using a pressurization rate of 400 bars h^{-1}. Volume was observed for at least 15 min after each pressure increment to be certain that equilibrium was achieved. Hence the data can be considered as quasi-equilibrium specific volumes. Three specimens were employed: linear PE, density 0.9794 g cm^{-3}, estimated crystallinity 85%; branched PE, density 0.9320 g cm^{-3}, estimated crystallinity 50%; and high molecular weight (HMW) linear PE, density 0.9268 g cm^{-3}, estimated crystallinity 50%. In all three cases, 17–18 isotherms were employed at about 10 K intervals from ca. 20 to 200 °C, with pressures to 2 kbars.

Table I
Pressure Coefficients, dK/dP, for Linear Polyethylene

transition or relaxation desig	nominal temp at $P = 1$ bar, K	dK/dP, K/kbar	method for dK/dP	ref
$T_{\mathrm{u}}{}^{a}$	492		–	16
T_{m}	403	27[g]	P–V–T	12
$T_{\alpha_{\mathrm{c}}}{}^{b}$	353	16–28[h]	*i*	17
$T_{\alpha_{\mathrm{a}}}{}^{c}$	293	17	*i*	
$T_{\beta}{}^{d}$	243	32	NMR	18
$T_{\gamma}{}^{e}$	150	13	NMR	18
$T_{ll}{}^{f}$	240	120	calcd	19

[a] A transition occurring near 1.2 T_{m} in n-alkanes and many crystalline polymers. Krüger[16] considers it to arise from breakup of smectic-like structures. [b] An intracrystalline relaxation discussed in the text. [c] An intercrystalline amorphous-phase relaxation discussed in the text. [d] A glass transition influenced by the presence of crystallinity. Our designation is T_g(u) although it frequently appears in the literature as T_β. [e] A secondary glassy-state relaxation, considered by some to be the true T_g of PE. [f] The liquid–liquid amorphous-phase relaxation. [g] Similar values were found for branched and HMW linear PE's based on tabulated data in ref 12. Values as high as 40 have been reported in the literature. [h] The high value of 28 is for an ethylene–vinyl acetate copolymer. Higher values are indicated for both linear and HMW linear PE in this report. [i] Pressurized torsion pendulum.

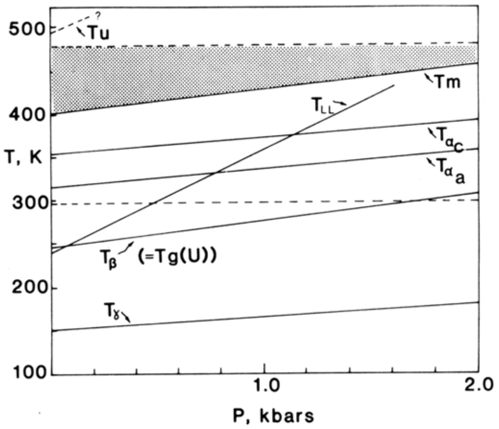

Figure 1. Loci in the T–P plane of all known transitions and relaxations for linear PE, suggesting a transition-free region in the cross-hatched trapezoidial area. Upper and lower dashed lines show range of isotherms studied in ref 12 for linear PE. (See Table I for details.)

Transition and Relaxation Behavior of PE in P-V-T Space

The multiple transition and relaxation behavior of branched and linear PE is well-known as a function of T at $P = 1$ bar and less well-known as a function of T and P at $P > 1$. Table I collects such information suitable for present needs.

Figure 1 is a temperature–pressure plot showing the loci for each of the transitions and relaxations listed in Table I. It is clear from this arrangement that there is a trapezoidal-shaped window between T_{m} and the top isotherm studied, through which one should not be able to observe any transition or relaxation. The polymer should be in the true liquid state except for the possible presence of secondary structure implied by the existence of T_{u}, which Krüger et al.[16] ascribe to a smectic-like structure. The top several isotherms can therefore be tested against the linear Tait equation along the entire isotherm.

At the same time, it is clear that the region between T_{m} and the lowest measured isotherm might reveal departures

Table II
Tait Equation Parameters for Liquid State of Linear PE

		linear least-squares regression[a]			calcd from arithmetic av of indiv values of b[b]					
isotherm, °C	no. of isobars	b	R^2[c]	SE in (P/b)(calcd), units of 10^{-2}	no. of values b	$\bar{b}$,[d] bars	σ[e]	range, bars	$\sigma/\bar{b}$, %	range/$\bar{b}$, %
199.7	12	696.28	0.99999	0.3289	12	696.58	1.4410	694.7–698.8	0.207	0.589
189.6	12	725.01	0.99998	0.4216	12	725.17	1.6245	722–728	0.224	0.827
180.9	12	763.13	0.99994	0.6857	11	766.82	1.6959	757–764	0.223	0.920
171.1	11	795.23	1.00000	0.1417	10	797.30	2.8302	795–804	0.355	1.129
165.4	9	821.42	1.00000	0.1204	8	823.75	1.5612	821–826	0.190	0.607
152.9	7	862.96	0.99999	0.0892	6	864.3	0.943	863–866	0.109	0.347

[a] Parameters of linear least-squares regression line of slope $1/b$ constrained to pass through the origin. [b] $1/b = (P/b)/P$. [c] Coefficient of correlation. [d] There is a mild oscillation of b about the average but no systematic trend across the isotherm. [e] Defined as $([\sum x^2 - (\sum x)^2/n]/n)^{1/2}$.

