methylene group) are comparable to the free energy of transfer of a methylene group ((1.08–1.32)kT) from water to hydrocarbon or micelle.[8,32] This observation points out the similarity between the binding of surfactant by polyelectrolyte and micelle formation, presumably because both processes involve a transfer of ionic surfactant from water to a highly charged and hydrophobic colloidal particle environment of surfactant–polyelectrolyte complex or micelle.[31]

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Secondary Transitions in Amorphous Polymers. 5. Linear Form of the Tait Equation Applied to Isotactic Poly(methyl methacrylate)

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ABSTRACT: An exact linear form of the Tait equation is used to analyze isothermal specific volume–pressure data on isotactic poly(methyl methacrylate) above its glass transition temperature. Since linear Tait behavior is obviously not obeyed in regions containing pressure-induced transitions, other polynomial and multisegment correlations are examined, with the standard error taken as the main criterion of model performance. An automatic computer technique has been developed to systematically test multisegment correlations of $y = f(P)$ data to locate intersection pressures, P^i, along individual isotherms. A three-segment correlation gives the best results on four high-temperature isotherms (138.2, 160.7, 174.5, and 190.2 °C), indicating the existence of secondary relaxations in the pressure range 1–2000 bars. These results are strengthened by good correlations of the determined transition points in a T–P plot, both among themselves and in comparison with prior results. Unambiguous interpretation of two lower isotherms (90.4 and 116.3 °C) is more difficult because of experimental uncertainties and the existence of the glass transition in the high-pressure region. Secondary relaxations above T_g include two liquid–liquid transitions, the intermolecular (T_{ll}) and the intramolecular ($T_{ll'}$), and a low-pressure glass transition, T_g(LP). Evidence for T_β elevated above T_g at high pressure is also found. Pressure coefficients for these transitions are given.

Introduction

The Tait equation has been used extensively in recent years to represent volume–pressure isotherms on polymers[1-13] and low molecular weight liquids.[14,15] In its integrated form, it is usually quoted as

$$1 - V/V_0 = C' \ln (1 + P/b) \tag{1}$$

where V is the specific volume in cm^3/g at pressure P, and V_0 is the corresponding volume at the reference pressure $P = 0$ bar. (Some authors use a reference pressure of $P_0 = 1$ bar,[14] but more generally, it is given as $P_0 = 0$ bar, even in cases where the tabulated data begin at $P = 1$ bar.[9]) C' is taken as a universal constant, having a value of 0.0894, as defined by Simha et al.[5-10] The parameter b is a constant along any isotherm for which there is no pressure-induced transition. In the presence of such a transition, the data points deviate from eq 1, and b effectively increases. The initial value of b between P_0 and the first

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pressure-induced transition encountered decreases as the temperature of the isotherm increases. Simha et al. have discussed this temperature dependence in detail for several polymers.[7]

Equation 1 is not particularly convenient for regression analysis of P–V–T data and thus has been used in modified forms at times. For example, Quach and Simha[5,6] observed the glassy-state β transition in atactic polystyrene (PS) using the differential form suggested by Wood[2]

$$\bar{K} = \kappa^{-1} = (b/C')(1 + P/b) \qquad (2)$$

where $\bar{K}$ is the bulk modulus and κ is the isothermal compressibility

$$\kappa = -(1/V_0)(\partial V/\partial P)_T = (C'/b)(1 + P/b)^{-1} \qquad (3)$$

One of us[16,17] has employed series expansions of the logarithmic term in eq 1 up to the first and second order. The resulting linear and quadratic approximations were used to locate transition pressures, P^{i}, as the intersections between two approximately straight-line sections. A first-order series expansion of the right-hand side of eq 3 has been used as another approximation.[16,17] These approximations yielded intersection pressures in the liquid and glassy states of polymers that generally agreed with those obtained from Wood's exact form.[2]

It is apparent that series approximations can be satisfactory only in a limited range of pressures, and their inadvertent use might distort the estimate of the Tait parameter b. The exact differential form[2] is not ideal either, since it may require precarious numerical differentiation of the data. Hence, we chose an exact linearized form of the Tait equation, given below by eq 4, for our analysis of second-order transitions in polymers.

We wish to point out that the subject of one secondary transition, the liquid–liquid transition (T_{ll}),[18–21] has been somewhat controversial, with criticism directed to the subjective, visual, and/or approximate methods of data treatment to date.[16,17] The term "relaxation" may be substitued for the several liquid-state transitions discussed herein. This report introduces an objective statistical analysis approach based on an exact linearized form of the Tait equation.

Linear Form of the Tait Equation

Strictly speaking, eq 1 is self-consistent only if $P_0 = 0$. Otherwise, the absolute pressure P should be replaced by the pressure difference $\Delta P = P - P_0$, where P_0 is the pressure at the reference state. Although the inconsistency would seem to be negligible if $P_0 = 1$ bar, it is significant enough to be detected in the statistical treatment. Thus we prefer to use a consistent form of the Tait equation that may be linearized as

$$y \equiv \exp[C'^{-1}(1 - V/V_0)] - 1 = (P - P_0)/b \qquad (4)$$

In the absence of any pressure-induced transitions, this form indicates that any V–P data described by the linearized Tait equation, plotted as $y(P)$, should follow a straight line with a slope of $1/b$ and an intercept of $-P_0/b$. While Simha et al.[5–10] treat C' as a universal constant, Prausnitz et al.[11,12] prefer to calculate a specific value of C' for each polymer. In any case, C' is usually a constant for all isotherms of a given polymer.

