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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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

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modulus, B), and α the thermal expansion coefficient. A sign is associated with Υ. By analogy with the ideal gas, for which $\Upsilon = -1$, one expects negative values of Υ. Positive values constitute an indication of the importance of nonpositional (e.g., intramolecular) sources of entropy.

The work reported here considers natural rubber and polycarbonate. These polymers were chosen in order to highlight the responses of what may be presumed to be rather representative exemplifications of true elastomers ($T > T_g$) and amorphous glasses ($T < T_g$).

The right-hand side (rhs) of eq 1 contains second derivatives of the volume which, of course, is the directly observed quantity in pressure dilatometry. Considerable care must be taken in the analysis of the data to avoid losing any real information if such subtle features are to preserved. On the other hand, it is equally important to ensure that the conclusions do not hinge on analysis of random errors in the necessarily limited data. Thus, a major portion of the following article is devoted to describing and justifying the techniques employed. In the Results and Discussion section the physical insight that emerges from that analysis will be emphasized.

Equipment and Materials

The pressure dilatometer used for this study has been fully described.[3] Indeed, the polycarbonate data analyzed here were obtained by P. Zoller some years ago and a report has been published.[4] The data on natural rubber are new and appear here for the first time. The apparatus is a bellows piezometer and provides direct, relative volume measurements for pressures in the range 100–2000 kg/cm^2 and temperatures between room temperature and 340 °C in this work. One independent determination of specific volume is additionally required.

The polycarbonate (PC) sample studied was an injection-molded sample of Lexan 101 with $v = 0.836$ cm^3/g at atmospheric pressure and 22 °C.[4] The natural rubber used was a piece of smoke sheet courteously supplied by R. Beckerbauer with $v = 1.01$ cm^3/g at ambient pressure and temperature.

Data were obtained in the isothermal mode, i.e., by equilibration at a given temperature and the sampling at intervals of 100 kg/cm^2 pressure. The resulting experimental output is a matrix of observed volumes associated with an ordered pair of temperature and pressure parameters. For example, in the case of natural rubber 20 pressures were sampled along 18 isotherms between 29.9 and 99.5 °C, inclusive: a total data set of 360 points.

Analysis

The isothermal data obtained at regular intervals of 100 kg/cm^2 is ideally suited to regression analysis by the method of orthogonal polynomials.[5] This method efficiently finds the best-fit polynomial,

$$V = a_0 + a_1P + a_2P^2 + \ldots$$

the highest order term with a statistically significant coefficient, and the residual sum of squares of deviations from the best fit. In order to be as circumspect as possible, the condition adopted for truncating this expansion was 99.5% confidence (F test) that the coefficient of the highest retained term was nonzero. All of the isotherms examined in this study required first, second, or third degree polynomials. Compressibilities and their pressure derivatives are then obtained by direct differentiation of the fitting polynomials.

No modification of the computed fits was made in order to impose a common form on all isotherms of a particular sample. Consequently, substantial variation in the pressure derivative to the compressibility (basically, the second derivative of the volume) occurs. This is probably an accurate reflection of the unavoidable uncertainty involved in obtaining information about such a subtle quantity at any single point. However, physical intuition suggests that the relevant factor in eq 1 ($k^{-2}[\partial k/\partial P]_T$ in the last term on the rhs) should be a slowly varying quantity for any condensed phase. Indeed, it has been proposed[6] that the Tait equation of state can be used for polymer melts and glasses with the factor c given by

$$1 - 1/c = -k^{-2}(\partial k/\partial P)_T = (\mathrm{d}B/\mathrm{d}P)_T \qquad (2)$$

as a universal constant ($c = 0.0894$). B is the bulk modulus, the reciprocal of k. Emboldened by this consideration, the *average* value of $(\mathrm{d}B/\mathrm{d}P)_T$ over the entire data set for any material phase has been computed for use in eq 1. The uncertainty ascribed to this quantity is simply the variance about its mean. This procedure can certainly be challenged as incompletely rigorous. In its defense there is expediency, objectivity, and the assignment of an uncertainty that reflects the magnitude of whatever real dependence T and P is actually present and yet ignored.