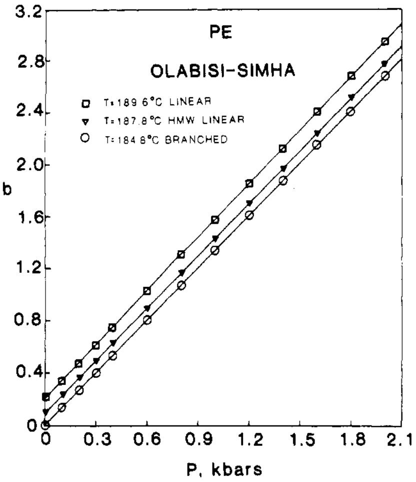

Figure 2. Equation 2 linear Tait plots for the indicated isotherms of linear, HMW linear, and branched PE's. The least-squares regression lines are displaced 0, 0.1, and 0.2 unit of P/b to avoid confusion near the origin.

from ideal Tait behavior. Since α_c is intracrystalline, it should be strongest in the linear PE data of ref 12. The intracrystalline α_a and $T_{ll'}$ both amorphous-phase events, should be stronger in the HMW linear PE and branched PE of ref 12. The liquid state and the α_c α_a regions will be examined in that order. All isotherms have been studied, including those just above T_m, in which pressure-induced freezing occurs.

Concerning the existence of the window in Figure 1, polyethylene is somewhat unique because its melting point is relatively low, as is dT_m/dP. Also, its glass temperatures and secondary relaxations occur far below room temperature and have relatively low pressure coefficients. Moreover, it is thermally stable in the absence of oxygen. T_g and T_β can be observed at $T >$ room temperature only at pressures in excess of 2 kbars.

Linear Tait Equation at $T > T_m$

Figure 2 shows for branched, linear, and HMW linear PE's eq 2 least-squares regression lines constrained to pass through $P/b = 0$ and $P = 1$, as required by eq 2. The upper two lines have been displaced vertically by 0.1 and 0.2 unit respectively to avoid confusion near $P = 1$. It is evident visually that the fits are extremely good. Slight differences in slopes arise in part because of small differences in temperature but also in part because of differences in structure.

Figure 3 shows the residuals patterns for these same three sets of data as plots of RES/SE against P. The patterns are nonrandom, but in a manner suggestive of secular changes rather than pressure-induced transitions. Secular changes might involve systematic errors in the pressure and/or the temperature readings. The residuals would be more random about zero, especially at low pressures, if unconstrained least-squares lines had been employed. Moreover, the standard errors in P/b(calcd) are so small in each case, that the RES/SE values appear to be large. The SE values in P/b(calcd) are from 0.16 to 0.32%, using a midrange value of P/b from Figure 2.

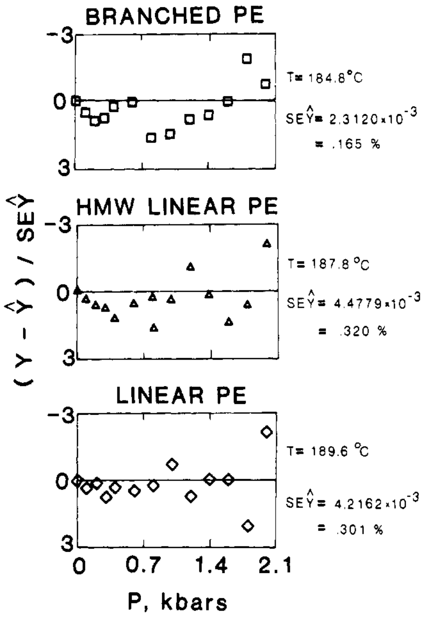

Figure 3. Residuals/standard error in P/b calculated, RES/$\mathrm{SE}(\hat{Y})$, for the three isotherms of Figure 2. The mild nonrandom pattern suggests the absence of any transitions or relaxations. Residuals are unweighted.

As a further check on the conclusion that the Figure 3 residuals patterns do not indicate real transitions, weighted and unweighted $y = P/b$ values were examined by the automatic intersection method. For linear PE, the one-line fit had the smallest standard error with both weighted and unweighted residuals. Branched PE actually showed the smallest standard error with a four-segment fit but the slope changes expressed as percentages were −1.63, +2.26, and −1.76%, i.e., too small to be significant and alternating in sign instead of all being negative as required for a major transition or relaxation (see Figure 9). HMW linear PE favored a two-line fit but the slope change was only −1.18%. Standard errors were smaller for weighted values by factors ranging from 18 to 29. Again we conclude that the Tait equation is obeyed quite well for all three types of PE shown in Figures 2 and 3.

Table II collects for linear PE the parameters derived from eq 2 plots of all liquid-state isotherms from 152.9 to 199.7 °C. The statistical parameters in this table appear to be consistent with high-quality data free from any

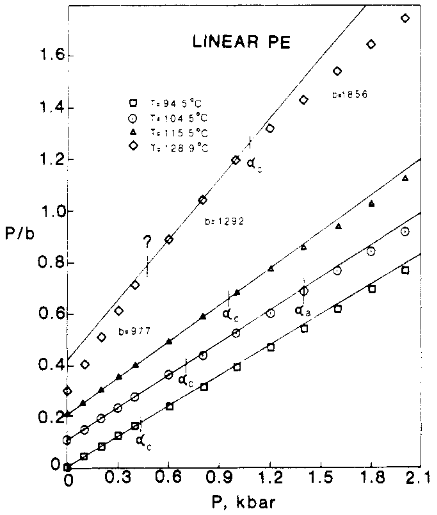

Figure 4. Tait eq 2 plots for the four indicated isotherms of linear PE in the α_c region. Each successive isotherm after the first is displaced vertically by 0.1 unit of P/b. Computerized regression lines are constructed through points as shown to emphasize deviations from Tait behavior at higher pressures. Slope change with question mark is explained in text.

