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Significance of Entropic Factors in Mechanical Deformation of Polymeric Glasses

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ABSTRACT: The formally entropic factors that influence the response of homogeneous polymeric materials to simple states of stress are examined. A very general derivation for the portions of the bulk and shear moduli that are entropic is given. This ratio of the entropic part to the total of the bulk modulus is given by the very simple formula $\Upsilon^* = B_1 - 10\alpha$ for a material that obeys the Tait equation of state in the limit of low pressure. Existing data on such materials are used to compute Υ^* for a number of polymeric glasses. Limitations of this analysis and fruitful directions for improving it are indicated. Entropic factors cannot be generally excluded when considering polymeric glasses.

Solids resist deformation. Their ability to resist is founded in the arrangement and interactions of their component molecules or atoms. From a thermodynamic point of view, their resistance to deformation can be decomposed into energetic and entropic contributions. The understanding and prediction of various moduli and other mechanical properties based on microscopic models is much more accessible when information is available on this most basic thermodynamic decomposition. A clear example can be found in the field of rubber elasticity. Here, the early experimental establishment that entropic factors dominated when a "good" rubber was extended permitted rapid and quite elegant development of a general theory with the assurance that particular details of the intermolecular forces were irrelevant.[1,2] Only the configurational choices available to a chain molecule by virtue of rotations about internal bonds are important in first approximation. Subsequent developments of both academic and practical importance right up through today are encouraged and derive their significance because of our appreciation for the molecular origin of rubber elasticity.

Recently, Theodorou and Suter[3] have reported computer simulations of the molecular origin of mechanical properties of polymeric glasses. In a very general development, they have produced a criterion for assessing the importance of entropic contributions to the bulk and shear moduli, together with a citation of relevant data on poly(methyl methacrylate).[4] In contrast to the classical case of rubber elasticity, they find that entropic effects are negligible in PMMA glass. However, just as in the historical example, this definite information proves to be invaluable for focusing attention on the important features of an initially hopelessly complex problem.

The present contribution rederives and extends the criterion introduced by Theodorou and Suter. Such a labor is clearly desirable in order to facilitate further, rational development of molecular understanding of the mechanical properties of polymeric glasses. Although we accept the conclusion of Theodorou and Suter[3] as regards PMMA, in the accompanying paper we report experimental data that demonstrate that entropic effects are by no means negligible in other polymeric glasses. First, a brief thermodynamic discussion is presented in order to place our results in context. Details of a new derivation of the Theodorou–Suter result (eq 16) are reserved for the appendix. Related expressions for simple states of stress in addition to hydrostatic compression are also deduced. Next, these results are specialized to the particular case of a material obeying the empirical equation of state due to Tait.[5] This equation is often approximately obeyed by amorphous polymeric materials.[6] Finally, we comment on the significance of some existing data and motivate the need for the experiments reported in the accompanying paper.

General Theory

The first law of thermodynamics is most often encapsulated by writing for the differential of the internal energy, U,

$$\mathrm{d}U = \delta q + \delta w \tag{1}$$

Here, q denotes heat, w denotes a generalized work done on the system, and δ reminds us that these quantities are path dependent. The heat change for a reversible transformation forms the usual basis for defining the entropy, S,

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$$dS = \delta q_{\mathrm{rev}}/T \qquad (2)$$

where T is the absolute temperature. Moreover, it is always possible to write any component of work as a product of generalized forces and displacements, viz.,

$$\delta w_x = \int F_x \, dx \qquad (3)$$

Combining eq 2 and 3 into eq 1 yields

$$dU = T\, dS + \sum_x \int F_x \, dx \qquad (4)$$

where the summation on x explicitly acknowledges contributions from any number of specific work terms. The final piece of formalism that we require is the Helmholtz free energy, A, defined by

$$A = U - TS \qquad (5)$$

Its differential is

$$dA = dU - T\, dS - S\, dT \qquad (6)$$

so that incorporating eq 4 yields

$$dA = -S\, dT + \sum_x \int F_x \, dx \qquad (7)$$

In the usual way[7] it is useful to observe that the thermodynamic state function A depends on T and all the generalized displacements, $\{x\}$, so that its total derivative is

$$dA = (\partial A/\partial T)_{\{x\}}\, dT + \sum_x (\partial A/\partial x)_{T,\{y\neq x\}}\, dx \qquad (8)$$

