molecule; $p - 1$ of these are cross-links and the rest must be involved in ring formation, since no unreacted double bonds were found after reaction. Thus

$$r = \frac{Rp - (p - 1)}{Rp} = (R - 1)/R + 1/pR \qquad \text{(A2)}$$

which is the relationship when p is replaced by P_n/P_{np}.

References and Notes

(1) Andrews, T. *Philos. Trans. R. Soc., London* **1869**, *159*, 575.
(2) van der Waals, J. D. Ph.D., Leiden, 1873.
(3) Weiss, P. *J. Phys. Radium* **1907**, *6*, 667.
(4) Huggins, M. L. *Ann. N.Y. Acad. Sci.* **1942**, *43*, 1.
(5) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(6) Ising, E. *Z. Phys.* **1925**, *31*, 253.
(7) Onsager, L. *Phys. Rev.* **1944**, *65*, 117.
(8) Kadanoff, L. P.; Götze, W.; Hamblen, D.; Hecht, R.; Lewis, E. A. S.; Palcianskas, V. V.; Rayl, M.; Swift, J.; Aspens, D.; Kane, J. *Rev. Mod. Phys.* **1967**, *39*, 395.
(9) Fisher, M. E. *Rep. Prog. Phys.* **1967**, *30*, 615.
(10) Stanley, H. E. "Phase Transitions and Critical Phenomena"; Oxford University Press: New York, 1971.
(11) Stanley, H. E., Ed. "Cooperative Phenomena near Phase Transitions"; M.I.T. Press: Cambridge, Mass., 1973.
(12) Widom, B. *J. Chem. Phys.* **1965**, *43*, 3892, 3898.
(13) Wilson, K. *Phys. Rev. B* **1971**, *B4*, 3174, 3184.
(14) Ma, S. K. *Rev. Mod. Phys.* **1973**, *45*, 589.
(15) Green, M. S., Ed. "Critical Phenomena"; Academic Press: New York, 1971.
(16) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(17) Flory, P. J. *J. Phys. Chem.* **1942**, *46*, 132.
(18) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.
(19) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
(20) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.
(21) Hammersley, J. M. *Proc. Cambridge Philos. Soc.* **1957**, *53*, 642.
(22) Kirkpatrick, S. *Rev. Mod. Phys.* **1973**, *45*, 574.
(23) Essam, J. W. In "Phase Transitions and Critical Phenomena"; Domb, C., Green, M. S., Eds; Academic Press: New York, 1973.
(24) Stauffer, D. *Phys. Rep.* **1979**, *54*, 1.
(25) Swinney, H. L. In "Photon Correlation and Light Beating Spectroscopy"; Cummins, H. Z., Pike, E. R., Eds.; Plenum Press: New York, 1974; p 331.
(26) Stockmayer, W. H. In "Advancing Fronts in Chemistry"; Twiss, S. B., Ed.; Reinhold: New York, 1975; Vol. I, pp 71-3.
(27) Weil, L. L., unpublished measurements (quoted in ref 26).
(28) Eschwey, H.; Hallensleben, M. L.; Burchard, W. *Makromol. Chem.* **1973**, *173*, 235.
(29) Eschwey, H.; Burchard, W. *Polymer* **1975**, *16*, 180.
(30) Eschwey, H.; Burchard, W. *J. Polym. Sci., Polym. Symp.* **1975**, *53*, 1.
(31) Schmidt, M. Ph.D. Thesis, Freiburg, 1980.
(32) Whitney, R. S.; Burchard, W. *Makromol. Chem.* **1980**, *181*, 869.
(33) Dobson, G. R.; Gordon, M. *J. Chem. Phys.* **1964**, *41*, 2389.
(34) Yamamoto, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971**, *2*, 799.
(35) Dobson, G. R.; Gordon, M. *J. Chem. Phys.* **1965**, *43*, 705.
(36) Feller, W. "An Introduction to Probability Theory"; Wiley: New York, 1968.
(37) Buttler, S.; Gordon, M.; Malcolm, G. N. *Proc. R. Soc. London, Sect. A* **1966**, *295*, 29.
(38) Burchard, W.; Ullisch, B.; Wolf, Ch. *Faraday Discuss. Chem. Soc.* **1974**, *57*, 56.
(39) Müller, M.; Burchard, W. *Makromol. Chem.* **1978**, *179*, 1821.
(40) Burchard, W. *Macromolecules* **1974**, *7*, 835, 841.
(41) Franken, I.; Burchard, W. *Br. Polym. J.* **1977**, *9*, 103.
(42) Gordon, M.; Parker, T. G. *Proc. R. Soc. Edinburgh, Sect. A* **1970**, *69*, 181.
(43) Good, I. J. *Proc. Cambridge Philos. Soc.* **1948**, *45*, 360.
(44) Gordon, M. *Proc. R. Soc. London, Sect. A* **1962**, *268*, 240.
(45) Ullisch, B. Ph.D. Thesis, Freiburg, 1977.
(46) Stauffer, D. 7th Discussion Conference "Polymer Networks", Karlovy Vary, 1980; *Pure Appl. Chem.*, in press.
(47) See: Stauffer, F. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1354.
(48) de Gennes, P. G. *J. Phys. (Paris)* **1977**, *38*, L-335.
(49) Daoud, M. *J. Phys. (Paris)* **1979**, *40*, L-201.
(50) Eschwey, H. Ph.D. Thesis, Freiburg, 1975.
(51) Burchard, W.; Bantle, S.; Müller, M.; Reiner, A. 7th Discussion Conference "Polymer Networks", Karlovy Vary, 1980; *Pure Appl. Chem.*, in press.

Pressure Dependence of Secondary Transitions in Amorphous Polymers. 1. T_{ll} for Polystyrene, Poly(vinyl acetate), and Polyisobutylene

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ABSTRACT: Wood's variation of the Tait equation and several approximations to the Tait equation developed herein have been employed to analyze isothermal volume–pressure data from the literature. Evidence for the T_{ll} transition and its pressure coefficient, dT_{ll}/dP, is given in detail for atactic polystyrene, poly(vinyl acetate), and polyisobutylene. Similar values obtained elsewhere by us on several methacrylates (atactic, isotactic, and cyclohexyl) are cited. Values of T_{ll}/T_g range from 1.15 to 1.20 except for a value of 1.32 for PIB. Application of these techniques to the determination of pressure coefficients for other transitions in the liquid and glassy states (but not T_g) is suggested. dT_g/dP values for the polymers cited, as given by the original authors or in the literature, vary from 20 to 30 K/kbar; values of dT_{ll}/dP are 2–5 times higher, or in the range 50–120 K/kbar. dT_{ll}/dP varies as $28000/T_g$. We suggest that T_{ll} determined from quasi-static $P-V-T$ data has a thermodynamic basis to the same extent that T_g does. We propose tentatively that isothermal values of $1 - V/V_0$ may change for some polymers in an essentially linear fashion as a function of pressure, with slope changes at each pressure-induced transition, and that the entire isotherm may be approximated in such cases by a Tait equation with a single value of b, so long as T is not too far above T_g.

Introduction

This is the first of a series of studies devoted to an analysis of published $P-V-T$ data on amorphous polymers, primarily to determine T_{ll} (at or near $1.2T_g$) and other transitions which may appear in the liquid state as well as their pressure coefficients and, on occasion, liquid-state compressibilities. When data permitted, glassy state transitions, T_β, T_γ, etc., and their pressure coefficients were also determined but will be reported in full in a later paper in this series.

$P-V-T$ data examined include those of Quach and Simha[1,2] and Öels and Rehage[3] for polystyrene (PS), Beret

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and Prausnitz[4] for poly(vinyl acetate) (PVAc) and polyisobutylene (PIB), McKinney and Goldstein[5,6] for PVAc, and miscellaneous methacrylate data by Simha and coworkers.[7-9] The data of Quach, Wilson, and Simha[10] on i-PMMA are treated in part 2.[11] Barlow's data[12] on polybutadiene will be reported on a later occasion. The tabulated data of Hellwege, Knappe, and Lehmann[13] were also considered but not used because their PS specimen was inadequately characterized and their PMMA data did not go to high enough temperature to observe T_{ll}.

Our general procedure involves analysis of isothermal V–P data by means of the Tait equation as well as variations of, and approximation to, the Tait equation. In addition to the P–V–T papers cited above, we have been guided extensively by the work of Breuer and Rehage on P–V–T studies of PS and thermodynamic implications of the results.[14] Papers by Gee[14] and Simha, Wilson, and Olabisi[16] on the Tait equation have been most helpful.

Definition of Terms

1. The Tait equation is commonly written as

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

where C is a constant of the order 0.2 and b is another "constant" which is in the range 1000–4000 bars for polymers. b decreases exponentially with temperature.[4,16] b also experiences step jumps at pressure-induced transitions, as will be seen later. V_0 is specific volume at a reference pressure, usually $P = 1$ bar, and V that at pressure P.