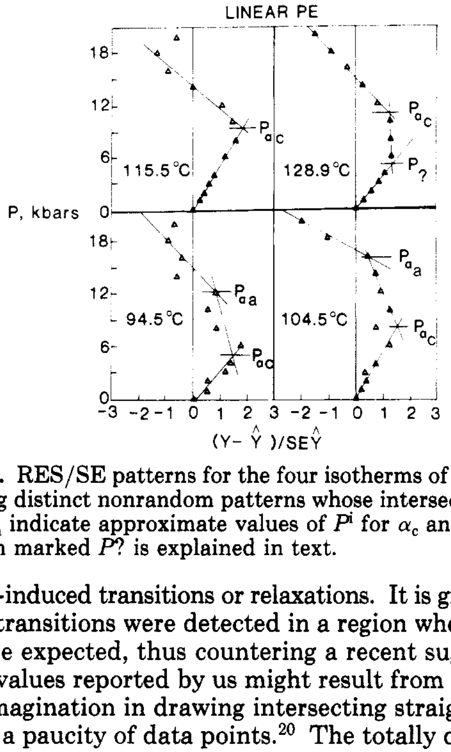

Figure 5. RES/SE patterns for the four isotherms of Figure 4, indicating distinct nonrandom patterns whose intersections for α_c and α_a indicate approximate values of P^i for α_c and α_a. Intersection marked $P?$ is explained in text.

pressure-induced transitions or relaxations. It is gratifying that no transitions were detected in a region where none was to be expected, thus countering a recent suggestion that T_{ll} values reported by us might result from an overactive imagination in drawing intersecting straight lines through a paucity of data points.[20] The totally different pattern in the α_c–α_a region (Figures 4 and 5) is in marked contrast to the results just shown.

α_c and α_a Processes

A dynamic mechanical loss peak lying just below T_m and commonly designated α_c was observed first by Schmieder and Wolf.[21] It was subsequently shown by Nakayasu et al.,[22] using creep studies, that there were two processes, α_a and α_c, with $T_{\alpha_c} > T_{\alpha_a}$. Extensive early background for α_c appears on p 358 of MacCrum et al.[23] Since α_c is intracrystalline in origin, it is best observed in polymer single crystals,[24] where there should be little or no interference from α_a. Alternately, one can use techniques that observe only the crystalline phase. For example, Peterlin and Meinel[25] measured the refractive index (RI) of a toluene suspension of linear PE single crystals as a function of temperature. Takayanagi et al.[26] used X-ray diffraction to measure the a and b axes of both branched and linear bulk-crystallized PE. We subsequently showed[27] from literature values of T_{α_c} the empirical relationship

$$T_{\alpha_c} = 0.85 + 25/T_m \text{ (K)} \tag{3}$$

which is consistent with α_c being a premelting process that might be considered as a precursor of T_m.[27]

Kajiyama et al.[28] subjected dynamic mechanical loss data on bulk-crystallized PE to mathematical analysis which resolved α_a and α_c with activation enthalpies of 32 and 46 kcal/mol, respectively. They discussed the nature of α_a as occurring in the amorphous phase between crystals. α_a is called a grain boundary relaxation whose detailed nature has been studied, for example, by Suehiro et al.[29,30]

Figure 5 of ref 28 is a plot of log f (Hz) against reciprocal T_{α_a} and T_{α_c} for linear PE (bulk crystallized) from which one can extrapolate to T_{α_a} (=25 °C; T_{α_c} = 55 °C at $f = 10^{-2}$ Hz). The effective frequency in a P–V–T experiment is of the order of 10^{-3}–10^{-4} Hz. T_{α_c} increases with stem length of the chain-folded crystallized PE, and stem length depends on thermal history.[31] However, we can expect that T_{α_a} and T_{α_c} at P = 1 bar will be near the temperatures just cited.

The existence of α_a and α_c, as well as the distinction between them, and their respective characteristics are thus well documented. Their detectability in P–V–T data remained to be determined. The refractive index and X-ray diffraction experiments indicate clearly that there is enhanced thermal expansion of the crystallites above T_{α_c}, which suggests that there should be an increase in compressibility. Hence α_c should be observable in isothermal V–P data and isobaric V–T data, which is indeed the case (see later). α_a has been designated as a viscoelastic process[28] and presumably it should be revealed in P–V–T data, since other viscoelastic processes such as the β relaxation are. This also was found to be correct.

Figure 4 gives Tait equation plots based on the data of Olabisi and Simha[12] for linear PE at the designated isotherms. A linear Tait equation regression line was computer drawn through the lowest isobars as shown, with sharp departure of the points at higher isobars evident by inspection. The intersection pressures are as indicated. Residuals plots for the same isotherms appear in Figure 5. There can be no doubt of a temperature-dependent departure from simple Tait behavior, indicative of a transition (relaxation), which we consider to be T_{α_c}. This is further confirmed by the automatic intersection search for the P/b–P data which locates exact intersections shown later in Figures 7 and 8.

The 104.5 °C isotherm residuals plot suggests a second transition near 1500 bars, which should represent T_{α_a}. It is too weak and/or at too high a pressure to show up in other isotherms. It is best observed, as predicted, in the HMW linear PE.

Plots similar to those of Figures 4 and 5 were computer drawn for HMW linear PE but are not shown. The main difference is that α_a is more readily observed than with linear PE.