Comparison with eq 7 shows

$$-S = (\partial A/\partial T)_{\{x\}} \qquad (9a)$$

$$F_x = (\partial A/\partial x)_{T,\{y\neq x\}} \qquad (9b)$$

Finally, the analogues of the classical Maxwell relationships can be obtained from the formal manipulations on eq 9:

$$\left(\frac{\partial S}{\partial y}\right)_{T,\{x\neq y\}} = -\left[\frac{\partial}{\partial y}\left(\frac{\partial A}{\partial T}\right)_{\{x\}}\right]_{T,\{x\neq y\}} = -\left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial y}\right)_{T,\{x\neq y\}}\right]_{\{x\}} = -\left(\frac{\partial F_y}{\partial T}\right)_{\{x\}} \qquad (10)$$

To this point, the development has been entirely general and very formal. It can also be extracted from numerous textbooks[7,8] so that some particularly compelling justification for reimposing it on the present audience is needed. That justification is to be found in the clarity with which particular assumptions can now be introduced to differentiate special cases that share the identical formal logic of eq 1–10. As a first example, consider the case of uniaxial tension imposed on an isotropic body. Then $F_x = f$, the uniaxial force; x becomes the conjugate length measured relative to an initial equilibrium rest position. Equations 5, 9b, and 10 combine to give

$$f = (\partial U/\partial x)_{T,V} - T(\partial S/\partial T)_{x,V} \qquad (11)$$

where V is the volume that when constant makes consideration of pressure–volume work nugatory. This is a form of the thermodynamic equation of state for rubber elasticity where the specification to constant volume is indeed appropriate. For ideal elastomers, the first term on the right-hand side (rhs) of eq 11 vanishes.[1] Then introducing the appropriate form of eq 10

$$(\partial S/\partial x)_{T,V} = -(\partial f/\partial T)_{x,V}$$

yields

$$f = T(\partial S/\partial x)_{T,V} \qquad (12)$$

Of course, this is the familar result that the origin of the retractive force in the ideal rubber (the negative of the applied force, f, in eq 12) is entirely entropic.

A second specialization is directly relevant to the present topic. Consider an isotropic body under hydrostatic pressure. Then $F_x = P$, the pressure; x becomes its conjugate displacement, V. Only pressure–volume work is acknowledged. These conditions reflect the paradigm of a pressure dilatometry experiment. We seek an expression analogous to eq 12 from which we learn how much entropic contribution there is in a material's response to such an experiment. Rather than work directly with the pressure, Theodorou and Suter[3] direct our attention to the bulk modulus, B, defined as

$$B = -V(\partial P/\partial V)_T \qquad (13)$$

or, equivalently, its reciprocal, k, the isothermal compressibility. In this instance eq 9b takes the explicit form

$$P = (\partial A/\partial V)_T$$

so that eq 13 can be developed as

$$\begin{aligned} B &= -V(\partial^2 A/\partial V^2)_T \\ &= -V[(\partial^2/\partial V^2)(U - TS)_T] \end{aligned} \qquad (14)$$

Clearly, the extent to which the formally entropic term is important in the bulk modulus can be measured in the second term on the rhs of eq 14. Let us adopt the ratio, Υ,

$$\Upsilon = \frac{VT}{B}\left(\frac{\partial^2 S}{\partial V^2}\right)_T \qquad (15)$$

as a convenient, dimensionless parameter for the significance of entropy. When $\Upsilon = 0$, then internal energy effects completely determine the bulk modulus. We shall reserve a discussion of the sign of Υ until we explicitly consider the Tait equation of state.

It is demonstrated in the Appendix that an elementary but lengthy thermodynamic derivation transforms eq 15 into the more useful form

$$\Upsilon = T\left[\left(\frac{\partial \ln k}{\partial T}\right)_P + \frac{\alpha}{k}\left(\frac{\partial \ln k}{\partial P}\right)_T\right] \qquad (16)$$

Thus, Υ can be obtained from the compressibility and thermal expansivity data generated in a pressure dilatometry experiment.

A third specialization that is experimentally practicable is simple shear. Here $F_x = f_s$ the shear stress (force per unit area to which it is applied) and $x = G$, the shear strain. An argument formally identical with that just given for Υ shows that for the shear analogue

$$\begin{aligned} \Upsilon_s &= -\frac{\epsilon T}{G}\left(\frac{\partial^2 S}{\partial \epsilon^2}\right)_{T,V} \\ &= T\left[\left(\frac{\partial \ln G}{\partial T}\right)_P + \frac{\alpha}{G}\left(\frac{\partial \ln G}{\partial P}\right)_T\right] \end{aligned} \qquad (17)$$

This result was also obtained by Theodorou and Suter with their formally more complex derivation. The present approach is complementary in the sense that for simple states of stress (the only ones of any real experimental significance) imposed on homogeneous samples, the present derivation requires neither restriction to vanishingly small strains nor to isotropic samples. It relies solely on general thermodynamics and the possibility of defining useful, effective moduli.