We have tested eq 4 on various liquid-state isotherms of polystyrene, poly(vinyl acetate), isotactic poly(methyl methacrylate) (iso-PMMA), poly(n-butyl methacrylate), and poly(dimethylsiloxane). Departures from linearity were found in each case. The most detailed test of the linear Tait equation is presented here for iso-PMMA.

Statistical Treatment of Data

The P–V–T data of Quach, Wilson, and Simha[9] on iso-PMMA was selected as the first test case for the objective statistical methods proposed in this report because (a) the polymer was well characterized, (b) a preliminary study[17] using other forms of the Tait equation suggested that the liquid–liquid relaxation was unusually strong, and (c) there was independent evidence for a T_{ll} at $P = 1$ bar.[22,23] Parameters used in this study are $P_0 = 1$ bar and $C' = 0.0894$.

It should be emphasized that the values of V for each liquid-state isotherm were obtained by the quasi-equilibrium method of Quach and Simha[6] whereby pressures were applied in increments of 100 or 200 bars at a pressurization rate of 400 bars/h, with a waiting period of at least 15 min after each step increase in pressure to ensure volume equilibrium. In view of the time effects noted by Höcker et al.[24] in the liquid state of polystyrene up to the T_{ll} region, we consider this procedure essential.

The present statistical analysis differs from the previous treatments in two key respects: (1) The data sets are subjected to an array of various correlation models, with the standard error, s, being taken as the main criterion for a "best" model. (2) Appropriate statistical weights are assigned to individual data points.

The first class of correlation models coming to mind are simple least-squares fits of all experimental points of an isotherm by polynomials of the first, second, third, etc. orders; these models will be referred to as simple linear, quadratic, cubic, etc. models. This type of behavior would be reasonable to expect if no particular transition event occurred in the examined range of pressures and all of the material constants were changing smoothly over the interval.

If however, a transition point is present, wherein some of the parameters of the Tait equation change abruptly, one should get a better statistical fit of the data (i.e., a lower standard error s) by fitting the two pressure ranges separately by two straight lines, to a first approximation. We call this correlation model a two-segment n_1/n_2 model, where n_1 and n_2 specify the number of data points fitted by the first and second line segments, respectively. An examination of the variation of the standard error as n_1 and n_2 are varied, subject to the condition $n_1 + n_2 = n$, where n is the total number of experimental points, gives some indication of the significance of the selected transition point. The extension of this concept to multisegment models with more than one transition point in the examined interval is evident and will be discussed in greater detail later in this report.

In no case are the various correlation models constrained to pass through the point corresponding to the reference state, $y = 0$, $P = P_0$. The determination of the volume at this point is subject to experimental error the same as at any other data point, and forcing a model through it would impose a systematic error on the rest of the data for a given isotherm.

The introduction of statistical weights into the analysis is desirable on the following grounds. It is reasonable to assume that the probable error in measuring the specific volume is independent of pressure. However, since the quantity y (eq 4) plotted in the linearized Tait equation is a nonlinear function of V, the probable error in calculated y then depends on the pressure. This dependence is corrected by assigning a statistical weight, w_i, to each point, where

$$w_i = \left(\frac{\mathrm{d}y}{\mathrm{d}V}\right)_i^{-2} = \left(\frac{C'V_0}{1 + y_i}\right)^2 \qquad (5)$$

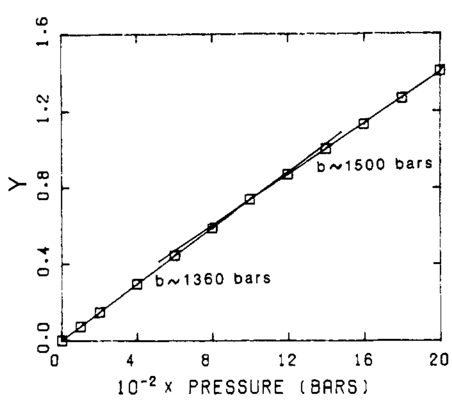

Figure 1. Apparent deviation of the 174.5 °C isotherm from linearized Tait behavior. The lines drawn through the experimental points are those chosen as the "best" fits from the two-segment n_1/n_2 model, where $n_1 = n_2 = 6$. The calculated value of b is ~1360 bars below the intersection and ~1500 bars above the intersection.

We note that the unweighted treatment would tacitly assume a probable error in V diminishing with increasing P like $(1 + y)^{-1}$, which is very unlikely.

The inclusion of the constants in the numerator of eq 5 ensures that the calculated standard error

$$s = [\sum_{i=1}^{n} w_i(y_i - \hat{y}_i)^2/(n - p)]^{1/2} \qquad (6)$$

gives the mean square-root deviation of the experimental points from the assumed model directly in terms of observed V. The number of degrees of freedom, p, is 2 for the linear, 3 for the quadratic, 4 for the cubic, etc. simple polynomial models. For a correlation model consisting of k linear segments, p is $3k - 1$. (Each additional linear segment augments p by 3, accounting for its slope, intercept, and the intersection pressure pinpointing the range of its validity.) The symbol $\hat{y}_i$ represents the value of y calculated for a pressure P_i for a given correlation model.