Freezing Range Isotherms

For isotherms above T_m at P = 1, application of pressure induces freezing at pressures noted by Olabisi and Simha[12] in their Table V. It was of interest to ascertain if the newly formed crystalline phase exhibited the α_a and/or the α_c processes. Figure 6 is a plot of four isotherms below, at, and above T_m at P = 1 for linear PE and HMW linear PE. The 91.5 °C isotherm reveals both α_c and α_a. Isotherms at 142.1 and 157.5 °C show a freezing process followed by a single strong slope change which is considered to be α_c with intensity enhanced by the high-temperature and/or

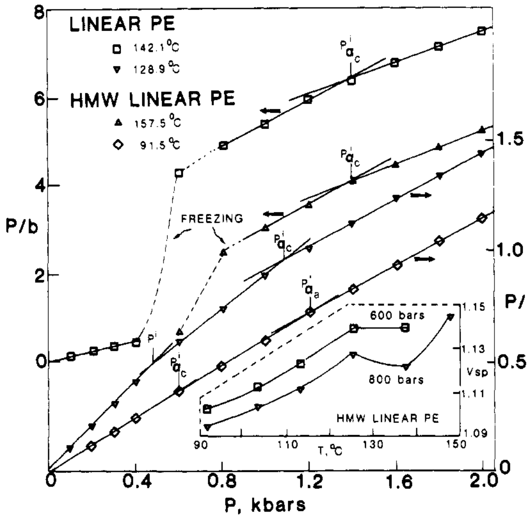

Figure 6. P/b plots below and in the freezing range for the indicated isotherms and polymers, showing the presence of the α_c process. The slope change at ca. 500 bars for the 128.9 °C isotherm represents a reversal of the premelting process (see text). The inset shows V_{sp}–T for two isobars of HMW linear PE in the premelting range showing a halt and a reversal in V_{sp}.

folded-chain crystals perfected more than normal by having been formed under pressure at higher than normal temperature.

The $P^i \sim 500$ bars intersection in the 128.5 °C isotherm was at first extremely puzzling. It seemed to represent a retrograde variation of α_c with pressure or else a failure of the linear Tait method. However, the following interpretation appears more likely in view of the proximity of this isotherm to T_m. The experimental evidence for the melting process proposed by Fulcher et al.[32] shows that, starting a few degrees below T_m, the thickness of the crystalline regions decreases rapidly while that of the amorphous regions increases. We suggest that application of hydrostatic pressure just below T_m reverses this process and gives prefreezing as the opposite of premelting, just as pressure applied to the melt, as in the 142.1 and 157.5 °C isotherms, induces freezing. The sharp increase in b from 977 bars below P^i to 1292 bars above P^i at 128.5 °C is consistent with such a picture.

A similar transition pressure was found at 500–600 bars for both the 103.4 and 113.7 °C isotherms of HMW linear PE (not shown). The prefreezing interpretation was suggested by noting the course of isobaric V_{sp}–T data at 600 and 800 bars in the temperature range 90–150 °C for HMW linear PE. This is shown as an inset to Figure 6. At 600 bars V_{sp} flattens out; at 800 bars V_{sp} decreases momentarily, just prior to the catastrophic melting process.

We are not aware of any previous mention of this reversal. However, the analogous situation with regard to T_g is known. For example, Quach and Simha[9] have shown a decrease in V_{sp} with T at 2 kbars on going from the glass to the liquid (see their Figure 5 for PS and their Figure 6 for PoMS). A similar effect was noted by Quach, Wilson, and Simha[11] at 1.2–2.0 kbars for isotactic PMMA (their Figure 2). See also Figure 6 of Hellwege et al.[36] for another example of PS.

Room-Temperature Isotherms of High Molecular Weight Linear Polyethylene

Because of its low amorphous content, we elected not to study linear PE around room temperature in search of possible amorphous-phase events but rather to concentrate on HMW linear PE and, to a lesser extent, on branched PE.

Table III
Approximate Strength of α_c and α_a Relaxations[a]

press, bars	$\Delta(d\rho/dT)$, 10^{-4} g cm^{-3} K^{-1} across T_{α_a}[b]	 across T_{α_c}[b]
	A. Linear PE	
1	*c*	2.66 (78)
300	0.24 (37)	2.77 (89)
600	0.46 (54)	3.21 (95)
800	1.07 (75)	*d* (101)
	B. HMW Linear PE	
1	0.53 (32)	2.57 (69)
300	1.08 (57)?	3.06 (89)?
600	0.88 (52)?	2.40 (83)?
800	2.30 (74)	*d* (104)

[a] Measured by approximate slope changes in density–temperature plots. [b] Numbers in parentheses are relaxation temperatures in °C. [c] Too weak to observe. [d] Too much curvature above T_{α_c}.

The 18.7 °C isotherm of HMW linear PE reveals a weak slope change in a P/b–P plot at about 300 bars and a stronger one near 1600 bars. The latter is most likely the T_β of Figure 1. Both processes occur in the 33.4 °C isotherms but at slightly higher pressures. At 44.0 °C there are complications from the α_a process.

The low-pressure process might be T_{ll}, for which we had previously assigned a value of 233 K at $P = 1$ bar.[33] We have developed[2] an empirical rule

$$dT_{ll}/dP = (28000T_g^{-1}) - 20$$

which leads to a pressure coefficient of about 125 K/kbar for $T_g(L) = 193$ K, where $T_g(L)$ is the lower T_g of amorphous PE. Such an extremely high-pressure coefficient gives a predicted locus starting at 233 K which cuts across T_{α_a}, T_{α_c}, and even T_m. Isotherms at 103.4 and 113.4 °C reveal sharp slope changes around 1100 and 1200 bars, respectively, both of which fall very close to the calculated T_{ll} line and to the left of the loci for T_{α_a}. Increases in b were 124 and 248 bars, respectively. Lack of isotherms below 18.7 °C and interference from T_{α_a} mean that assignment of this event to T_{ll} is very tentative. The points and the line are shown in Figure 8.