We prefer to use an alternate form of the Tait equation employed by Simha and co-workers,[8,16] namely

$$1 - V/V_0 = C' \ln (1 + P/b) \qquad (2)$$

where C' is assumed to have the universal value of 0.0894. Beret and Prausnitz[4] prefer to calculate C for each polymer but that did not appear necessary for our studies.

2. Wood[17] has proposed several variations of eq 2 by taking the derivative

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

where κ is the compressibility. Inversion gives

$$\bar{K} = \kappa^{-1} = (b/C')(1 + P/b) \qquad (4)$$

where $\bar{K}$ is the bulk modulus. One sees that at $P = 0$

$$b = C'\bar{K} \qquad (5)$$

Wood demonstrated for several rubbers that the bulk modulus does indeed increase linearly with P and that a pressure-induced transition such as T_g appears as a step jump in $\bar{K}$. The straight-line portions above and below the discontinuity have essentially identical slopes but different intercepts. We demonstrate herein that similar behavior is found at T_{ll}, while Quach and Simha[1,2] demonstrated similar behavior for T_β ($T < T_g$) in PS.

3. Compressibilites and Bulk Moduli: Compressibilities are usually designated as κ_l for the liquid state above T_g. We define κ_{ll} as the compressibility above T_{ll}, so that κ_l holds for $T_g < T < T_{ll}$. Similarly for the bulk moduli, one can write $\bar{K}_g$, $\bar{K}_l$, and $\bar{K}_{ll}$. Literature discrepancies about κ_l may arise from κ_l vs. κ_{ll}.

4. T_g(LP): This term was introduced by Quach and Simha[2] to signify a glass formed at low pressure in distinction to T_g(HP), the glass formed by compressing the liquid at high pressure and cooling.

5. T_{ll}: This signifies a liquid–liquid transition temperature found at about $(1.2 \pm 0.05)T_g$ in most amorphous polymers and copolymers. Its characteristic features have been described by Gillham and Boyer.[18-21]

The existence and nature of T_{ll} have been controversial, and discussed in detail elsewhere.[18-21] Patterson, Bair, and Tonelli[22] proposed that for PS, T_{ll} may have a kinetic origin but not a thermodynamic basis. In reaching this conclusion, they ignored without explanation the finding by Höcker, Blake, and Flory[23] of a discontinuity in the coefficient of volumetric expansion, α, at ca. 170 °C for anionic PS of $\bar{M}_n = 51\,000$. Höcker et al.[23] noticed that this behavior corresponded to an apparent third-order transition. Patterson et al.[22] also missed an explicit reference by Wilson and Simha[9] to a liquid–liquid transition in poly(cyclopentyl methacrylate), based on a slope change above T_g in a V–T plot at $P = 1$ bar.

We suggest that the showing herein of discontinuities in compressibility near $1.1T_g$ to $1.2T_g$ and a pressure dependence for T_{ll}, obtained for quasi-equilibrium P–V–T data, will add thermodynamic support to the kinetic evidence for T_{ll} which has been recognized. This is not meant to imply that T_{ll} is an equilibrium-type transition.

6. T_{ll}': A transition or relaxation process lying 30–50 K above the T_{ll} process has been observed on several occasions.[18-21] It is designated for the moment as T_{ll}'. One reviewer notes the need for a clear distinction between a transition phenomenon and the temperature at which it occurs. Thus, it is proper to refer to T_{ll} and T_{ll}' transition temperatures. This is to be inferred throughout when not explicitly stated. We consider the T_{ll} transition phenomenon to arise from intermolecular effects. T_{ll}' from intramolecular causes:[21] By the same token, T_g should signify the glass transition temperature, although this is not common usage in the literature.

7. Volumes and Expansivities: Some authors provide tabular values of specific volumes, symbol V_{sp}, in cm^3 g^{-1}. Others provide only relative volumes, V_{rel} (dimensionless) as V_p/V_0, defined in connection with eq 1 and obtained directly from the experimental data. We calculate V_{rel} from V_{sp} at pressure P and V_{sp} at a reference pressure, commonly, but not always, $P = 1$ bar. Hellwege et al. employ a relative volume, $(V_{200} - V_p)/V_0$, where V_{200} is the specific volume at 200 bars.

We use thermal expansivity, $\beta = (\partial V/\partial T)_P$, in cm^3 g^{-1} deg^{-1} in Figure 1; in contrast, the coefficient of thermal expansion, $\alpha = (1/V)(\partial V/\partial T)_P$ is in units of deg^{-1}.

8. Intersection Pressures: We later introduce intersection pressures, P^i, as the intersection of two linear, or nearly linear, segments of a V–P isothermal plot. n is an integer which increases with the number of the intersection, i.e., 1, 2, 3, starting at low pressure. If the nature of the pressure-induced transition causing this intersection is known, the same reviewer commented, consistent with remarks in item 6, then one can speak of P_{ll} and P_{ll}' transition pressures. Other designations such as P_g and P_β should also be used. In the absence of such specific information, we employ the general designation P^i, where the superscript i denotes "intersection".

9. Apparent Third-Order Transition: T_{ll} has been termed on several occasions[20,21,23] as an "apparent third-order transition" in the Ehrenfest sense that it appears as a discontinuity in the second derivative of volume, V, or heat content, H, with respect to T. In view of many similarities in behavior between T_g and T_{ll}, it is our belief that the transition is only weaker and more diffuse than, but not different in kind from, T_g. Emphasis should be on the word "apparent".

If T_{ll} transition temperature is that at the intersection of two quadratics in H, or V, it is clear that there will be a discontinuity in $\mathrm{d}^2H/\mathrm{d}T^2$ or $\mathrm{d}^2V/\mathrm{d}T^2$. Hence, in the

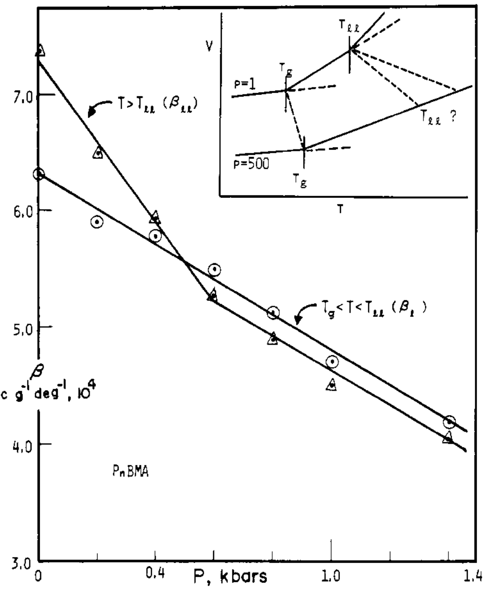

Figure 1. Inset: schematic V–T plots near T_g and T_{ll} at $P = 1$ and $P = 500$ bars, showing the apparent disappearance of the liquid transition under hydrostatic pressure. Main figure shows a numerical example of thermal expansitivity, β, above and below T_{ll} for PnBMA. At pressures of ca. 500 bars and above $\beta_{ll} \equiv \beta_l$. A continuous curve can be drawn through the triangles.

sense that we use it herein, the term "third-order transition" is a commentary on $H = f_1(T)$ or $V = f_2(T)$ rather than an attempted description of the nature of the transition. Similar remarks apply if a derivative quantity $C_p = \mathrm{d}H/\mathrm{d}T$ or $\alpha = (1/V)(\partial V/\partial T)_p$ follows two intersecting first-degree equations.

We have shown that the V–T data of Höcker et al.[23] follow two quadratics above T_g,[20] as do the V–T data of Wilson and Simha on poly(cyclopentyl methacrylate)[21] at $P = 1$ bar. Höcker et al.[23] found a slope change for α for the same PS data. We found a slope change in C_p for data on synthetic rubbers.[21]

In the present study, comments as to whether a certain body of data shows second- or third-order transition behavior are basically a shorthand commentary on the data, which may not have sufficient data points and/or accuracy to provide an exact answer as to apparent order of the transition.

Isobaric V–T Plane vs. Isothermal V–P Plane

Original attempts to determine T_{ll} from P–V–T data involved regression analysis of the region above T_g in the V–T plane. It soon became apparent from an exhaustive analysis of V–T data by Olabisi and Simha[8] on PnBMA that this procedure could not succeed for the reason presented in Figure 1. The inset to this figure shows schematically that even when T_{ll} can be observed at $P = 1$ bar, T_{ll} is obliterated by pressure at $P = 500$ bars and higher and is difficult to locate at $P = 300$–500 bars. On the basis of point-to-point derivatives, values of expansivity in the liquid state just above T_g, namely, β_l in cm^3 g^{-1} deg^{-1}, were obtained. Figure 1 is a plot of β_l and β_{ll} against P. It is evident that T_{ll} can be readily observed at $P = 1$ bar, possibly at $P = 200$ bars, but only with difficulty or not at all at higher pressures (see Figure 13 of ref 21 for V–T plots at high P).