Applications with the Tait Equation. The Tait equation[5] is empirical but often an exceptionally good equation of state for polymer melts and amorphous solids.[6,9] Let us focus initially on the entropic contributions to the bulk modulus. One justification for this preeminence is the availability of data. Other justification will be forthcoming. Following Gee[10] we write the Tait equation in the form

$$V(P,T) = V(0,T)[1 - c[\ln [1 + P/B_{\mathrm{Tait}}(T)]]] \tag{18}$$

where $V(0,T)$ is the zero (or atmospheric) pressure volume as a function of temperature, c a constant, and B_{Tait} a material-dependent quantity of the form

$$B_{\mathrm{Tait}} = B_0 \exp(-B_1/T) \tag{19}$$

From eq 18 and 19 and the definition of k we have for a material obeying the Tait equation

$$k = \frac{V(0,T)c}{V(P + B_{\mathrm{Tait}})} \tag{20}$$

so

$$(\partial k/\partial P) = k^2 - k/(B_{\mathrm{Tait}} + P) \tag{21a}$$

or when $P = 0$

$$(\partial k/\partial P)_{T,P=0} = k^2(1 - 1/c) \tag{21b}$$

and we have as well

$$\left(\frac{\partial k}{\partial T}\right)_P = \frac{c}{V(B_{\mathrm{Tait}} + P)}\left(\frac{\partial V(0,T)}{\partial T}\right)_P - \frac{V(0,T)c}{V^2(B_{\mathrm{Tait}} + P)}\left(\frac{\partial V}{\partial T}\right)_P + \frac{V(0,T)cB_1B_{\mathrm{Tait}}}{V(B_{\mathrm{Tait}} + P)^2} \tag{22a}$$

or when $P \rightarrow 0$

$$(\partial k/\partial T)_{P=0} = kB_1 \tag{22b}$$

Substituting eq 21b and 22b into eq 16 and carrying out the trivial simplification required gives the simple result

$$\Upsilon^* = T[B_1 + \alpha(1 - 1/c)] \tag{23a}$$

where the asterisk reminds us that this is restricted to a material obeying the Tait equation in the limit $P \rightarrow 0$. Nanda and Simha[6] report the empirical result that c has a nearly universal value of 0.0894, so that to an approximation surely better than that involved in postulating Tait-like behavior itself, we can rewrite this last result even more tersely as

$$\Upsilon^* = T(B_1 - 10\alpha) \tag{23b}$$

It is instructive to imagine actually measuring Υ^* using this result. Reference to van Krevelen's compendium[11] shows $\alpha \sim 10^{-4}$ for a vast array of polymer glasses (Table 4.11, pp 70–72) whereas $B_1 \sim 3 \times 10^{-3}$ (p 78) and for the range of practical interest $T \sim 10^2$. Evidently, α and B_1 should be known to at least ±10% in order to confidently infer information from Υ^*. Since these quantities are first and second derivatives of the quantity (volume) actually measured, the demands on experimental precision are not trivial. Indeed, it becomes quite suspect to combine and use data on glasses of the same material that have not seen identical handling history. Table I records the heuristic results of a series of calculations based on literature data.

Table I
Computed Values of Υ^* by Using Literature Reports of B_1 and α[a]

polymer	T_g, K	B_1, 10^{-3} K^{-1}	α, 10^{-4} K^{-1}	Υ^* (300 K)[b]
poly(vinyl acetate)	305	0.89[c]	2.790	−0.56[f]
		0.97[d]	2.790	−0.53[f]
		2.637[e]	3.074	−0.13[f]
polystyrene (PS)	373	2.999	2.34	0.20
		4.31	2.86	0.44
PS/PPO 80/20 (w/w)		3.53	2.85	0.20
PS/PPO 60/40		3.08	2.74	0.10
PS/PPO 50/50		3.11	2.49	0.19
PS/PPO 40/60		2.98	2.32	0.20
PS/PPO 20/80		2.33	2.11	0.07
poly(2,6-dimethylphenylene oxide) (PPO)		2.00	2.09	0.03
poly(methyl methacrylate)	378	3.229	2.32	0.27
		3.164[g]	2.66[g]	0.15
		2.6[h]	2.1[h]	0.15
		1.27[i]	1.87[i]	−0.18[j] (0.07)
poly(cyclohexyl methacrylate)	380	2.983	2.28	0.21
polycarbonate (Lexan 101)	423	2.609	2.63	−0.01
poly(bisphenol A 2-hydroxypropane-1,3-diyl ether)	341	5.79	3.00	0.84
polysulfone	459	1.543	2.17	−0.19