Isobaric V–T Data

In principle, one should be able to locate T_{α_c} in isobaric V–T plots. In practice, it is not simple as we noted on a previous occasion (Figure 28 of ref 34) since premelting appears to start just above T_{α_c}, resulting in marked upward curvature in the V_{sp}–T plots. Curvature is not as marked near T_{α_a}. We found that curvature was slightly less in both regions for density–temperature plots (not shown) for linear and HMW linear PE's at several isobars each. Plots of ln ρ vs. $(T, \mathrm{K})^{1.5}$ were free of curvature for linear PE. Numerical values of the slope changes, $\Delta(d\rho/dT)$, across T_{α_a} and T_{α_c} are collected in Table III. While the values listed are approximate because of slight curvature in the plots, they confirm expectations, namely, that α_c is much stronger than α_a in linear PE while α_a(HMW linear) is stronger than α_a(linear), consistent with the origin of α_a in the amorphous phase. The reverse situation appears to be true for α_c, confirming the origin of α_c in the crystalline phase.

Such T_{α_a} and T_{α_c} values are, of course, independent of any assumption about the existence or validity of the Tait equation and moreover provide values of these quantities at low pressures nor normally accessible to eq 2 treatment.

Pressure Dependence of T_{α_c} and T_{α_a}

Having examined all pertinent isotherms, we constructed temperature–pressure maps for linear PE in Figure 7 and for HMW linear PE in Figure 8. Pressure coefficients in

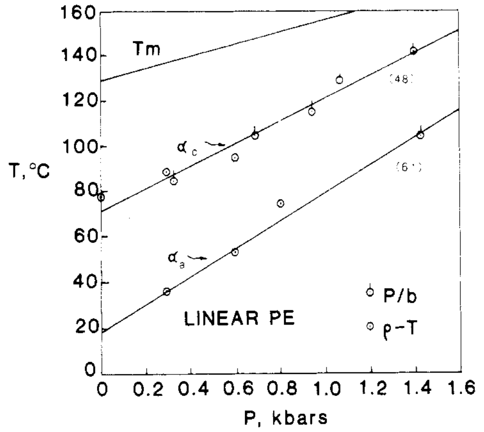

Figure 7. Temperature–pressure map for linear PE based on best values of P_n^i for each isotherm examined. Numbers in parentheses are pressure coefficients in K/kbar.

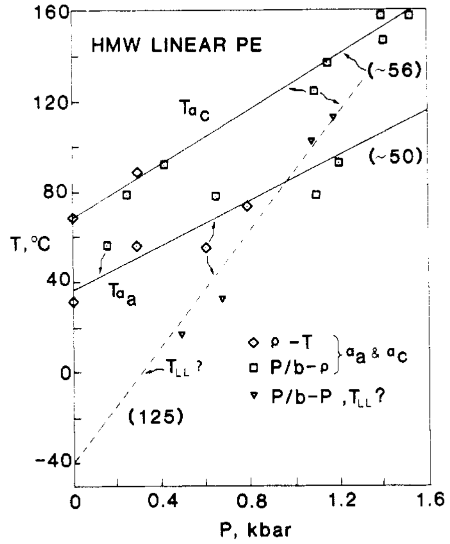

Figure 8. Same as Figure 7 but for HMW linear PE. The line cutting across T_{α_c}, T_{α_a}, and T_m possibly represents T_{ll}.

K/kbar are shown beneath each line. Several general statements can be made:

(a) The pattern is relatively unambiguous for linear PE compared to HMW linear PE.

(b) The latter pattern is clearly complicated by the presence of a third process, tentatively labeled T_{ll}. T_{α_c} is better defined for each polymer than is T_{α_a}.

(c) In Figure 7, the slope is greater for T_{α_a} than for T_{α_c} whereas the situation is reversed in Figure 8. This presumably represents an interplay between morphology and crystallinity and their combined effect on compressibility.

(d) We have no explanation as to why our pressure coefficients are so much higher than those of Parry and Tabor[17] unless it is a consequence of their dynamic technique (1 Hz) in contrast to the quasi-equilibrium approach of Olabisi and Simha.[12] The fact that isothermal V–P results at higher pressures were consistent with isobaric P–T results at low pressure strengthens confidence in our results.

(e) We believe that this is the most exhaustive analysis of the α_c–α_a region of PE yet presented in terms of quasi-equilibrium data.

b-*P* Data

It is well-known that the Tait parameter b increases significantly under isothermal conditions across a primary transition such as T_g.[8-12] We noted its increase across a weak secondary relaxation such as T_{ll}.[1,2,6] As already evident from Figure 2 and Table II, b is constant across the high-temperature isotherms of PE because there are no pressure-induced processes above T = 175 °C. There should be step increases in the α_a and α_c regions.

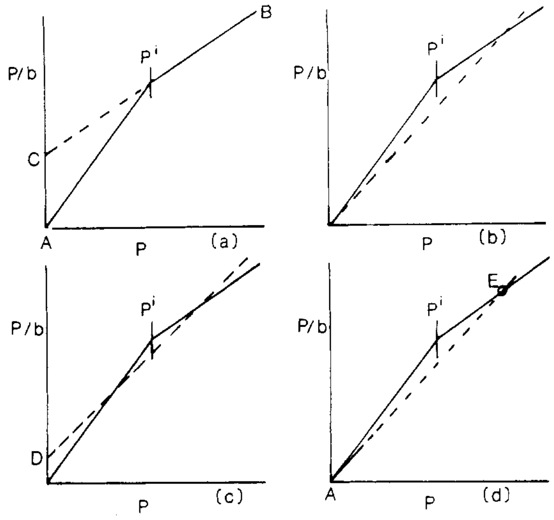

Figure 9. Schematic P/b–P plots with origin at A (P = 1, P/b = 0), a transition at pressure P^i, and definitions of various regression lines and methods to calculate b as follows: (a) method of locating new origin at C for line P^i–B; (b) least-squares line constrained to pass through A with intercept at $-(1/b)$; (c) unconstrained least-squares lines with positive intercept at D; (d) incorrect method to calculate b above P^i as reciprocal of slope of line A–E.