In addition to the standard error, there are two other quantities to watch in judging various models: (1) For the reference state of $P_0 = 1$ bar, the computed intercept, $y_{P=0}$, expected from eq 4 is $-1/b$, with an error bar of $\pm s/w_{P=0}{}^{1/2}$. Any intercept lying far outside these limits suggests that the examined correlation model is not well obeyed. (2) Another criterion tied to the significance of detected transition points is the difference between the slopes of two consecutive line segments, as well as the trend the slopes exhibit in multisegment correlations. If the slopes differ by no more than 1–2%, we would be reluctant to consider such a fit as a meaningful confirmation of the multisegment model. In terms of slope trends, one would expect the slope $(1/b)$ to decrease upon traversing a transition point since the compressibility is a monotonic decreasing function of b (cf. eq 3).

Detailed Analysis of Polynomial and Two-Segment Models Applied to the 174.5 °C Isotherm. The 174.5 °C isotherm of iso-PMMA has been chosen to illustrate the application of the simple polynomial and two-segment n_1/n_2 correlation models. We feel that the number of experimental points for a single isotherm (12) does not warrant correlation by a multisegment model of three or more segments. The deviation from linearity in plotting the linearized Tait function, eq 4, against pressure for this isotherm is particularly clear, as shown in Figure 1. Data points up through P = 1000 bars follow linear Tait behavior well (residuals are random about zero with a correlation coefficient of r^2 = 0.9999); above that point the deviation from linearity is quite obvious.

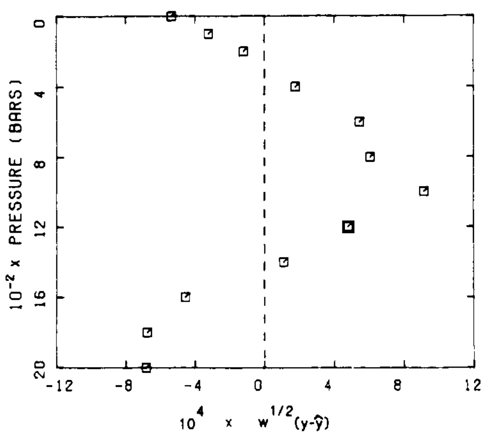

Figure 2. Weighted residuals for the simple linear model applied to the 174.5 °C isotherm. The distinctly nonrandom pattern attests to the poorness of fit of the linear model.

Table I
Simple Polynomial Correlation Model ($y = c_0 + c_1P + c_2P^2 + \ldots + c_mP^m$) Applied to the 174.5 °C Isotherm of iso-PMMA[a]

m	$c_0 \times 10^3$	$c_1 \times 10^4$, bar^{-1}	$s \times 10^4$, cm^3/g
1	6.01	7.12	5.75
2	−2.72	7.61	2.12
3	−2.22	7.56	2.22
4	0.306	7.05	1.30
5	22.1	2.68	18.5

[a] The higher coefficients, c_j for $j > 1$, are not listed.

Table II
Two-Segment n_1/n_2 Correlation Model ($y = a_k + P/b_k$, k = 1, 2) Applied to the 174.5 °C Isotherm of iso-PMMA[a]

	first segment		second segment		
n_1/n_2	$a_1 \times 10^4$	$b_1^{-1} \times 10^4$, bar^{-1}	$a_2 \times 10^2$	$b_2^{-1} \times 10^4$, bar^{-1}	$s \times 10^4$, cm^3/g
3/9	−7.67	7.37	2.50	6.97	4.70
4/8	−7.02	7.36	3.87	6.87	3.34
5/7	−9.77	7.39	5.27	6.78	2.34
6/6	−7.19	7.37	7.07	6.67	1.08
7/5	−8.72	7.38	6.92	6.68	1.10
8/4	0.955	7.33	6.21	6.72	1.96
9/3	14.5	7.28	2.75	6.90	3.14

[a] The standard error, s, is calculated from eq 6.

The nonlinearity of the overall dependence is even more apparent in a plot of residuals.[25] Figure 2 shows a plot of weighted residuals, $w^{1/2}(y - \hat{y})$, vs. pressure, for the simple linear correlation model. The distinctly nonrandom residual pattern along the pressure axis indicates the inappropriateness of the simple linear model for this data set.

Table I gives the results for the simple polynomial correlation model. Comparing standard errors, a linear fit is clearly not the best fit; the optimal correlation (minimum standard error) is obtained for a fourth-order polynomial. In going to the next higher polynomial (m = 5), the standard error increases sharply by more than an order of magnitude. The poor performance of the linear and fifth-order fits in terms of s is paralleled by the intercept results; c_0 is barely in the range of $-c_1 \pm sw_{P=0}{}^{-1/2}$ for the linear fit, far outside the range for the fifth-order fit, but well within the expected interval for the other polynomial correlations.

The results for the two-segment n_1/n_2 correlation model are given in Table II. As one may have anticipated from the residuals pattern shown in Figure 2, the best two-segment fits are obtained by splitting the data as 6/6 or 7/5; i.e., the intersection pressure should be very close to the seventh experimental point, $P_7 = 1000$ bars. Any other two-segment fit has a substantially larger standard error. Comparing the two-segment model with the simple polynomial model (Table I) indicates that the 6/6 correlation is the "best" fit overall since it gives the smallest standard error. Also, the intercept, a_1, is surprisingly close to $-1/b_1$, attesting to the internal consistency of the two-segment model and justifying our substitution of P in eq 1 by $P - P_0$ in eq 4.