[a] Unless otherwise noted, all date are taken from the survey article by Zoller.[9] [b] Υ^* is computed by using eq 23b with T = 300 K unless otherwise noted. [c] Data from ref 12; glass formed by cooling from the melt under the pressure of measurement. [d] Data reported by Zoller[9] taken from ref 12; glass formed by cooling from the melt under atmospheric pressure. [e] Data from ref 12; glass formed by cooling from the melt under 800 bar pressure. [f] T = 293 K because of limitations on data. [g] Values estimated by using data in Table II of ref 15. [h] Values estimated by using data plotted in Figures 17 and 18 of ref 16. [i] Values taken from the data on α, k, and $(\partial k/\partial T)_p$ from Koppelmann et al.[4] as reported by Theodorou and Suter.[3] [j] T = 293 K. Value in parentheses is computed using all the data of Koppelmann et al.[4] and the complete eq 16.

There are four instructive features of Table I. First is the considerable variability in both α (cf. PMMA) and B_1 (cf. PS) from study to study. Clearly, the doubts expressed in the preceeding paragraph are now confirmed and we must conclude that extant literature is inadequate for drawing firm conclusions on the magnitude of Υ^*. Second, the report of McKinney and Simha[12] demonstrates that the method of glass formation can remarkably change even relative values of Υ^*. Their data on poly(vinyl acetate) suggests that the entropic contribution to the bulk modulus depends on the details of molecular organization. It can be influenced by processing, an important conclusion that severely limits the significance of generalizations based on any limited number of glasses. Third, the data on PMMA[3,4] give values of Υ (from eq 15) and Υ^* (from eq 23b that differ in sign and in absolute magnitude by a factor of 3. From this we conclude that the simplicity of eq 23b is chimerical. If we insist upon the Tait equation, then we must acknowledge nonuniversal values of c for polymeric glasses examined at this quite demanding level. For PMMA, $(1 - 1/c = k^{-2} (\partial k/\partial P)_T = -5.5 \neq -10)$. It will be preferred to numerically fit dilatometric data instead of postulating any equation of state. Fourth, the surveyed literature produces both positive and negative values for Υ^*. With reference to eq 15, we note that V, T, and B are always positive. Thus, the sign of Υ^* (or Υ, of course) is reporting on the sign of $(\partial^2S/\partial V^2)_T$, i.e. that of the derivative with respect to volume of the isothermal kinetic pressure. Ordinarily, physical intuition would suggest that this sign ought to be negative (consider the limiting case of an ideal gas where $(\partial^2U/\partial V^2)_T \equiv 0$). Positive values imply that an increase in entropy is taking place upon compression: the contrapositive of the usual formulation of rubber elasticity (vide supra). Possibly other sources besides the accessible configurations of chain molecules will be important in any special case, but those are certainly the most obvious and first to be considered for macromolecules. Parenthetically, it should be pointed out that large negative values of Υ^* do *not* necessarily imply the absence of configurational entropy, because we do not know a priori the volume at which all chains are relaxed. Glasses are complicated. However, while many conceivable molecular explanations (including the configurational entropy of chain molecules) are consistent with $\Upsilon^* < 0$, the list is vastly smaller for positive values and speculation is less ambiguous.

The observation that Υ can be of either sign highlights the complications involved in interpreting its magnitude. As should be clear from eq 14, the necessarily positive bulk modulus is the sum of the two terms; either one of which can be positive or negative. Thus, Υ can be arbitrarily large and of either sign, so that we would prefer that the adjective "nonnegligible" be associated with entropic contributions giving rise to "large" absolute values of Υ. Values near unity *may* signify complete dominance of entropic factors, but more detailed analysis is needed.