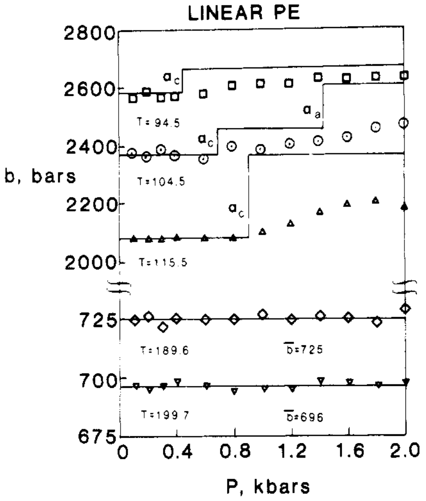

Figure 10. Top three plots: b vs. P in the α_c region of linear PE. Points represent b calculated in relation to the origin A–E of Figure 9 while solid lines show true b values calculated below P^i from the slope A–P^i and above P^i by the slope C–P^i–B. Bottom two lines are values of b for melt isotherms.

There are two methods for calculating b, indicated in Figure 9. One is to use the origin, P = 1, P/b = 0, as the reference. This is convenient but wrong, as we noted in Figure 2 and the related discussion of ref 2. Instead, once a pressure-induced transition occurs, a transformed material is present and its isothermal V–P behavior should be referred to a new origin at P^i and the related value of P/b or at the extrapolated value of P/b at P = 0. Fortunately, the automatic intersection method of Šolc gives both the intercept and the slope of the line passing through P/b at P^i, or, if there are several intersection pressures, the lines through P_1^i, P_2^i, etc. b is the reciprocal of any such slope.

We suggest one reason that these secondary relaxations have been missed is that b is calculated with regard to the

Table IV
Strength of α_c and α_a from Δb[a]

isotherm, °C	Δb, bars across α_c	 across α_a
A. Linear PE		
89.5	74	[b]
94.5	71	[b]
104.5	85	155
115.5	294	[c]
128.9	511	[c]
B. HMW Linear PE		
79.2	67	37
91.5	34	127
103.4	40	117
113.4	36	223

[a] Δb is the increase in the Tait parameter, b, across α_c and α_a, calculated from automatic slopes. [b] Too weak to measure. [c] Out of pressure range.

original origin. The change in b is minimal, as seen in Figure 10. Even so, one notes occasional examples in published data where b does increase slightly across an isotherm (see Figures 3 and 4 of ref 9).

Figure 10 compares the two methods for linear PE in the α_c region. The points refer to $P = 1$, $P/b = 0$ as the origin. The solid lines are taken from the automatic intersection method. The points both suggest a diffuse transition and also underestimate the value of b above T_{α_c}. The lines suggest an extremely abrupt and relatively strong transition. The truth may be in between, but closer to the solid lines as regards intensity.

It is our belief that the present study constitutes the first detailed analysis of α_a and α_c behavior based on isothermal V–P and isobaric V–T data in linear PE. The pressure coefficients are likely the most reliable yet reported.

Table IV collects representative strengths of the α_a and α_c relaxations based on the change in b across P^i, namely, Δb, where b below P^i is the inverse of the slope for A-P^i in Figure 9 and b above P^i is the inverse of the slope C-P^i-B in Figure 9. These slopes are calculated by the automatic intersection search method of Šolc.[6]

Constrained vs. Unconstrained Tait Lines

Polyethylene data provide an opportunity to test the use of constrained vs. unconstrained P/b plots as represented in Figure 9. This is readily done by comparing a transition-free isotherm in linear PE such as 189.9 °C with one of the α_c region such as 115.5 °C. Constrained P/b plots satisfy the Tait criterion for linearity but might be considered to put undue weight on a single point, $P/b = 0$ at P(ref) = 1 bar, even though this point is used to calculate all values of P/b. An unconstrained line represents a least-squares fit to all P/b values, giving them equal weight. At 189.9 °C the equation for the constrained line is

$$Y_c = -0.0013793 + 0.0013793P \tag{4a}$$

with slope and intercept identical as they must be for a reference pressure of 1 bar. The equation of the unconstrained line is

$$Y_u = -0.00029077 + 0.0013781P \tag{4b}$$

The intercept is essentially zero, and the two slopes are nearly identical. For the 115.4 °C isotherm, the equation of the constrained line is

$$Y_c = -0.00046226 + 0.00046226P \tag{5a}$$

In sharp contrast, the unconstrained line equation is

$$Y_u = +0.0086812 + 0.00045554P \tag{5b}$$

The large positive intercept, compared to the numerical value of the slope, a factor of 19, is prima facie evidence for one or more pressure-induced transitions, as was already evident in the P/b plot of Figure 4 or in the schematic P/b–P plot of Figure 9. Hence the linear regression line equation for an unconstrained fit is an extremely simple test for a pressure-induced transition or relaxation. The magnitude of the positive unconstrained intercept is a measure of the strength of the transition at pressure P_1^i or, if there are several transitions, of their combined strengths.