It is well-known that pressure diminishes the magnitude of the expansivity $\alpha_l - \alpha_g$ at T_g. An example for PVAc appears in Table 9c of the McKinney–Goldstein paper.[5] The slope change at T_{ll} is weaker than that at T_g. For example, from the PnBMA data in ref 8, we calculate $\beta_l - b_g$ as 2.3×10^{-4} cm^3 g^{-1} deg^{-1}, which is 2 times the corresponding quantity at T_{ll}. Even so, $\Delta\beta$ at T_g in PnBMA is unusually weak because of the strong β relaxation. A more common value of $\Delta\beta$ at T_g is 4×10^{-4} cm^3 g^{-1} deg^{-1}.

Linear regression analysis of PVAc V–T data at $P = 0$ shows $\beta_l = 6.134 \times 10^{-4}$ cm^3 g^{-1} deg^{-1} and $\beta_{ll} = 6.1325 \times 10^{-4}$ cm^3 g^{-1} deg^{-1} for $\Delta\beta = 0.191 \times 10^{-4}$ cm^3 g^{-1} deg^{-1} or $\Delta\alpha = 0.221 \times 10^{-4}$ deg^{-1} compared to $\Delta\alpha$ at $T_g = 4.141 \times 10^{-4}$ deg^{-1}. At 200 bars, for which $T_{ll} = 85$ °C, values of ΔV for 5 °C intervals from 70 to 85 °C average 0.002 94 cm^3 g^{-1}; from 85 to 100 °C the average is 0.0028 cm^3 g^{-1}. These results are based on data in Table 1, ref 5.

Considerations such as these demonstrated that enhanced compressibility above T_{ll} was sufficient to neutralize or even reverse any potential increase in thermal expansion at T_{ll}. This conclusion suggested working in the V–P plane to determine possible discontinuities in κ_l at T_{ll}. Wood's variations of the Tait equation seemed ideally suited to this purpose.

Application of eq 3 and 4 to V–P data on PVAc and PS quickly revealed a discontinuity in b at T_{ll}, equivalent to a discontinuity $\kappa_{ll} - \kappa_l$ in compressibility. Plots of $\bar{K}$ vs. P and κ vs. P indicated quite clearly the existence of T_{ll} at $P > 1$ bar. We later show examples of both kinds of plots. However, these methods sometimes proved unsatisfactory for one or more of the following reasons: (1) inherent weakness of the T_{ll} transition compared with that at T_g; (2) scatter in point-to-point derivatives; (3) limited number of data points; (4) multiple transitions over the pressure region being studied.

We therefore developed tractable approximations to the Tait equation which, though potentially less accurate, would eliminate some of the problems inherent in eq 3 and 4.

We might add, parenthetically, that PnBMA was likely the least favorable choice to use with the isobaric V–T plane, mainly because of the extremely bulky side groups. Poly(cyclohexyl methacrylate) was an equally bad choice. a-PS and i-PMMA showed some evidence of T_{ll} in V–T plots but only at moderate pressures, generally less than 0.6–0.8 kbar. Such V–T plots will be presented on a later occasion.

Approximations to the Tait Equation

The logarithmic term in eq 2 can be expanded[26] as an infinite series in P/b so long as $P/b \leq 1$:

$$1 - V/V_0 = C'(P/b)[1 - (1/2)(P/b) + (1/3)(P/b)^2 - +] \qquad (6)$$

This suggests a linear increase in $1 - V/V_0$ when P/b is small, say less than 0.3–0.4. Since b makes a step jump at the first pressure-induced transition, the range of eq 6 is then extended to higher pressures. Alternately, as an approximation, one can write

$$P^{-1}(1 - V/V_0) \cong (C'/b)[1 - P/2b] \qquad (7)$$

which is indeterminate near $P = 0$ but may be used in the range $0.2 < P/b < 0.6$–0.8. The first derivative of eq 6 gives the compressibility:

$$\kappa_l \cong C'[1 - P/b + -] \qquad (8)$$

This same expression is obtained by series expansion of $(1 + P/b)^{-1}$ in eq 3. Use of eq 8 requires calculation of point-to-point derivatives and hence suffers the limitations already discussed in connection with Wood's eq 3 and 4.

Equations 6 and 7 are quite convenient when the original authors of P–V–T data give tabulated values of V/V_0, as in ref 4 and 13. More commonly, values of V_{sp} in cm^3 g^{-1}

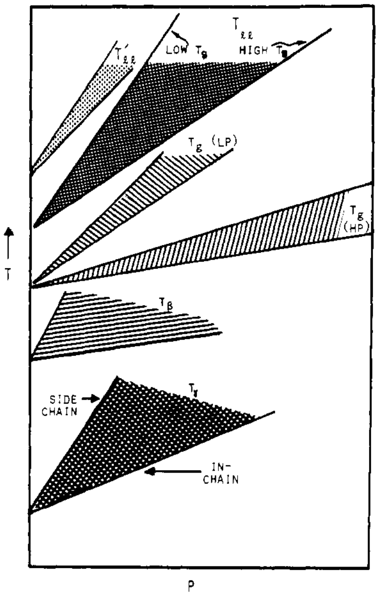

Figure 2. Schematic illustration of the transition temperature–pressure plane indicating the normal expected locations of the several transitions at $P = 1$ bar and how they might increase with pressure. Actual examples for specific polymers appear later. This figure uses experimental findings to date.

are used. By a double-logarithmic expansion of eq 2 one obtains

$$\ln (V_{sp}/V_0) = -(C'P/b)[1 - P/2b + (1/3)(P/b)^2 + C'P/2b(1 - P/b) + -] \quad (9)$$

A useful approximation for small P/b is

$$\ln V_{sp} = \ln V_0 - C'P/b[1 - (P/2b) + -] \quad (10)$$

which we use with the first term only for P/b less than 0.3–0.4, and

$$P^{-1} \ln (V_{sp}/V_0) \cong -(C'b)[1 - P/2b] \quad (11)$$

which is indeterminate near $P = 0$. Obviously one can employ log in eq 9–11.

Hence a series of convenient approximations to the Tait equation may be employed in evaluating V–P data. In general, we prefer to use several approximations such as eq 6, 7, 8, and 10, as well as the exact eq 4, because each one provides a slightly different viewpoint of the same data.

The parameter b in eq 1 and 2 may be determined by trial and error to give the best fit to data in a V–P isotherm. This can be a tedious procedure unless computer regression techniques are employed. However, the initial slope in eq 6 is C'/b while the intercept in eq 8 is also C'/b. Small variations in these first approximations to b can then be made to achieve a better fit of the data to eq 1 and 2. The newer, higher value of b above each pressure-induced transition can be estimated from the form of eq 4–11.

Transition Temperature–Pressure Plane

Even though major interest centered on the T_{ll} transition, it soon became apparent that one should be aware of all transitions in the T–P plane because of possible crossovers. Figure 2 is a schematic depiction of this plane and was constructed with the following basic facts or assumptions.

1. Amorphous polymers and copolymers will exhibit a small number of transitions and relaxations at $P = 1$ bar.
2. The most prominent of these is the glass transition, T_g, whose location as a function of pressure is usually given by the authors of the P–V–T data.
3. Other glass transitions, determined by various thermal histories, may be given, as in the data of Quach and Simha for PS[1,2] and McKinney and Goldstein for PVAc.[5]
4. Most polymers will have a glassy state relaxation, designated T_β, usually lying at or near $0.75T_g$ for $P = 1$ bar.
5. There may be one or more additional glassy state relaxations found at decreasing temperatures, T_γ, T_δ, T_ϵ, etc., all lying below T_β in the order indicated.
6. T_{ll} is usually to be found in the range $(1.15–1.25)T_g$ at $P = 1$ bar. It is weak compared to T_g by any test method, as already noted.
7. All of these transitions are expected to have positive pressure coefficients, dT/dP, whose magnitude cannot be predicted a priori.
8. dT_g/dP is most studied and usually falls in the range 15–30 K/kbar.
9. Experience to date places dT_{ll}/dP at 2–5 times dT_g/dP, consistent with the greater amount of free volume in the liquid state. We show elsewhere[11] that $dT_{ll}/dP = 28000/T_g$, where dT_{ll}/dP is in K/kbar.
10. dT_β/dP is generally greater than dT_g/dP, with the result that T_β crosses the T_g(HP) line at elevated pressure and appears in the liquid region at elevated pressure, as shown by Quach and Simha for PS.[1,2] If the side group is bulky, as with PnBMA, then $dT_\beta/dP \gg dT_g/dP$ and the T_β–P locus may even cross the T_{ll}–P locus.
11. The schematic drawing in Figure 2 clearly suggests the correct procedure to use for plotting V–P isotherms to determine intersection pressures, P^i_n. For example, some 20–40 K above $1.2T_g$ at $P > 0$ one might expect to observe slope changes in plots of $1 - V/V_0$ vs. P or log V_{sp} vs. P as follows:

$$P^i_1 = T_{ll} \qquad P^i_2 = T_g(\text{LP}) \qquad P^i_3 = T_\beta$$

These pressures P^i_1 should move to higher values as isotherms of higher temperature are followed: Some 50 K above T_{ll} at $P > 0$, one may observe T_{ll}' vs. P^i. If one starts at an isotherm 20–40 K above T_g, the slope changes should occur at $P^i_1 = T_g$(LP), $P^i_2 = T_\beta$, and $P^i_3 = T_g$(HP). For an isotherm below T_g, a common pattern is $P^i_1 = T_\beta$, $P^i_2 = T_\gamma$, although these may be reversed.
12. Conversely, one may prefer to start in the glassy state when data permit, locating β and γ transitions, for which it is desirable to have quasi-static values from the literature at $P = 1$ bar. One then follows these secondary processes at ever higher isotherms, picking up the glass and low-pressure glass processes until one is well into the liquid state.
13. It is clear from Figure 2 that the liquid state may be a more active region in terms of multiple transitions than was hitherto generally suspected. One inherent weakness of most sets of P–V–T data is the lack of sufficient data points in a V–P isotherm to resolve these multiple transitions accurately. This problem is alleviated by several practices: (a) using all of the V–P isotherms that are available, especially in the liquid state; (b) using multiple forms of the Tait equation, starting with eq 4 and then several approximate forms, eq 6–11; (c) using data by several authors whenever possible. Figure 10 provides a good example on PVAc with two sets of authors, offering a combined total of seven isotherms and several different methods.

The actual sequence in b is rather important. If eq 4, starting at the highest isotherms, exhibits several step jumps in $\bar{K}$ and, hence, in b, it follows that that isotherm cannot be represented by eq 1 and 2 with a single value of b. This is generally confirmed by eq 3 plots. Equation 7 or 11 is then next in accuracy because of the term $P/2b$

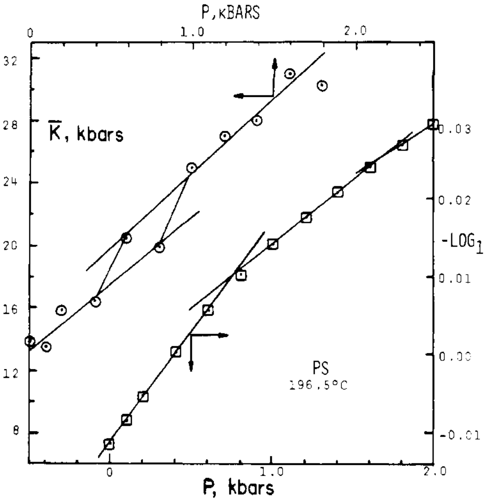

Figure 3. Top curve: bulk modulus $\bar{K}$ vs. pressure for a-PS at 195.6 °C (data of Quach and Simha[2]); bottom curve: same data plotted as $-\log V_{sp}$ against pressure. Discontinuities in $\bar{K}$ near 0.5–0.9 kbar and a slope change in $-\log V$ at 0.76 kbar indicate T_{ll} temperature, suggesting, respectively, second- and third-order transitions for T_{ll}.

in the approximation forms. We then rely on the first term in eq 6 or eq 10 for the lowest temperature isotherms still expected to show a slope change at T_{ll}.

It is important to emphasize that we are not interested in the exact representation of P–V–T data since that is already covered in the literature via eq 1 and 2. Rather we seek to locate transition pressures around which slope changes occur.

Following this detailed introductory material, actual V–P data can now be analyzed. a-PS is treated first because of extensive background material in ref 1–3 and 13–16. PVAc is then treated with data from two sets of authors.[4,5] PIB and methacrylates then follow.

Polystyrene

Quach and Simha[1,2] have published tabulated V_{sp} values at 8 temperatures above T_g at 12 pressures up to 2000 bars. Regression analysis of V–T data at P = 1 bar suggested but did not prove the existence of a T_{ll} transition near 163 °C but did locate T_g at 95 °C. Hence, isothermal V–P data were analyzed at T = 173.5, 184.9, and 195.6 °C.

Figure 3 compares Wood's method, namely, eq 4, with the log V–P plot for a set of PS data from Quach and Simha.[2] These data emphasize some ambiguity in the Wood plot compared to greater certainty in the log V method. This example should not be construed as a general criticism of Wood's method, which is a rigorous variation of the Tait equation, in contrast to our approximation.

Figure 4 is plot of log V against P for three PS isotherms, showing the progressive change in P at T_{ll} with temperature. Figure 4 shows other transitions occurring in the V–P plane. Not given are plots for 140.2 °C which show breaks corresponding to T_g(LP) and T_g(HP) at 690 and 1330 bars, respectively, and a plot for 52.7 °C which shows a slope change for T_β at 1000 bars. Figure 5 is a plot of log V_{sp} vs. P and of $1 - V/V_0$ vs. P for data from Öels and Rehage[3] on anionic PS, M_n = 20 400, at 196.6 °C. Breaks in the first plot occur at 415 and 800 bars. The former may be T_{ll}';[18] the latter is T_{ll}. Figure 6 is a plot of T_{ll} vs. P from Figures 4 and 5. The line as drawn has a slope dT_{ll}/dP = 60 K/kbar or about twice the value of dT_g/dP given by Quach and Simha (31.6 K/kbar). The higher value for T_{ll} is consistent with the greater amount of free volume at T_{ll} than at T_g.

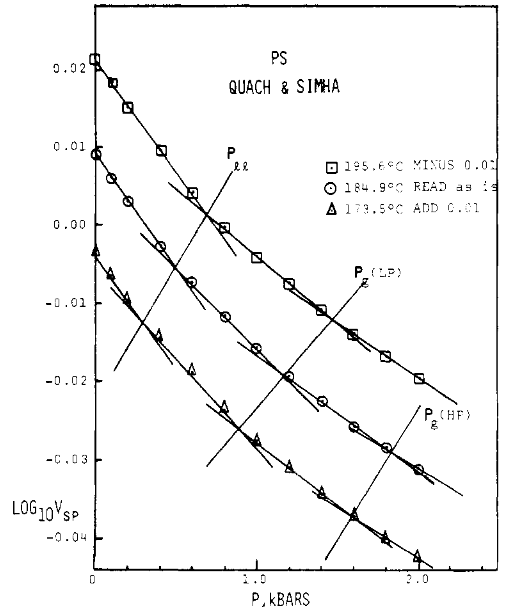

Figure 4. Isothermal log V_{sp}–P PS plots at (top to bottom) 195.6, 184.9, and 173.5 °C (data of Quach and Simha[2]). Loci for P_{ll}, low-pressure glass (P_g(LP)), and high-pressure glass (P_g(HP)) are indicated. Curves are shifted as follows: middle, read scale directly; top, subtract 0.01 from scale reading; bottom, add 0.01 unit.

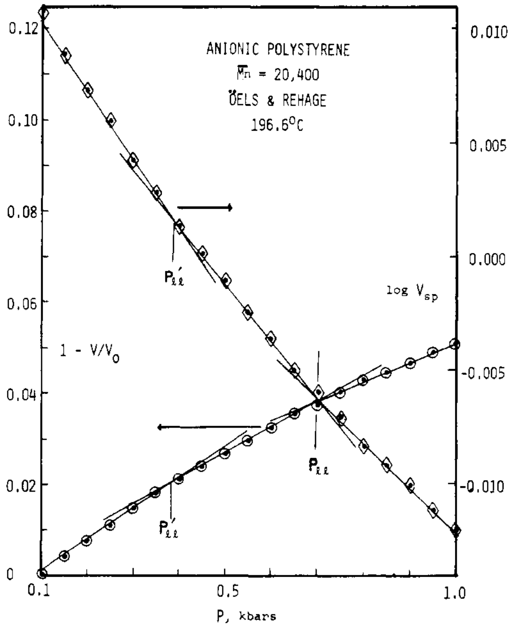

Figure 5. log V_{sp}–P and $1 - V/V_0$–P plots for anionic PS, $\bar{M}_n$ = 20 400 at 196.6 °C. Data of Öels and Rehage.[3]

Also shown on Figure 6 are the loci for the low- and high-pressure glasses, T_g(LP) and T_g(HP), as defined and determined by Quach and Simha for T_β. Loci for these three transitions are taken from Figure 8 of ref 2. This method of plotting demonstrated that T_{ll} is distinct and separable from the glassy transitions in PS at elevated pressures.