Discussion and Summary

Equation 16 is the central focus of this report. It was previously obtained by Theodorou and Suter.[3] The rederivation provided here requires only the specialization to pressure–volume work (appropriate for dilatometry experiments) applied to homogeneous materials, thus broadening the apparent applicability of the result. The close formal relationship between the Theodorou–Suter equation and the familiar demonstration of the entropic basis of rubber elasticity has been emphasized. Specialization produced by assuming an equation of state (here the Tait equation) results in some simplification. However, as demonstrated by application to available literature, this simplification is illusory because of the approximate nature of existing equations of state. Neither these equations nor the existing data are precise enough to permit definite conclusions concerning the importance of entropy to the bulk deformation of polymeric glasses.

What can be definitely concluded is that the question is still open. Certainly the absolute value of several of the Υ^* quantities tabulated in Table I are astoundingly large. A bulk modulus as for poly(bisphenol A 2-hydroxypropane-1,3-diyl ether) that is possibly 84% entropic at a temperature 40 °C below T_g is significant—even if in error by a factor of 2 or 3. Moreover, the large dependence on glass formation history [e.g., poly(vinyl acetate)] vitiates any claim to the universal insignificance or criticality of entropic contributions. Only detailed numerical analysis of very precise dilatometric data can settle this question. In the accompanying paper some initial work along this line is presented.

We have implied that some major component of the still vaguely identified entropic contribution to the bulk modulus of polymeric glasses arises from molecular motions identical with those identified with true rubber elasticity. This speculation is not entirely novel. Yannas and Luise[13] have proposed rotation about backbone bonds as a crucial mechanism of polymeric mechanical response. Much earlier Bowden[14] argued that the absolute value of mechanical moduli implicated conformational adjustments in deformations. Obviously, the entropy associated with accessible configurations that totally dominates mechanical response for networks above T_g (i.e., in true elastomers) must play a reduced role in the regime $T < T_g$. However, its role can be considerably reduced without becoming negligible. For conceptual and, in view of its process dependence, for practical reasons, the quantitative significance of entropic contributions to mechanical response is a crucially important question. Further work is imperative.

Appendix

Here we present the derivation of eq 16 in the text. The starting point is eq 15, which defines the fraction of the bulk modulus, B, that originates in formally entropic terms. This fraction will be denoted Υ and recapitulating eq 15 shows

$$\Upsilon = VT/B(\partial^2 S/\partial V^2)_T \tag{A1}$$

From the definition of the Helmholtz free energy, A, and the fact that it is an exact differential the well-known Maxwell relation[8]

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V \tag{A2}$$

follows at once. In the situation at hand, only PV work is possible so that

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right]_T = \frac{\partial^2 P}{\partial V \partial T} = \left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right]_V \tag{A3}$$

Thus, substituting eq A2 into eq A1 and employing eq A3 yield

$$\Upsilon = \frac{VT}{B}\left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right]_V \tag{A4}$$

But from the definition of B (see eq 13 in the text)

$$\Upsilon = \frac{-T}{B}\left(\frac{\partial B}{\partial T}\right)_V \tag{A5}$$

Now dA is a perfect differential depending only on T and V for our situation. If we are far from phase transitions, second-order transitions and third-order transitions (whatever reality those might have), then these characteristics are likewise enjoyed by the second derivatives of A. Thus

$$\mathrm{d}(B/V) = \mathrm{d}\left[\left(\frac{\partial^2 A}{\partial V^2}\right)_T\right] = \left[\left[\frac{\partial}{\partial T}\left(\frac{\partial^2 A}{\partial V^2}\right)_P\right]\mathrm{d}T + \left[\frac{\partial}{\partial P}\left(\frac{\partial^2 A}{\partial V^2}\right)_T\right]\mathrm{d}P\right]$$

or more succinctly

$$\mathrm{d}(B/V) = \left[\frac{\partial}{\partial T}(B/V)_P\,\mathrm{d}T + \frac{\partial}{\partial \mathrm{P}}(B/V)_T\,\mathrm{d}P\right] \tag{A6}$$

In order to proceed with eq A6 it will be convenient to have two auxiliary results in hand. Now V is a perfect differential as is A, so, justified exactly as was eq A6, we obtain

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P$$

from which it follows that

$$0 = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V \tag{A7a}$$

Upon rearrangement

$$(\partial P/\partial T)_V = \frac{-(\partial V/\partial T)_P}{(\partial V/\partial P)_T}$$

and by utilization of the definitions of the thermal expansivity, α, and the isothermal compressibility, k,

$$(\partial P/\partial T)_V = \alpha/k \tag{A7b}$$

Either of the equivalent expressions, eq A7a or A7b, constitutes the first auxiliary result. The second is nothing more than the interrelationship between the derivatives of B and those of its reciprocal, k. Since

$$B = 1/k$$

it follows for any variables x and y that

$$\left(\frac{\partial B}{\partial x}\right)_y = -\frac{1}{k^2}\left(\frac{\partial k}{\partial x}\right)_y \tag{A8}$$