The situation for the second line segment of the two-segment model requires some explanation. In all of the correlations of Table II, its intercept, a_2, is relatively large (on the order of 10^{-2}) and well beyond the expected error range. Furthermore, the slope, $1/b$, was noted to decrease by 9.5% from the first line segment to the second for the two best fits. These observations suggest clear and systematic deviations from linearized Tait behavior for the second line segment.

The reason for a simultaneous change in both the intercept and slope parameters has been discussed in one of our previous papers.[17] With C' kept constant in eq 1, a mere stepwise change in b occurring at a transition point would require a corresponding stepwise change in the volume V. However, the transitions discussed in this paper are not first-order transitions, and thus, the volume remains constant over a transition. Although a linearized Tait function may explain V–P behavior quite well over the first line segment of a two-segment model, it appears unsuitable for describing the higher pressure range second segment.

This problem can be resolved in one of two ways. First, the transition point, P^i, could be declared as a new reference state for the second line segment with modified values of P_0 and V_0 defining the new origin.[17] Second, one could acknowledge and adjust for pressure-induced transitions by replacing unity in the logarithmic term of the general Tait equation by an intercept parameter, a, whereby we write

$$1 - V/V_0 = C' \ln [a + (P - P_0)/b] \qquad (7)$$

We utilize the second option in this paper for our multisegment correlation models; it seems more convenient since it does not require a change in the definition of the plotted quantity over a transition. The intercept for a second or subsequent line segment need not be $-P_0/b$, which is required for a simple linear model. The simultaneous change in the a and b parameters across a transition point is related as

$$\Delta a / \Delta b \approx P^i / b^2 \qquad (8)$$

Three-Segment Model Applied to the Liquid-State Isotherms. The application of a multisegment correlation model of three or more segments may be unwarranted in analyzing any single isotherm because of the limited number of experimental data points. However, we feel justified in at least examining what a three-segment model may indicate for a series of isotherms, e.g., to see if there is a correlation of intersection pressures over a range of isotherms.

In this section we discuss the application of a three-segment $n_1/n_2/n_3$ correlation model to a set of six isotherms in the liquid region of iso-PMMA—90.4, 116.3, 138.2, 160.7, 174.5, and 190.2 °C. All isotherms have 12 experimental data points, except the 116.3 °C isotherm, which has 11 data points. The 1600-bar point of the 116.3 °C isotherm deviates substantially from the remaining 11 points in both the linear Tait plot and the corresponding residuals pattern and has thus been deleted from the statistical analysis.

A computer program (available upon request) has been written for an HP 1000 F Series computer to systematically break a set of data into a specified number of segments, linearly interpolate the data points within each segment, and determine the intersection points between adjacent segments. The program also computes an overall standard error for each multisegment correlation generated according to eq 6.

Ideally, for a given intersection pressure, P^i should lie between pressure coordinates of the last data point of a left-hand segment and the first data point of a right-hand segment; we refer to such a situation as a "no overlap" case. Because of experimental errors in the data, the point of intersection of two adjacent segments may at times fall within the pressure interval of one of them. In this situation, we judge the seriousness of the intersection displacement by a "percentage of overlap", which is the fraction of an adjoining segment of data points into which the intersection point has penetrated.

Obviously, the most confidence can be placed in correlations that do not overlap into an adjoining segment. Even correlations having low standard errors should be viewed with some suspicion in terms of their "best" fit status if they require significant overlap. The program takes into account several allowed ranges of overlap and selects several best correlations (least overall standard error) for each level as specified by the user.

We generally request a printout of the three lowest standard error correlations for three levels of overlap—0%, up to 25%, and up to 50%. In principle, this protocol could lead to nine choices for "best" fit correlations. Frequently though, in relaxing the overlap restriction from 0% to 25% and then to 50%, little effect is noted on obtaining additional alternate correlations with lower standard errors, and often identical correlations are selected as best fits at several levels of overlap.

Table III lists all of the three-segment correlations selected by the computer program as best fits (three for each level of overlap) for all six isotherms. The results are tabulated according to increasing standard error, s, for each isotherm. Table III also lists the intersection pressures, percentages of overlap, and the slopes of the straight-line segments, from which the Tait parameter, b, and the percent change in b are calculated.

Since there is no case where a single correlation is distinctly superior to the rest of them, we define as "best" fits a group of up to three correlations with overlaps of no more than 10% and with standard errors ranging no more than 10% above the best of them. These correlations are printed in boldface in Table III. The average range of intersection pressures, P_j^i, for the "best" correlations is 35 bars for $j = 1$ and 119 bars for $j = 2$. The higher value for the range of the second intersection point is mainly due to correlations for the 90.4 and 116.3 °C isotherms, where the range of intersection pressures was 251 and 148 bars, respectively.

Comparison of Polynomial and Multisegment Models. We have also applied the simple polynomial model (up to the fifth order) and multisegment correlations of two and four lines to all six liquid-state isotherms. Table IV summarizes the single best fits for all models examined for each isotherm. The standard errors for the best models are printed in boldface with the second best contenders in italics.