The V–P data of Öels and Rehage on PS provide an excellent example of a sufficient number of data points to demonstrate linear segments interacting at transitions. We have shown by regression analysis that these segments are linear within experimental error. In a later paper we plan to analyze this data in more detail and also the PBD data of Barlow,[12] together with synthetic data based on the Tait equation. As indicated earlier, most tabulated P–V–T data

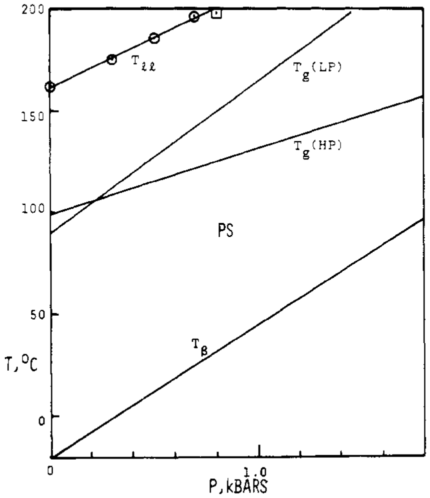

Figure 6. T_{ll}–P plot for a-PS with T_{ll} values from Figures 4 and 5. Slope of the line is dT_{ll}/dP = 60 K/kbar. Also shown without data points are the loci for three glassy state transitions from Quach and Simha.[2]

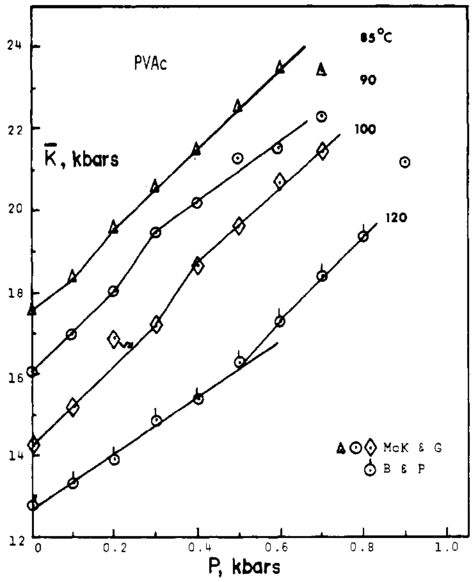

Figure 7. Bulk modulus vs. P for PVAc. Top three plots represent data of McKinney and Goldstein;[5] bottom, Beret and Prausnitz.[4] Curves have been shifted as follows: 90 °C, scale reading correct; 85 °C, subtract one unit from indicated units; 100 °C, add one unit; 120 °C, add two units.

lack sufficient points to provide completely unambiguous plots of $1 - V/V_0$ or $\ln V_{sp}$ against pressure.

Poly(vinyl acetate) (PVAc)

Liquid-state P–V–T data of McKinney and Goldstein[5] from 35 to 100 °C and up to 800 bars were studied along with the relative volume data of Beret and Prausnitz[4] at six temperatures from 64 to 120 °C and pressures up to 1000 bars. Both sets of data, when treated either by eq 4 or eq 10, show evidence for T_{ll} and permit an estimate of dT_{ll}/dP. Typical data plots are shown in Figure 7 for bulk moduli vs. P and in Figure 8 for $\log V_{sp}$ or $\log V_{rel}$ vs. P.

Figure 9 is an eq 8 type plot of κ_l vs. P with a slope change at T_{ll} and, hence, a discontinuity in $d\kappa_l/dP$. Scatter in κ_l discouraged us from presenting similar plots on all other sets of data.

Figure 10 shows T_{ll} as a function of pressure, using values of T_{ll} from both sets of authors[4,5] as read from Figure 8. Linear regression analysis carried out by us for the liquid-state V–T data of McKinney and Goldstein at P = 0 suggests but does not prove a T_{ll} between 65 and 70 °C. The line as drawn in Figure 9 corresponds to dT_{ll}/dP of 64 K/kbar. Examination of Figure 7 of ref 5 shows that our T_{ll} is distinct from any of the three T_g–P loci which McKinney and Goldstein reported. Also shown in Figure 10 is our estimate of the locus of T_g(LP) in the T–P plane.

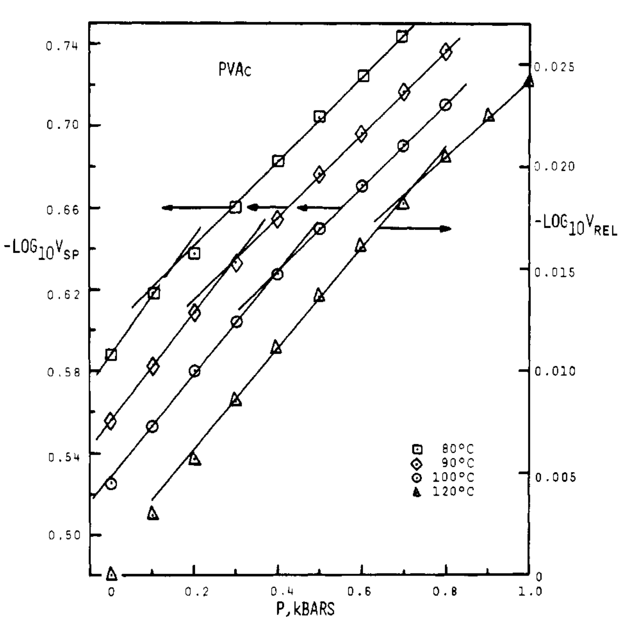

Figure 8. PVAc data: top three curves are $-\log V_{sp}$–P from McKinney and Goldstein;[5] bottom curve, $-\log V_{rel}$–P from Beret and Prausnitz.[4]

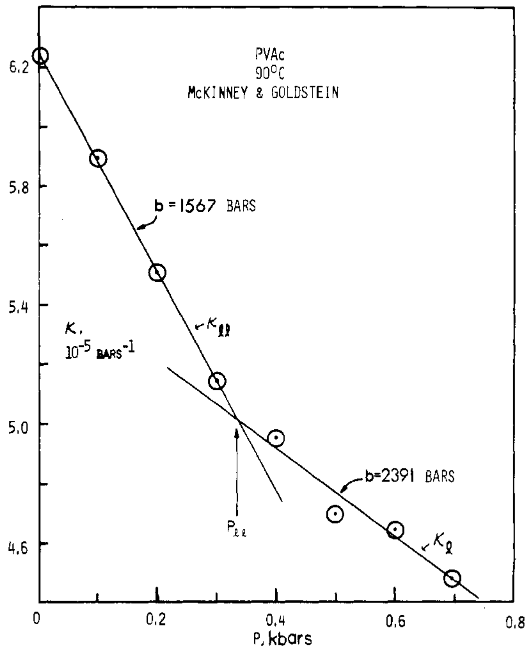

Figure 9. Compressibility–P plot according to eq 5 for PVAc data at 90 °C from ref 5. The discontinuity in $d\kappa/dP$ at P_{ll} is indicative of a third-order transition. Upper b calculated from intercept, lower one from slope.

It is evident that the 90 °C PVAc data of McKinney and Goldstein[5] shown in Figure 8 as linear in $\log V_{sp}$–P and in Figure 9 as κ vs. P cannot be simultaneously true mathematically since the slope of $\log V_{sp}$ vs. P is κ_l. The former indicates T_{ll} as a second-order transition and the latter plot shows T_{ll} as a third-order transition. In this case the straight lines drawn in Figure 8 depict an average slope.

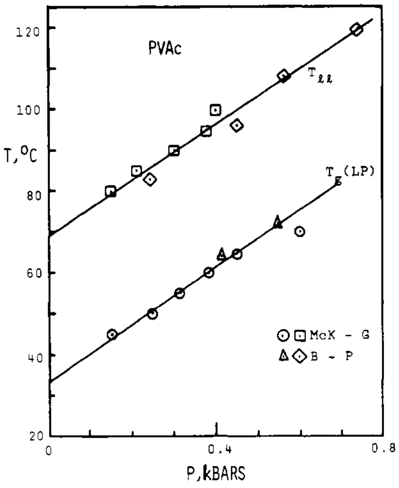

Figure 10. Top line: T_{ll} vs. P for PVAc, based on data in Figure 6 and ref 4 and 5. dT_{ll}/dP = 70 K/kbar. Bottom line: locus for low-pressure glass based on log V_{sp}–P plots not shown.

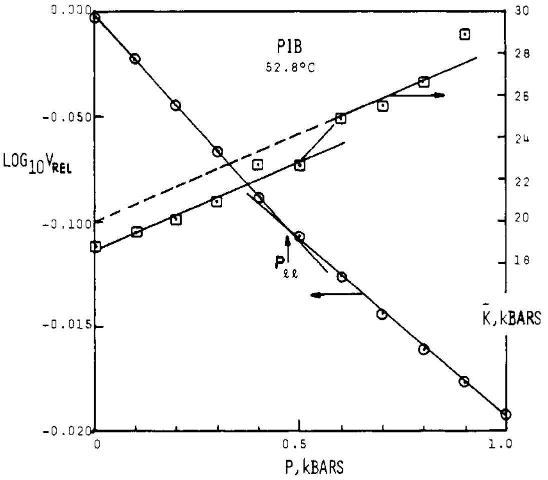

Figure 11. Comparison of eq 4 plot and eq 10 representation for PIB at 52.8 °C from data of Beret and Prausnitz.[4]

The volume data of ref 5 were subjected to a double-smoothing operation as depicted by their eq 5. We prefer to work with raw data since smoothing may introduce a prejudice. For the data available, Figure 9 is rigorously correct. Figures 8 and 9 give nearly identical values of T_{ll}.