With these in hand, we differentiate both sides of eq A6 with respect to temperature at constant volume

$$\left[\frac{\partial(B/V)}{\partial T}\right]_V = \frac{\partial}{\partial T}\left(\frac{B}{V}\right)_P + \frac{\partial}{\partial P}\left(\frac{B}{V}\right)_T\left(\frac{\partial P}{\partial T}\right)_V$$

expand the composite differentials on the rhs

$$\left[\frac{\partial(B/V)}{\partial T}\right]_V = \frac{1}{V^2}\left[V\left(\frac{\partial B}{\partial T}\right)_P - B\left(\frac{\partial V}{\partial T}\right)_P + \left[V\left(\frac{\partial B}{\partial P}\right)_T - B\left(\frac{\partial V}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V\right]$$

and rearrange to produce

$$\left(\frac{\partial B}{\partial T}\right)_V = \left[\left(\frac{\partial B}{\partial T}\right)_P + \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial B}{\partial P}\right)_T\right] + \frac{B}{V}\left[\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\right] \tag{A9}$$

According to eq A7a the last term in brackets is identically zero. The remainder of the rhs can be rewritten with eq A7b and A8 (with $(x,y) = (T,P)$ or (P,T) as appropriate) yielding

$$\left(\frac{\partial B}{\partial T}\right)_V = -k^{-2}\left[\left(\frac{\partial k}{\partial T}\right)_P + \frac{\alpha}{k}\left(\frac{\partial k}{\partial P}\right)_T\right] \tag{A10}$$

Inserting this equivalence into eq A5 and slight simplification generates the final desired result

$$\Upsilon = T\left[\left(\frac{\partial \ln k}{\partial T}\right)_P + \frac{\alpha}{k}\left(\frac{\partial \ln k}{\partial P}\right)_T\right] \tag{A11}$$

It is instructive to emphasize the generality of this result. Its derivation rests on only the most general thermodynamics for a system capable only of pressure–volume work and under conditions far enough from phase transitions to ensure the existence of derivatives up to and including third order for the free energy. In particular, it is not limited to small deformations nor to any molecular level details beyond the requirement of homogeneity needed to profitably define an effective bulk modulus.

Registry No. PS, 9003-53-6; PPO, 25322-69-4; PPO (SRU), 24938-67-8; PPO (homopolymer), 25134-01-4; poly(vinyl acetate), 9003-20-7; poly(methyl methacrylate), 9011-14-7; poly(cyclohexyl methacrylate), 25768-50-7; poly(bisphenol A 2-hydroxypropane-1,3-diyl ether), 108773-34-8; Lexan 101 (SRU), 24936-68-3; Lexan 101 (homopolymer), 25037-45-0.

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Measurements of Entropic Factors in the Mechanical Deformation of Polycarbonate and Natural Rubber

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Received January 12, 1987

ABSTRACT: The formally entropic factors that influence the mechanical response of polymers are determined for natural rubber and polycarbonate. The methods of data analysis are described. Natural rubber and the melt of polycarbonate are characterized by $\Upsilon \sim -^1/_2$. Polycarbonate glass in the low-pressure limit has $\Upsilon \sim +^1/_2$. These values indicate that the entropic factors cannot be neglected. However, over the experimentally accessible range of pressure and temperature, polycarbonate glass shows a fortuitous cancellation of effects and the average value of Υ is approximately zero.

The accompanying paper[1] presents a derivation and discussion of an experimentally realizable measure of the contribution from formally entropic factors to material moduli. In this paper, appropriate experimental results are to be presented and examined. The central result of the previous discussion is the equation (first given by Theodorou and Suter[2]) for Υ (the ratio of the formally entropic term to the whole of the bulk modulus) in terms of measurable quantities from pressure dilatometry. Equation 16 of ref 1 is

$$\Upsilon = T\left[\left(\frac{\partial \ln k}{\partial T}\right)_P + \frac{\alpha}{k}\left(\frac{\partial \ln k}{\partial P}\right)_T\right] \tag{1}$$

where T is the Kelvin temperature, P the pressure, k the isothermal compressibility (the reciprocal of the bulk

0024-9297/87/2220-1851$01.50/0