At the same time, the magnitude of the standard error in Y will be greater for the constrained line than for the unconstrained line. It, too, is a measure of the strength of one or several pressure-induced transitions. A log–log plot (not shown) of unconstrained intercepts vs. constrained standard errors is linear with unit slope over 2 orders of magnitude of each variable. The correlation fails as both quantities approach zero.

This technique of comparing the parameters of constrained lines is very simple to apply but does not readily locate intersection pressures. By comparing results for the first four or five data points, the first eight to ten data points, and all of the points, one can make a rough judgment of where the transition(s) is (are) located.

Dependence on Pressure of Isothermal Compressibility and Bulk Modulus

Independently of any assumptions about the exact dependence of some function of V on P, one can invoke the definition of isothermal compressibility, κ, as

$$\kappa = -(1/V)(\partial V/\partial P) \tag{6}$$

and calculate κ for any body of isothermal V–P data. One can also calculate the bulk modulus, $\bar{K}$, as $(\kappa)^{-1}$. It was known from early P–V–T studies on polymers that a discontinuity in κ (and hence in $\bar{K}$) occurred across T_g. $\Delta\kappa$ at T_g was then used to check the several Ehrenfest relationships as was done, for example, by Breuer and Rehage,[35] Hellwege et al.,[36] Heydemann and Guicking,[37] and Oels and Rehage.[38] None of these papers was concerned with the Tait equation, which was first employed on polymers by Nanda and Simha[39] and by Gee.[8]

We first calculated κ and then $\bar{K}$, using point-to-point derivatives $\Delta V/\Delta P$ for the 189.6 °C isotherm of linear PE. A hand plot of $\bar{K}$–P appeared linear to the eye. A linear regression line for the $\bar{K}$–P plot had the equation

$$\bar{K} = 7909 + 11.50P \tag{7}$$

with $R^2 = 0.9924$ and a standard error in $\bar{K}$(calcd) of 665 bars, which is 3.3% of a midrange value of 20000 bars for $\bar{K}$. Residuals were random, with eight crossovers from plus to minus for 12 data points. Scatter was greater than in Figure 2 but such is typical of point-to-point derivatives. The absence of any transition across this isotherm was confirmed. A plot of κ–P (not shown) was curved continuously concave upward.

Figure 11 shows a $\bar{K}$–P plot of this isotherm, along with the 115.4 °C isotherm of linear PE and the 79.2 °C isotherm of HMW linear PE. The latter two show discontinuities in $\bar{K}$ at pressure corresponding to α_c and α_a, respectively, whose values from Figures 7 and 8 are indicated with vertical arrows.

Hence this simple exercise confirmed what was already known from application of eq 2 to these same isotherms. Of course, we were aware of Wood's treatment[40] of eq 1, from which he derived the result

$$\bar{K} = (b/C')(1 + P/b) \tag{8}$$

whose slope is $1/C' = 11.186$. The slope of the regression

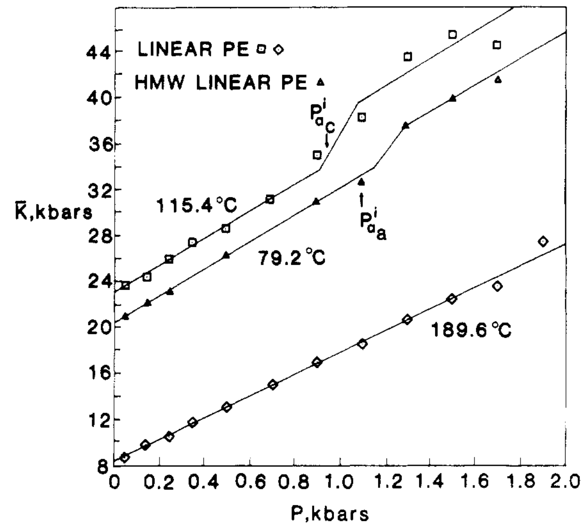

Figure 11. Bulk modulus obtained from point-to-point derivatives, $V_i(\Delta P/\Delta V)$, for the indicated PE's at the listed isotherms. Intersection pressures from linear Tait plots are indicated.

line for the 189.6 °C isotherm is 11.499. Wood further demonstrated the presence of a step jump in $\bar{K}$ resulting from the glass transition of natural rubber data which he used as a test case. The step jumps in α_a and α_c in Figure 11 are consistent with Wood's prediction.

Isobaric V-T Data above T_m

As a check on conclusions already reached, the isobaric V_{sp}-T data were examined above T_m at pressures of 1, 100, and 200 bars for the two linear PE's. There was no evidence for any transition, thus confirming the isothermal V-P results.

In the case of HMW linear PE, V_{sp} data at 178.3 °C appeared to be in error for all three pressures and were discarded, leaving only five points from 147.2 to 199.5 °C. The data appeared to be exactly linear at all three isobars. In fact, standard errors were slightly greater for quadratic and cubic fits than for the linear; with linear PE, seven data points were used from 142.1 to 199.7 °C. Standard errors were marginally better for quadratics and cubics but coefficients for the cubic alternated in sign for all pressures. The point at 142.1 °C may have been too close to T_m.

Discussion of Results

The isothermal V-P data of Olabisi and Simha[12] offer an opportunity to subject the Tait equation to two very rigorous tests: (a) its ability to provide an exact description of V-P data across isotherms for which there are no known pressure-induced transitions. (b) its ability to detect two well-known weak secondary relaxation processes, α_a and α_c, by means of departures from an exact linear form of the Tait equation and to estimate their pressure coefficients, $\mathrm{d}(T_{\alpha_a})/\mathrm{d}P$ and $\mathrm{d}(T_{\alpha_c})/\mathrm{d}P$.