Polyisobutylene (PIB)

The existence of T_{ll} in PIB has been amply demonstrated based on dynamic mechanical loss results and adiabatic calorimetry data, both of which have been reviewed by Gillham and Boyer.[27] DSC and other data were summarized by Enns and Boyer.[28] We consider the quasi-static value of T_{ll} to be 264 K, which, with the literature T_g value of 200 K, gives a quite high T_{ll}/T_g value of 1.32.

Beret and Prausnitz[4] presented relative volumes on a PIB of $\bar{M}_v$ = 36 000 at five temperatures from 52.8 to 110 °C and pressures to 1000 bars. We have examined these data by the methods of eq 4 and eq 10. Figure 11 compares these two methods at 52.8 °C, which places T_{ll} conveniently near the midrange of pressure. The two methods show a difference of 0.075 kbar in the location of T_{ll}. Figure 12 summarizes the variation of T_{ll} with pressure by both methods. Results at 84.8 and 110 °C may be doubtful because they are both near the upper limit of pressure covered.

Also shown is a point at 30 °C based on density–pressure data at 30 °C for PIB by Singh and Nolle.[29] Their data are in graphical form. However, these authors state that κ is 2.4 × 10^{11} cm^2/dyn from 0 to 348 bars and 1.8 × 10^{11} from 348 to 689 bars. We assume that this apparent discontinuity in κ at 344 bars indicates T_{ll}. Indeed, this datum point fits very well on Figure 12. The line as drawn in Figure 12 corresponds to dT_{ll}/dP of 120 K/kbar, at least up to 60 °C.

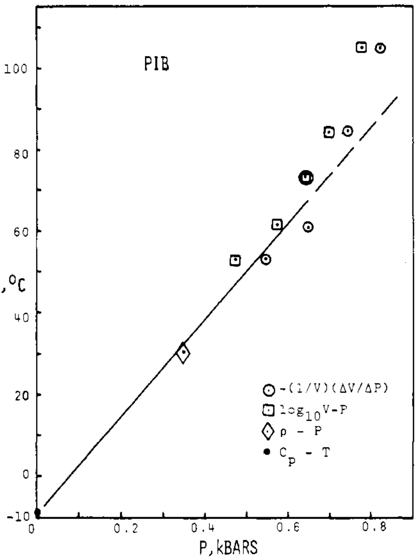

Figure 12. Variation of T_{ll} with P for PIB by several methods. The line corresponds to dT_{ll}/dP = 120 K/kbar up to about 60 °C. All data from ref 4 except density–pressure point from ref 29.

Table I
Summary of Thermodynamic Parameters

polymer[a]	T_g,[b] K	T_{ll},[b] K	T_{ll}/T_g[b]	dT_g/dP[c]	dT_{ll}/dP[c]
1. PIB	200	264[d]	1.32	24[k]	120[f]
2. PnBMA	293[e]	358[f]	1.20	20.4[e]	75[f,m]
3. PVAc	298	343[f]	1.15	22[k]	64[f]
4. i-PMMA	323[g]	383[h]	1.19	21.1[g]	70[h]
5. PS	368[f]	436[f]	1.18	31.6[l]	60[f]
6. a-PMMA	378[e]	[i]		23.6[e]	66[n]
7. PCHMA	380[e]	438[j]	1.15	22.4[e]	50[j]

[a] Arranged in order of increasing T_g. [b] At P = 1 bar. [c] K/kbar. [d] Reference 28. [e] Reference 7. [f] This report. [g] Reference 10. [h] Reference 11. [i] DSC value from ref 34. [j] Reference 21. [k] Reference 35. [l] Reference 2. [m] Tentative value. [n] Estimated by us from DSC values at 1 and 136 atm given by Panke and Wunderlich in ref 34.

The apparent upswing in T_{ll} above ca. 70 °C or 0.7 kbar with data from eq 4 and eq 10 plots might possibly represent T_{ll} combined with a glassy transition such as T_g(LP) or T_β. dT_g/dP has a normal value of 24 K/kbar (see Table I) and cannot be involved. PIB is usually considered not to have a β relaxation although a weak one has been observed by torsional braid analysis at a frequency of about 1 Hz.[27]

Methacrylate Polymers

Wilson and Simha[9] observed a T_{ll} at P = 1 bar in V–T data on poly(cyclopentyl methacrylate) (PCPMA) and poly(cyclohexyl methacrylate) (PCHMA). Olabisi and Simha[7] later gave P–V–T data on PCHMA. We have analyzed these data with log V_{sp} plots in the glassy and liquid states (plots not shown herein).[21] These data provide evidence for the pressure dependency of T_{ll}, T_g(LP), T_β, and T_γ in addition to T_g(HP) by the authors.[7] Values of dT_g/dP and dT_{ll}/dP appear in Table I.

A detailed study of data in ref 7 on PnBMA was complicated by the very strong pressure dependence of T_β, namely, 218 K/kbar, and for T_g(LP), of 240 K/kbar. The high value of T_β is probably a direct consequence of the important role played by the flexible *n*-butyl side group. This is consistent with the dielectric data of Williams and Edwards.[30,31] We present in Table I a tentative value for $\mathrm{d}T_{ll}/\mathrm{d}P$. No log V–P plots are included herein.

V–P isotherms on i-PMMA based on the tabulated data of Quach, Wilson, and Simha,[10] showing pressure coefficients for T_{ll}, T_β, and T_g(LP), are presented elsewhere.[11] Except for T_g, transition behavior of this polymer has been controversial, as we discussed in a recent review.[32] Whereas the V–T data of Wilson and Simha[9] at $P = 1$ bar did not indicate a T_{ll}, we found evidence for it in other atmospheric pressure V–T data.[32] We also presented literature data showing that the intensity of the β relaxation did not go to zero for pure i-PMMA.[32] Both showings were confirmed by our V–P analysis.[11]

While P–V–T data on a-PMMA have been presented by two sets of authors,[7,13] temperatures do not reach the T_{ll} region, possibly because of concern about thermal decomposition. Table I contains a provisional value of $\mathrm{d}T_{ll}/\mathrm{d}P$ which we calculated from DSC values of T_{ll} at $P = 1$ bar and $P = 136$ atm given by Panke and Wunderlich.[34]

Discussion of Results

Table I summarizes values of T_g, T_{ll}, T_{ll}/T_g, $\mathrm{d}T_g/\mathrm{d}P$, and $\mathrm{d}T_{ll}/\mathrm{d}P$ for the polymers analyzed herein and elsewhere.[11,21] Entries are arranged in order of increasing T_g. These points seem clear:

1. T_{ll}/T_g is relatively constant but high for PIB, as has been noted elsewhere.[27,28]
2. $\mathrm{d}T_g/\mathrm{d}P$ shows little variation.
3. $\mathrm{d}T_{ll}/\mathrm{d}P$ varies inversely with T_g. In fact, we have shown[11] that

$$\mathrm{d}T_{ll}/\mathrm{d}P = 28000/T_g\ (\mathrm{K}) - 20 \tag{12}$$

which is strongly influenced by the high value of T_{ll} for PIB. $\mathrm{d}T_{ll}/\mathrm{d}P$ is in K/kbar.

We suggest[11] that this implies a direct dependence on the expansion of free volume above T_g, which is proportional to $\Delta\alpha = \alpha_l - \alpha_g$ and, hence, via the Simha–Boyer[33] empirical result, proportional to $0.11/T_g$.

Equation 12 has several useful functions. It implies that the techniques we have used to locate T_{ll} in the isothermal V–P plane and to determine $\mathrm{d}T_{ll}/\mathrm{d}P$ are generally correct, or at least self-consistent. Secondly, it has predictive powers. Beret and Prausnitz published tabulated P–V–T data on poly(dimethylsiloxane) (PDMS) from 25 to 70 °C.[4] In view of the low T_g and low estimated T_{ll} of about −90 °C, we doubted that T_{ll} could be observed in their data. Equation 12 predicted a $\mathrm{d}T_{ll}/\mathrm{d}P$ of 170 K/kbar. It was immediately evident that pressures of 0.7 kbar and greater should bring T_{ll} into their range of measurements. This has now been verified. We are delaying publication, pending the location in the literature of other P–V–T data on PDMS.

In addition, eq 12 has diagnostic ability. We have used it to check a value of $\mathrm{d}T_{ll}/\mathrm{d}P$ for a-PMMA reported by Panke and Wunderlich,[34] as indicated in Table I.