The results in Table IV clearly indicate that the three-segment correlation is the best model for the four

Table III
Three-Segment $n_1/n_2/n_3$ Correlation Model Applied to the Six Liquid-State Isotherms of iso-PMMA[a]

temp, °C	$n_1/n_2/n_3$	$s \times 10^4$, cm³/g	$P_1{}^i$, bar	$P_2{}^i$, bar	overlap, %	$b_1{}^{-1} \times 10^4$, bar⁻¹	$b_2{}^{-1} \times 10^4$, bar⁻¹	$b_3{}^{-1} \times 10^4$, bar⁻¹	% change in Tait b: b_1 to b_2	% change in Tait b: b_2 to b_3
190.2	3/4/5	1.75	158	1133	21/0	8.68	7.90	7.40	9.9	6.8
	3/5/4	**1.76**	180	1271	**10/0**	8.68	7.85	7.33	10.6	7.1
	2/6/4	**1.80**	199	1284	**0/0**	8.65	7.84	7.33	10.3	7.0
	2/5/5	**1.87**	194	1167	**0/0**	8.65	7.86	7.40	10.1	6.2
	3/6/3	2.05	203	1414	0/0	8.68	7.81	7.24	11.1	7.9
174.5	7/3/2	**0.82**	1058	1734	**0/0**	7.38	6.54	7.05	12.8	−7.2
	6/4/2	**0.88**	1036	1774	**6/0**	7.37	6.60	7.05	11.7	−6.4
	3/3/6	1.43	589	1025	47/3	7.37	7.36	6.67	0.1	10.3
	3/4/5	1.45	444	996	7/1	7.37	7.39	6.68	−0.3	10.6
160.7	4/4/4	**1.36**	448	1154	**0/8**	7.28	6.73	6.23	8.2	8.0
	4/3/5	**1.38**	463	1225	**0/3**	7.28	6.70	6.20	8.7	8.1
	3/5/4	**1.44**	410	1142	**1/7**	7.29	6.76	6.23	7.8	8.5
	3/2/7	3.47	388	757	0/0	7.29	6.97	6.40	4.6	8.9
	6/4/2	3.60	912	1683	0/0	7.06	6.31	6.17	11.9	2.3
	7/2/3	3.74	1070	1546	0/0	7.01	6.11	6.27	14.7	−2.6
138.2	2/4/6	0.89	293	944	16/0	6.55	6.30	5.72	4.0	10.1
	3/3/6	**0.93**	236	952	**0/0**	6.65	6.29	5.72	5.7	10.0
	3/4/5	**0.98**	270	1029	**0/0**	6.65	6.23	5.70	6.7	9.3
	5/2/5	1.69	713	1085	0/0	6.42	6.05	5.70	6.1	6.1
116.3[b]	5/4/2	0.83	333	1524	45/0	5.80	5.61	5.21	3.4	7.7
	4/5/2	**0.96**	439	1571	**0/0**	5.84	5.56	5.21	5.0	6.7
	3/6/2	**0.98**	379	1555	**0/0**	5.87	5.57	5.21	5.4	6.9
	4/4/3	**1.01**	441	1423	**0/4**	5.84	5.56	5.32	5.0	4.5
	3/5/3	1.04	377	1394	0/0	5.87	5.58	5.32	5.2	4.9
90.4	4/5/3	**1.64**	470	1483	**0/0**	5.52	4.91	4.52	12.4	8.6
	4/4/4	**1.69**	467	1405	**0/1**	5.52	4.92	4.58	12.2	7.4
	4/6/2	**1.78**	488	1656	**0/0**	5.52	4.88	4.37	13.1	11.7
	3/5/4	1.83	372	1345	0/0	5.61	4.97	4.58	12.9	8.5

[a] The standard error, s, is calculated from eq 6. "Best" fits as specified in the text are given in boldface. [b] The 1600-bar data point was deleted from the statistical treatment for this isotherm.

Table IV
Comparison of Best Polynomial and Multisegment Correlation Models for the Six Liquid-State Isotherms of iso-PMMA As Specified in the Text[a]

	polynomial		two-segment			three-segment			four-segment		
temp, °C	order	$s \times 10^4$, cm³/g	n_1/n_2	$s \times 10^4$, cm³/g	overlap, %	$n_1/n_2/n_3$	$s \times 10^4$, cm³/g	overlap, %	$n_1/n_2/n_3/n_4$	$s \times 10^4$, cm³/g	overlap, %
190.2	4	*1.91*	6/6	2.99	0	3/5/4	**1.76**	10/0	3/3/4/2	2.76	35/0/0
174.5	4	**1.30**	6/6	*1.09*	2	7/3/2	**0.82**	0/0	6/2/2/2	*1.10*	13/3/0
160.7	3	*1.57*	6/6	2.74	0	4/4/4	**1.36**	0/8	4/3/2/3	2.61	0/20/0
138.2	3/4	*1.03*	6/6	1.39	0	3/3/6	**0.93**	0/0	2/4/4/2	1.40	16/0/44
116.3[b]	4	**0.86**	4/7	1.53	0	4/5/2	*0.96*	0/0	–	–	–
90.4	4	**0.98**	5/7	1.98	0	4/5/3	*1.64*	0/0	3/3/3/3	1.72	0/45/0

[a] Best fits are given in boldface; second best contenders are in italics. [b] The 1600-bar data point was deleted from the statistical treatment for the 116.3 °C isotherm. As a consequence, a four-segment correlation cannot be tested because 11 points are insufficient in calculating such a correlation.