Moreover, α_a and α_c are detected, albeit less exactly, as a function of pressure from isobaric V-T plots at $P \leq 800$ bars. This method requires no assumptions about the existence or the validity of the Tait equation. The isothermal V-P and the isobaric V-T analyses provide complementary data which mutually support each other.

Polyethylene is unusual, if not unique, for such purposes for the following reasons:

(a) Its transition and relaxation behavior is well documented over regimes of pressure and temperature far beyond those involved in the present studies.

(b) Its known transitions and relaxations occur in convenient temperature regions at $P = 1$ bar, with relatively low pressure coefficients.

(c) Its thermal stability in the absence of O_2 is excellent.

Summary and Conclusions

The following are the principal conclusions from this study:

1. The classical Tait equation, although empirical in origin, provides a remarkably accurate mathematical description of high-quality isothermal V-P data on PE for $T > T_m$ isotherms considered, a priori, to be free of pressure-induced transitions and relaxations. b is constant across the entire isotherm.
2. At the same time, the linear form of the Tait equation, used in conjunction with appropriate statistical tools, is a sensitive method of locating weak secondary transitions in PE, such as α_a and α_c, which were known, a priori, to exist.
3. If there are n such transitions per isotherm, $n + 1$ Tait equations, each with its own intercept and slope $(1/b)$, are needed to describe that isotherm. In general, with $P \leq 2$ kbars, $1 < n \leq 3$.
4. Assuming that there is nothing unique about PE (account being taken of crystallinity), it follows that when a departure from linear Tait behavior is detected in an unknown polymer by using the procedures advocated in this study, the implied transition should be considered real (and not an artifact), subject to confirmation of its existence by independent physical methods, at least at $P = 1$ bar, if not at high pressures.
5. The need to select a new origin and slope for the Tait equation after each pressure-induced transition, as first suggested in an earlier study,[2] has been amply confirmed. (See Figure 10.)
6. The literature assignment of α_c to the crystalline phase and α_a to the amorphous phase is also confirmed.
7. Four methods for the correct interpretation of isothermal V-P data have been presented. In order of increasing complexity, these are as follows: (A) Woods method to calculate bulk modulus from point-to-point derivatives $V_0(\Delta P/\Delta V)$ (subject to error but locates $P_n{}^i$, and permits estimates of C' and b's); (B) comparison of standard errors and intercepts for constrained vs. unconstrained lines through $Y = P/b$ data (does not determine intersection pressures directly); (C) linear regression analysis with residuals (such programs are available for computers with memory disks (our specific procedures are detailed in ref 13); slopes $(1/b)$ and intercepts for each Tait line can be determined); (D) the automatic intersection search method of Šolc (This calculates intersection pressures, $(P_n{}^i)$ and slopes $(1/b)$ as well as intercepts for each of the Tait lines. This, and its several subroutines are thus far unique to our Institute but could become a standard routine.) Once the P/b vs. P values are card punched, we routinely use methods B-D.

The above points have been demonstrated fully for linear and HMW linear PE's, but to a much lesser extent for branched PE. Exploratory tests in the α_c-α_a region indicated that it behaved similar to HMW linear PE.

Acknowledgment. We are indebted to Professor Robert Simha, Case Western Reserve University, for discussions about the nature of the Tait equation and to Professor Geoffrey Gee, FRS, retired, from the University of Manchester, England, for discussion, correspondence, and advice about working with the Tait equation. It should not be inferred that either of them necessarily agrees with any of our conclusions. Dr. Paul Zoller of Du Pont provided a P-V-T manuscript on PS prior to publication. We wish to record our special appreciation to Professor Motowo Takayanagi, retired, Kyushu University, who was a guest lecturer at MMI in 1975. We questioned him at length concerning these α_a and α_c processes whose nature was just beginning to emerge, in large part from his researches. Professor Suehiro has kindly provided us with recent reprints. Mrs. Kathleen Panichella conducted the extensive regression analysis studies. Mrs. Panichella also prepared the line drawings.

Appendix I

It was of interest to apply the technique of this paper to two *n*-alkanes for which *P–V–T* data were available. Grindley and Lind[41,42] studied *n*-heptadecane over a wide range of temperatures and pressures. We chose the 110 °C isotherm data with pressures to 4800 bars at 200-bar increments. Visually, eq 2 appeared to be followed quite well, with $R^2 = 0.99988$ unconstrained and $R^2 = 0.99981$ constrained. However, the residuals in the form of RES/SE values were distinctly nonrandom in a pattern that suggested a quadratic or cubic fit.[13] Standard errors in P/b(calcd) were 0.2666×10^{-1}, 0.38756×10^{-2}, and 0.56608×10^{-1} for polynomials of degree one to four, respectively. The residuals patterns were more nearly random for the second- and third-degree polynomials than for the other two.

We also studied the *n*-octadecane data of Cutler et al.[43] at two temperatures: 115 °C to 4479 bars and the 135 °C isotherm to 5512 bars. Values of R^2 were 0.99993 and 0.99996, respectively, indicative of good fits. The RES/SE values were nonrandom in both cases but with no identifiable pattern such as those in our standard patterns.[13]

There was no evidence for the T_u process discussed in Table I although it has been observed in *n*-alkanes by Pietralla and Krüger[44] using kinematic viscosity, by Denny and Boyer with DSC,[45] and by Krüger et al.[46] on a PE of $\bar{M}_n = 2230$ by Brillouin scattering.

Registry No. Polyethylene (homopolymer), 9002-88-4.

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