The basic thesis of this study has been that certain functions of volume such as $1 - V/V_0$ or $\ln V_{sp}$ can be approximated as linear in P over limited pressure ranges, with slope changes at each pressure-induced transition. This thesis seems amply verified by numerous examples given herein and elsewhere.[11,12] We are now examining an alternate hypothesis which states (1) that $1 - V/V_0$ and/or $\ln V_{sp}$ are nearly linear in P over limited pressure ranges between multiple transitions in the liquid state and (2) that the Tait equation with a single value of b gives a remarkably good representation of $1 - V/V_0$ and/or $\ln V_{sp}$ over the entire set of straight-line sections. However, representation of such data by eq 1 or 2 leads to a set of residuals R, where $R = [(1 - V/V_0)$ observed $- (1 - V/V_0)$ calculated from the exact Tait equation at constant $b]$ such that the R's are not random about zero.

This hypothesis has been tested rigorously with the Öels and Rehage data on PS shown in Figure 5, with the PBD data of Barlow[12] not yet discussed, and less rigorously, because of a paucity of data points, on i-PMMA. This hypothesis, if proven generally true, will reconcile our studies on the liquid state with previous investigations of the Tait equation. Moreover, it does not vitiate any of graphs and conclusions presented thus far, except Figure 9. We have not yet applied this new hypothesis to the glassy region.

Semicrystalline Polymers. Our experience to date suggests that crystallinity inhibits the appearance of T_{ll} at $P = 1$ bar. However, available evidence suggests that the pressure coefficient for melting, $\mathrm{d}T_m/\mathrm{d}P$, tends to be small.[36,37] For some semicrystalline polymers, $\mathrm{d}T_m/\mathrm{d}P$ might be considerably smaller than $\mathrm{d}T_{ll}/\mathrm{d}P$. It is thus possible, in principle, to bring T_{ll} above T_m. A preliminary examination of P–V–T data on both linear and branched polyethylene, as tabulated by Olabisi and Simha[8] and by Hellwege et al.,[13] using eq 4, 6, 8, and 10, does indeed show evidence for multiple transitions in the melt and in the semicrystalline state. We have not yet fully deciphered these results but there may be evidence for T_{ll}. Analysis is hampered by the well-known difficulties with multiple transitions in PE at atmospheric pressure.

Other P–V–T Data. The P–V–T data discussed in this paper, as well as in ref 11 and 21, and the unpublished studies on PBD, PDMS, and PE do not represent all of the available literature but rather the systems which we have chosen to study thus far because the polymers are standard ones with data from several sets of authors.

Application of Ehrenfest Equations to T_{ll}

H.-G. Elias, Director of our Institute, suggested that we test the Ehrenfest equations, normally employed for T_g at T_{ll}, namely

$$\mathrm{d}T_g/\mathrm{d}P = \Delta\kappa/\Delta\alpha \tag{13}$$

and

$$\mathrm{d}T_g/\mathrm{d}P = TV\Delta\alpha/\Delta C_p \tag{14}$$

As is known (ref 3 and 13–15 and elsewhere) eq 14 is more nearly correct than eq 13. The several quantities on the right-hand side of eq 13 and 14 are readily measured at T_g. However, they are smaller and more difficult to determine at T_{ll}. This is especially true of $\Delta\alpha$. Thus far these quantities, when known, are not available on identical specimens. Moreover, there is a problem with the apparent order of the transition. There is no ΔC_p at T_{ll} but simply an endothermic slope change indicative of an apparent third-order transition. Slope changes in $\ln V_{sp}$–P plots suggest a $\Delta\kappa$ but a Figure 9 type plot indicates a discontinuity in $\mathrm{d}\kappa/\mathrm{d}P$.

Since T_{ll} may be more nearly an equilibrium transition than is T_g, a test of these or similar equations will be of interest. Any further discussion of this topic is premature.

One reviewer points out that eq 13 and 14 properly refer to a second-order transition temperature, T_2, and that our inquiry should concern whether or not T_{ll} relates to T_2. In practice, many authors do employ eq 13 and 14 as if $T_g \equiv T_2$.

Summary and Conclusions

1. $P-V-T$ data from the literature have been employed for the first time to demonstrate the existence of a liquid-liquid transition, T_{ll}, above T_g and to determine its pressure coefficient, dT_{ll}/dP.

2. It has been found experimentally that isobaric $V-T$ data may reveal T_{ll} under favorable conditions at P of one to several hundred bars but not at higher pressures and hence are not suitable for estimating dT_{ll}/dP.

3. This results because enhanced compressibility above T_{ll} weakens or destroys the tendency for enhanced thermal expansion above T_{ll}.

4. Isothermal $V-P$ data take advantage of this enhanced compressibility and allow one to determine T_{ll}, dT_{ll}/dP, and κ_{ll}, in additin to the normal liquid-state compressibility κ_l.

5. These isothermal $V-P$ data have been analyzed by Wood's exact variation of the Tait equation and by several approximations to the Tait equation developed herein. These equations permit some function of volume, or its temperature derivative, to be plotted as linear in P. These plots consist of two or more straight-line sections whose intersections define transition pressures, P^i, and whose slopes are proportional to compressibilities.

6. Such plots reveal the liquid state ($T > T_g$) of polymers to be more active than has been generally realized. A liquid-state isotherm might reveal, under rare circumstances, the following transition pressures in sequence: P_{ll}', P_{ll}, P_g(LP), and P_β.

7. Pressure coefficients dT_{ll}/dP are reported in Table I for PIB, PnBMA, PVAc, i-PMMA, PS, and PCHMA. Polymers still under study include PBD, PDMS, and PE.

8. dT_{ll}/dP varies inversely with T_g or, as first shown in ref 11

$$dT_{ll}/dP = 28000/T_g - 20 \qquad (15)$$

This equation has both diagnostic and predictive capabilities.

9. The techniques described above have also been applied to the glassy state to reveal, when data permit, T_β and T_γ as well as their pressure coefficients. Discussion of this material is planned for a later paper in this series.

10. These techniques are not suitable for T_g, at which there is a major change in the Tait parameter b.

11. These $P-V-T$ data suggest that T_{ll} has a thermodynamic basis to the same extent that T_g does. A kinetic basis for T_{ll} has been recognized for some time.

12. As a general rule with published data, pressure intervals are too large, and the number of isotherms too few, to permit precise determinations of pressure coefficients.

13. We are exploring the possibility that $1 - V/V_0$ and $\log V_{sp}$ may be nearly linear with P, at least for some polymers, in the liquid state over the short pressure intervals between multiple transitions, with slopes which show a step decrease at each transition.

14. It also appears possible, again for some polymers such as PS, PBD, and i-PMMA, that such data over the entire pressure range can be approximated by the exact Tait equation, (1) or (2), with a single value of b.

15. Such results do not explain the pressure dependence of κ_l, which is known to exist (see, for example, ref 14), but do give the discontinuity $\kappa_{ll} - \kappa_l$ at T_{ll}.

16. Our basic rationale is that if Wood's technique of plotting bulk modulus, $\bar{K}$, against P (namely, eq 4) for a given isotherm reveals one or more step jumps in $\bar{K}$, there will be one or more step jumps in b, and data for that isotherm cannot be represented exactly by eq 1 or 2 over the entire pressure range with a single value of b. However, it may be approximated by eq 1 or 2 with an average value of b.

Acknowledgment. We are indebted to Professor G. Rehage for tabulated $P-V-T$ data on PS, to Dr. L. A. Wood for ref 24, giving compressibility data on PIB, to Kevin Battjes and Steven Keinath of MMI for computer analysis of data, to T. Alfrey of Dow Chemical Co. and Dr. K. Solc, MMI, for discussion of Tait equation approximations, and to Lisa Richards Denny for line drawings. The basic impetus for this study resulted from discussions with Frenkel and Baranov[38] about the tentative interpretation of T_{ll} phenomena in terms of phase dualism. This involves competition between the entropic tendency of macromolecules to be gaslike far above T_g and the energetic tendency to form liquidlike polymer-polymer contacts just above T_g. The latter should be favored by hydrostatic pressure. Positive values of dT_{ll}/dP are thus consistent with their views. We currently have plans for mutual exploration of this subject. Their application of phase dualism for formation of extended-chain crystals of PE under pressure has been published.[39,40] A related publication by Lobanov and Frenkel has now appeared.[41] Finally, the advice of two reviewers of the manuscript is very much appreciated and is taken into account in this and future work.