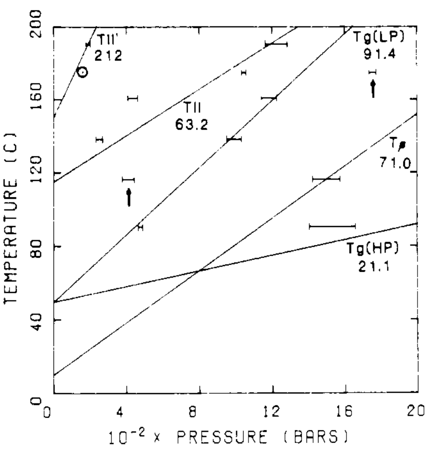

Figure 3. Transition intersection pressures for six liquid-state isotherms of iso-PMMA. The bars specify the range of intersection pressures given by the "best" fit three-segment correlations of Table III. The T_g(HP) line was previously defined by Quach et al.[9] The other transition lines are least-squares fits computed for the midpoints of the P^i ranges, each constrained to pass through the accepted transition temperature at $P = 1$ bar (10 °C for T_β, 49.7 °C for T_g(LP), 115 °C for T_{ll}, and 150 °C for $T_{ll'}$). The numeric values are the pressure coefficients, dP/dT, for the transition lines as drawn, in units of degrees Kelvin per kilobar (K/kbar). The arrows denote P^i ranges not included in the calculated lines. The circle identifies a low-pressure intersection point determined for the 174.5 °C isotherm when the $P = 2000$ bar data point is deleted from the analysis (see text).

highest isotherms and the second best contender for the two lowest isotherms. For the 116.3 °C isotherm, either a second- or fourth-order polynomial was found to be marginally better than the optimal three-segment model, and a second-, third-, or fourth-order polynomial was a better fit for the 90.4 °C isotherm.

In our opinion, the 116.3 °C isotherm deserves less confidence than the other isotherms. As mentioned earlier, the 1600-bar point was removed from the data set prior to statistical treatment because of its obvious deviation from neighboring points. How much the results may be affected by the event leading to the 1600-bar anomaly is difficult to estimate.

We are equally suspicious of the lowest isotherm; it is unique in being the only one extending into the glass transition range at its high-pressure end. The T_g may impress enough nonequilibrium character on the data so as to distort the results of the analysis. Another factor contributing to the anomalous behavior of the 90.4 °C isotherm may be the presence of three transition points (see Figure 3). It is apparent that the more transition points in a given interval, the easier it is to fit the data with a smooth polynomial.

We believe that the good performance of the three-segment model for the four highest isotherms is statistically significant and reflects the real physical behavior of iso-PMMA in the examined range of pressures and temperatures. The standard errors for this model average 17% lower than those of the next best fits. Equally important, there is no consistent pattern among the second best contenders. At 190.2 °C, a fourth-order polynomial is the second best model, at 174.5 °C, two- or four-segment correlations are comparable second contenders, at 160.7 °C, a third-order polynomial is selected, and at 138.2 °C, third- or fourth-order polynomials are equally preferred as second best fits.

The two-segment model is clearly inferior. On the average, the standard error is 63% higher than that of the three-segment model. Also, the resulting intersection pressures are generally close to the midpoint of the pressure interval and do not vary in a systematic manner with increasing temperature as is characteristic of pressure-induced transitions.

The average standard error for the four-segment model is similarly higher (58%); additionally, these poor results are achieved only at the expense of large overlaps. As a group, the closest contenders are the polynomial correlations. Yet, even here the correlations are distinctly inferior with no systematic pattern of a "best" order of the polynomial.

One of the reviewers felt that breaking a set of data into increasing numbers of linear segments would automatically lead to lower standard errors and thus better fitting correlations. Equation 6 ensures that this in not necessarily the case; multisegment correlations are heavily taxed by the increase in the variable p in the denominator of eq 6. In the present analysis, we note that all four-segment correlations are inferior to the corresponding three-segment models. We also note that for an analogous statistical treatment of the $P-V-T$ behavior of various polyethylenes[26] in a temperature range in which no pressure-induced transitions are expected, a simple linear correlation fits the experimental data better than any other model.

In addition to examining the least standard error, we consider the percentage change in the Tait parameter, b, over a transition point a measure of the significance of the model. For the 16 correlations designated as "best" fits in Table III, the average percent change in b is 9.1% for the lower pressure intersection and 7.7% for the higher pressure intersection. In contrast, analogous results on various polyethylenes[26] show negligible changes in b over consecutive segments, on the order of 1–2%, which may alternate in sign.

We are not proposing that a three-segment correlation will be the best model for all polymers over all temperatures. However, for the liquid-state isotherms of iso-PMMA examined herein, with their attendant pressure-induced transitions, the three-segment model is the statistically best one. It leads to the lowest overall standard error of any model, shows significant magnitude increases in the Tait parameter across transitions, and indicates transition intersection pressures that vary systematically with temperature as shown in Figure 3. The bars indicate the intersection pressure ranges of the designated "best" fit correlations for each isotherm given in Table III for the three-segment model. The superimposed pressure-dependent transition lines will be discussed below.