References and Notes

(1) Quach, A.; Simha, R. *Macromolecules* **1971**, *4*, 268.
(2) Quach, A.; Simha, R. *J. Appl. Phys.* **1971**, *42*, 4592.
(3) Oels, H.-J.; Rehage, G. *Macromolecules* **1977**, *10*, 1036. (This reference is based on the Doctoral Dissertation of H.-J. Oels, Technical University of Clausthal, Feb 11, 1977. We are indebted to Professor Rehage for providing us with requested numerical $P-V-T$ data on PS.)
(4) Beret, S.; Prausnitz, J. J. *Macromolecules* **1975**, *8*, 536. Tables of relative volume as a function of P may be obtained as supplementary material from the American Chemical Society (MACRO-75-536).
(5) McKinney, J. E.; Goldstein, M. *J. Res. Natl. Bur. Stand., Sect. A* **1974**, *75A*, 331.
(6) McKinney, J. E.; Simha, R. *Macromolecules* **1974**, 7, 894.
(7) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 206.
(8) Olabisi, O.; Simha, R. *J. Appl. Polym. Sci.* **1977**, *21*, 149.
(9) Wilson, P. S.; Simha, R. *Macromolecules* **1973**, *6*, 902.
(10) Quach, A.; Wilson, P. S.; Simha, R. *J. Macromol. Sci., Phys.* **1974**, *B9*, 533.
(11) Boyer, R. F. *Colloid Polym. Sci.* **1980**, *258*, 760.
(12) Barlow, J. W. *Polym. Eng. Sci.* **1978**, *18*, 238. Dr. Barlow has additional data at pressures intermediate to the ones tabulated in the published paper. He will furnish these on request.
(13) Hellwege, K.-H.; Knappe, W.; Lehmann, P. *Kolloid Z. Z. Polym.* **1962**, *183*, 110.
(14) Breuer, H.; Rehage, G. *Kolloid Z. Z. Polym.* **1967**, *216/217*, 159.
(15) Gee, G. *Polymer* **1966**, *7*, 177.
(16) Simha, R.; Wilson, P. S.; Olabisi, O. *Kolloid Z. Z. Polym.* **1973**, *251*, 402.
(17) Wood, L. A. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 703.
(18) Gillham, J. K.; Boyer, R. F. *J. Macromol. Sci., Phys.* **1977**, *B13*, 497.
(19) Gillham, J. K. *Polym. Eng. Sci.* **1979**, *19*, 749.
(20) Boyer, R. F. *Polym. Eng. Sci.* **1979**, *19*, 732.
(21) Boyer, R. F. *J. Macromol. Sci., Phys.* **1980**, *B18*, 455.
(22) Patterson, G. D.; Bair, H. E.; Tonelli, A. E. *J. Polym. Sci., Polym. Symp.* **1976**, *54*, 249.
(23) Höcker, H.; Blake, G. J.; Flory, P. J. *Trans. Faraday Soc.* **1971**, *67*, 2251.
(24) Enns, J. B.; Boyer, R. F. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18* (2), 475.
(25) Enns, J. B.; Boyer, R. F.; Ishida, H.; Koenig, J. L. *Polym. Eng. Sci.* **1979**, *19*, 756.
(26) Burington, R. S. "Handbook of Mathematical Tables and Formulas"; Handbook Publishers, Inc.: Sandusky, Ohio, 1933 (or any handbook of mathematical formulas such as the

"Handbook of Chemistry and Physics").
(27) Boyer, R. F.; Gillham, J. K. *Org. Coat. Plast. Chem.* **1979**, *41*, 430.
(28) Enns, J. B.; Boyer, R. F. *Org. Coat. Plast. Chem.* **1978**, *38* (1), 387.
(29) Singh, H.; Nolle, A. W. *J. Appl. Phys.* **1959**, *30*, 337.
(30) Williams, G.; Edwards, D. A. *Trans. Faraday Soc.* **1966**, *62*, 1329.
(31) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *67*, 2793.
(32) Boyer, R. F.; Richards-Denny, L.; Elias, H.-G.; Gillham, J. K. *Org. Coat. Plast.* **1980**, *42*, 682.
(33) Simha, R.; Boyer, R. F. *J. Chem. Phys.* **1962**, *37*, 1003. Boyer, R. F.; Simha, R. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 33.
(34) Panke, D.; Wunderlich, W. *Proc. 4th ICTA, Budapest* **1974**, *2*, 35–42.
(35) O'Reilly, J. J. *J. Polym. Sci.* **1962**, *57*, 429.
(36) Baer, E.; Kardos, J. L. *J. Polym. Sci., Part A* **1965**, *3*, 2827.
(37) Kijima, T.; Imada, K.; Takayanagi, M. *Rep. Prog. Polym. Phys., Jpn.* **1973**, *16*, 225. These authors note that dT_m/dP tends to increase with T_m.
(38) Frenkel, S.; Baranov, V. G. Institute of Macromolecular Compounds, Leningrad, USSR, personal discussions (Oct 1978).
(39) Frenkel, S.; Baranov, V. G. *Polymer* **1977**, *18*, 228.
(40) Baranov, V. G.; Frenkel, S. *J. Polym. Sci., Part C* **1977**, *61*, 351.
(41) Lobanov, A. M.; Frenkel, S. Ya. *Vysokomol. Soedin.* **1980**, *22*, 1045.

Static and Dynamical Properties of Polystyrene in Carbon Tetrachloride. 1. Characteristic Frequency in the Dilute, Intermediate, and Semidilute Regions[†]

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ABSTRACT: Dynamical properties, in terms of the characteristic frequency Ω or $1/\tau$, of polystyrene ($\bar{M}_w \sim 1 \times 10^7$) in carbon tetrachloride have been studied from dilute to semidilute polymer concentrations of 0.117 wt % at 18 and 25 °C over a range of scattering angles by means of single-clipped photon correlation of scattered light. In dilute solutions, the dynamical structure factor $S(K,t)$ obeys the form derived by Dubois-Violette and de Gennes, provided that the K range has excluded translational motions of isolated coils as well as fast localized segmental motions. We have also achieved a scaling of Ω/K^2 vs. $Kr_g^{*\dagger}$ by using the Benmouna–Akcasu theory[14] whereby we can determine both the diffusion coefficient and the radius of gyration ($r_g^{*\dagger}$) by making line-width measurements at more accessible scattering angles, e.g., 90°, for high molecular weight polymer samples. We observed a change in Ω, representing an anomalous behavior whose dynamics has not been reported previously. The anomalous phenomenon can be observed only under appropriate conditions but becomes masked for low molecular weight polymers and/or when the probe length (K^{-1}) is inappropriate. It suggests a special property of polymer coils dealing with intermolecular interactions and polymer entanglement.

I. Introduction

In a recent series of articles,[1-6] we reported our studies of static and dynamical properties of polystyrene in *trans*-decalin from around the Θ temperature to about 20 °C above the Θ temperature. We used a low molecular weight polystyrene sample[1-4] ($\bar{M}_w = 179\,300$) in order to avoid observation of Rouse–Zimm motions of polymer coils and examined the changes of osmotic compressibility, diffusion coefficient, and frictional coefficient as a function of temperature and concentration from dilute to concentrated polymer solutions. At finite molecular weight, we observed gradual changes of osmotic compressibility as a function of concentration at various fixed temperatures (20, 30, and 40 °C). Only traces of simple power law relations could be established. By means of a histogram method of data analysis,[7-9] we succeeded in separating the fast pseudogel motions from translational diffusion motions of polymer coils. This pseudogel mode is responsible for the anomalous increase in the variance of the line-width distribution function $G(\Gamma)$ from the dilute to the semidilute region.

By repeating our studies with a high molecular weight polystyrene sample[5,6] ($\bar{M}_w = 1 \times 10^7$), we examined the static and dynamical properties of large polymer coils in the intermediate-K region, where internal motions of polymer segments can play an important role. In dilute solutions, the behavior of the characteristic frequency ($1/\tau$) associated with the dynamical structure factor $S(K,t)$ for an isolated Gaussian coil in the presence of excluded-volume effects has been studied by de Gennes[10] and by Daoud and Jannink.[11] For an unperturbed isolated Gaussian chain in the Zimm limit without excluded-volume effects, Dubois-Violette and de Gennes[12] obtained the characteristic frequency

$$1/\tau = (1/6\pi\sqrt{2})(k_BT/\eta_0)K^3 \tag{1}$$

with a preaveraged Oseen tensor while Akcasu and Gurol[13] obtained a corresponding characteristic frequency

$$\Omega = (1/6\pi)(k_BT/\eta_0)K^3 \tag{2}$$

in the limit of initial decay rate, where $t \to 0$ and k_B, T, and η_0 are the Boltzmann constant, the temperature, and the solvent viscosity, respectively. For small values of K for which $Kr_g \ll 1$, $S(K,t)$ is an exponential function of time with a decay constant $\Gamma = DK^2$, where D is the translational diffusion coefficient and r_g is the radius of gyration of the polymer coil. In the large-K limit for which $Kl \gg 1$, $\Gamma = (k_BT/\xi_0)K^2$, which corresponds to a simple diffusion of segments, with $D_s = k_BT/\xi_0 = k_BT/3\pi\eta_0 l$ and l being the statistical segment length.

In a recent communication, we reported the observation of a dynamical change representing a new anomalous region which occurs before the overlap concentration C^* ($=M/N_A\rho_s r_g^3$, with ρ_s, M, and r_g being the solvent density,

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