Discussion of Results

We begin by noting the general similarity of Figure 3 to the corresponding $T-P$ map shown as Figure 5 of ref 17; both are based on the same $V-P$ data for iso-PMMA.[9] Intersection pressures for the latter figure were obtained by using various approximations to the Tait equation, with the intersection pressures, P^i, estimated by subjective judgment. The good agreement with Figure 3, where intersection pressures are objectively determined, results in part from the quality of the starting data. Another contributing factor is the relatively high inherent intensity of the liquid–liquid process, T_{ll}, in iso-PMMA compared to its strength in other systems, e.g., polystyrene (PS) or poly(vinyl acetate) (PVAc). Table V of ref 27 indicates that the intensity of T_{ll} in iso-PMMA (60% isotactic content) is several times greater than in either PS or PVAc, based on the change in thermal expansivity, $\Delta\alpha$, across T_{ll}.

The specific temperatures selected as the anchor points ($P = 1$ bar) for the transition lines in Figure 3 are based largely upon data from the literature. Reference-state transition temperatures are discussed in detail in the sections following.

Liquid–Liquid Transitions. An analysis of ^{13}C NMR spectra collapse temperatures obtained by Axelson and Mandelkern for iso-PMMA placed T_{ll} at 110 °C at $P = 1$ bar.[23] An examination of slope changes in b–T plots also suggests a T_{ll} around 110 °C as P approaches zero.[28] Analysis of isobaric V–T data at $P = 1$, 100, and 200 bars[27] likewise suggests a T_{ll} approaching 110 °C as P goes to zero. The T_{ll} intersection pressure ranges at 138.2 and 160.7 °C in Figure 3 appear to favor a somewhat higher value of T_{ll} at $P = 1$ bar though. A higher value of 140 °C has also been observed by DSC[22] but it may be high as a consequence of a heating rate of 10 K/min. Considering all of these results, we feel justified in selecting a T_{ll} anchor point at 115 °C.

An extensive DSC study on a number of polymers identified a $T_{ll'}$ transition process ranging some 30–40 degrees above T_{ll}.[29] For the present analysis we assign an approximate $T_{ll'}$ transition temperature anchor point at 150 °C at $P = 1$ bar. The 190.2 °C isotherm shows an intersection pressure for T_{ll} at 1200 bars and a well-defined second transition at about 200 bars. We ascribe this low-pressure event to a $T_{ll'}$ relaxation. $T_{ll'}$ is believed to be an intramolecular relaxation process involving a barrier to rotation of a side group about the polymer backbone. Conversely, T_{ll} is thought to be intermolecular in origin, arising from the thermal disruption of segment–segment interactions.[20,30]

The results for the 174.5 °C isotherm were initially disconcerting, with intersection pressures assigned at 1050 and 1750 bars. The 1050-bar intersection is unquestionably due to T_{ll}, but the 1750-bar intersection does not appear to correlate with any transition process in Figure 3.

Since compressibility is a monotonic decreasing function of the Tait parameter b, the slopes in multisegment correlations should decrease from lower to higher pressure ranges, with b conversely increasing over transition intersections. However, we note that the change in b is negative in going from the second to the third line segment in both the 7/3/2 and 6/4/2 models for the 174.5 °C isotherm (see Table III); we further note that this was the only case where such an inconsistency occurred. Additionally, a closer examination of the residuals plot for this isotherm (Figure 2) led us to suspect the accuracy of the $P = 2000$ bar data point.

The statistical treatment of the 174.5 °C isotherm with the 2000-bar point removed still selects a three-segment model as the "best" fit, now breaking the data as 2/5/4. The intersection pressure between the first and second segments of this new correlation is 160 bars. This revised intersection point is denoted by the circle in Figure 3 and correlates well with the $T_{ll'}$ transition line.

Low- and High-Pressure Glass Transitions. Some comments are in order concerning the T_g(LP) line where "LP" refers to a low-pressure glass. This term was introduced by Quach and Simha[6] in connection with their P–V–T study of atactic PS. They defined T_g(LP) as the intersection of an extrapolated $T < T_g$ isobaric V–T line with the corresponding $T > T_g$ isobar. In PS, the T_g(LP) so determined has a pressure coefficient about 3 times greater than that of the conventional T_g, which Quach and Simha designate as a high-pressure glass, T_g(HP).[6] One of us (R.F.B.) has detected T_g(LP) as an intersection pressure in high-temperature isotherms of atactic PS,[16] without recourse to knowledge of the $T < T_g$ isobaric lines. Although this result seemed unusual and was unexpected at the time, the values of T_g(LP) were consistent with those obtained by Quach and Simha.[6]

For the case of iso-PMMA, Quach et al.[9] did not discuss T_g(LP), and moreover, they provided tabulated isobaric V–T data for only two glassy-state isotherms. However, Figure 3 indicates a rather well-defined T–P line, which we ascribe to T_g(LP), originating at or near T_g(HP) at $P = 1$ bar. The T_g(LP) intersection pressures appear to end at the 160.7 °C isotherm, likely because they cannot be resolved at higher temperatures in view of their close proximity to the T_{ll} line. While T_g(LP) had been considered by one of us (R.F.B.) to be a hypothetical glass temperature obtained only conceptually and by extrapolation, it appears to have a real existence, being observed both in Figure 5 of ref 17 via approximation methods and in Figure 3 from an exact linear Tait approach.

The T_g(HP) line shown in Figure 3 is that previously defined by Quach et al.[9] They give the pressure coefficient of T_g(HP) as 21.1 K/kbar and a value of 49.7 °C as the glass transition temperature at atmospheric pressure.

β Relaxation. The T_β line shown in Figure 3 cutting across the T_g(HP) line is defined only approximately by the intersection pressure range at 116.3 °C. However, its anchor point at $P = 1$ bar has been rather well defined by several independent measurements. Gillham et al.[31] have reported a $T < T_g$(HP) or β relaxation at 7 °C ($f = 1.14$ Hz) at $P = 1$ bar on a specimen of 91.5% isotacticity. Quach et al.[9] found a slope change in the coefficient of expansion at 10 °C for 100% isotactic content material. Our selection of an anchor point at 10 °C at $P = 1$ bar for the T_β line is further confirmed by the results of a two-segment correlation of the 26.2 °C isotherm.

The β relaxation has been considered to be much weaker in isotactic PMMA than in its syndiotactic counterpart.[22,31,32] The intensity of T_β appears to increase with temperature, even though pressure is also increasing, based upon the observed increase in b across T_β.

General Considerations. Overall, the intersection pressure ranges identified by the "best" fit three-segment models given in Table III correlate quite well with known transition processes. In only two instances a pressure range was calculated that did not correlate with a transition. In one of those cases (174.5 °C) a deviant experimental point at $P = 2000$ bars was deemed responsible for the discrepancy.

Unquestionably, the loci of intersection pressures could have been delineated more precisely if we had experimental V–P data available at more frequent intervals instead of at every 200 bars. Unfortunately, much of the P–V–T data provided in the literature offers a paucity of experimental points. The location of the transition lines might not change substantially if more data were available for analysis, but a greater degree of confidence would be placed in them.

Finally, we call attention to the general utility of two statistical procedures used extensively in developing this report. The computer program written by one of us (K.Š.) to automatically search for and select optimal multisegment correlations and their attendant intersection points is generally applicable to any $y = f(X)$ data. It has, for example, been used to conveniently locate T_{ll} temperatures in isobaric V–T data.[27] The residuals method illustrated in Figure 2 is also general to $y = f(X)$ and has been used extensively on V–T[27,33] and b–T data[28] recently.

Summary

For systems obeying Tait behavior, V–P data may be represented by a linearized form of the Tait equation, linear in pressure with a slope of $1/b$. However, most V–P isotherms we have examined to date for several amorphous polymers deviate from Tait behavior because of one or more pressure-induced transitions. A computational procedure has been devised and tested for ascertaining the extent to which experimental isothermal V–P data follow the linear Tait function given by eq 4. The present analysis was carried out on six liquid-state isotherms of isotactic PMMA using the tabulated P–V–T data of Quach et al.[9]

Deviations from Tait behavior result in characteristic nonrandom residuals patterns from which intersection pressures can be estimated.[25] A more rigorous objective approach to defining intersection pressures has been developed. A computer program was employed to systematically test a number of multisegment correlations, select several optimal choices based on the lowest standard errors and maximum allowed overlaps, and calculate the corresponding intersections. Intersection pressures obtained from the automatic search method generally agree with the results obtained from more subjective approximation methods[17] or residuals patterns.

Our analysis of multisegment models consisting of from two to four linear segments and simple polynomial models up to the fifth order identified a three-segment correlation as the "best" overall model to locate systematic deviations in Tait behavior for the six liquid-state isotherms examined for iso-PMMA.

A master plot of isotherm temperature vs. intersection pressure was constructed from which pressure coefficients, $\mathrm{d}T/\mathrm{d}P$, can be estimated for a number of transition processes. Although the number of experimental points per isotherm was limited to 11 or 12 points, the T–P plot provides an overall check on the method and lends credence to the concept of using systematic deviations from Tait behavior to define transitions in amorphous polymers. Our analysis of the liquid state of iso-PMMA reveals two liquid-state relaxations (T_{ll} and $T_{ll'}$), a low-pressure glass transition (T_g(LP)), and a sub-T_g β relaxation (T_β), which moves into the $T > T_g$ liquid range at higher pressures.

Analogous studies are in progress on several additional polymer systems, viz., branched and linear polyethylene (PE),[26] atactic polystyrene (data from three sets of authors), and poly(*o*-methylstyrene).[34] The results on PE, using the data of Olabisi and Simha,[10] show that isotherms in the range 180–200 °C, judged a priori to be free of any pressure-induced transitions, do indeed follow the linear form of the Tait equation remarkably well.[26] Hence, the deviations from Tait behavior reported herein cannot be ascribed to any deficiency in the empirical Tait equation itself.

Note Added in Proof. After completion of the manuscript, a study of seven PMMA's of known tacticities by the method of thermally stimulated current (TSC) was completed.[35] T_g increases linearly with syndiotactic triad content and T_{ll} increases linearly with syndiotactic diad content with correlation coefficients, R^2, of 0.9704 and 0.9633, respectively. iso-PMMA shows a T_{ll} current peak at 94 °C and a $T_{ll'}$ current peak at 146 °C, in reasonable agreement with the $P = 1$ bar values of Figure 3.

Registry No. Isotactic poly(methyl methacrylate), 25188-98-1.

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