In principle, extraction of $\alpha = V^{-1}(\partial V/\partial T)_P$ is identical with that for k. Unfortunately, it is very inconvenient in practice to demand data collection at precisely regular temperature intervals. Thus, the method of orthogonal polynomials or existing alternatives must be abandoned. Custom inclines one to use polynomials in T, and experience shows that with increasing pressure the variation of V with T decreases. For these reasons, the present analysis looks to the data taken at lowest pressure (100 kg/cm^2) in order to define the appropriate polynomial order. Again, the very stringent condition of failure of the null hypothesis at 99.5% confidence level is used to truncate the expansion. Then this same form (quadratic in all systems studied to date) has been assumed for the other isobars. The uncertainty in α is assessed by computing the standard error of estimate, S_e,

$$S_e^2 = \frac{1}{N - m - 1}\sum_{i=1}^{N}(V_i - V'_i)^2 \qquad (3)$$

for the best-fit (quadratic so $m = 2$) polynomial over the N data points of each cross-plotted isobar. Here V_i is the observed volume and V'_i is the corresponding prediction of the fitting equation. Then using standard formulas[7] for the variance in each coefficient of the fit, the uncertainty in the slope is obtained as the appropriately weighted sum of variances. The total change in V over the temperature ranges employed is large compared to the uncertainty in any single volume measurement. Thus, the uncertainty in that slope is essentially the uncertainty in α.

In contrast, the uncertainty in any specific value of k is comparable to the relative change in k with T. Thus, only a linear fit was attempted, resulting in a constant estimate of $\mathrm{d}k/\mathrm{d}T$ along any isobar. The uncertainty in this quantity is better than the variation one might expect from the absolute uncertainty in the component k values. This reaffirms the smoothness and presumptive quality of the data.

Finally, the criteria used to reject data as systematically flawed deserves mention. In general, the raw data can be examined to try and identify consistently odd isotherms or particular pressures. Occurrence is most easily remediated by repeating the entire experiment. The data described below are free of such obvious anomolies. We have also checked the data for peculiar sensitivity to a few unusual points by recalculating fitting functions with particular points excised. Again, no grounds for systematically suspicious observations could be found.

Results and Discussion

Natural Rubber. The experimental data for natural rubber are displayed in Figure 1. The specific volume of 1.101 cm^3/g under ambient conditions is in exact agree-

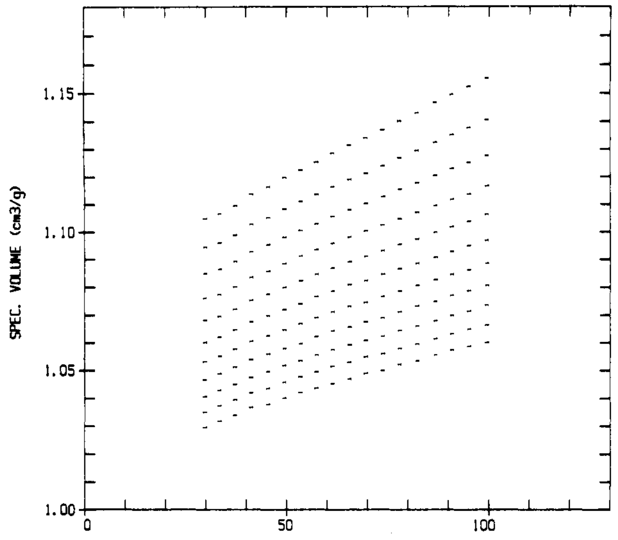

Figure 1. Specific volume vs. temperature for natural rubber. The data (corrected to the initial specific volume 1.101 cm^3/g as determined with a Micromeritics Model 1320 autopycnometer) shown are for alternate pressures (200, 400, ..., 2000 kg/cm^2) and for the extrapolation to $P = 0$ for each isotherm.

Table I
Representative Values of Derived Quantities for the Data Plotted in Figure 1[a]

quantity	conditions	this work[b]	Scott[c]
$\alpha \times 10^4$	$T = 45.5, P = 100$	6.6 ± 0.3	6.5
	$T = 45.5, P = 500$	5.9 ± 0.2	5.6
	$T = 45.5, P = 1000$	5.5 ± 0.2	na[d]
	$T = 45.5, P = 2000$	4.8 ± 0.4	na
$k \times 10^5$	$P = 400, T = 33.5$	4.23 ± 0.05	4.3
	$P = 400, T = 57.4$	4.56 ± 0.08	4.8
	$P = 400, T = 78.0$	4.80 ± 0.2	5.1
	$P = 400, T = 99.5$	5.2 ± 0.3	na
$(dk/dT)_P \times 10^7$	$P = 100$	2.39 ± 0.07	2.4
	$P = 500$	1.54 ± 0.04	1.8
	$P = 1000$	0.92 ± 0.02	na
	$P = 2000$	0.78 ± 0.03	na
$k^{-2}(dk/dP)_T$	averaged	−9.7 ± 0.5	−11.8

[a] Values extrapolated from the work of Scott[7] are given for comparison whenever possible. Scott's data were taken on samples with 3–31% sulfur and under conditions $10 \leq T \leq 85$ °C and $0 \leq P \leq 800$ bar = 816 kg/cm^2. Units: T, °C; P, kg/cm^2; α, °C^{-1}; k, cm^2/kg. [b] Computed as described in the text; all uncertainties are 95% confidence intervals. [c] Evaluated from equations or data in ref 8. [d] na = not available; Scott's study did not encompass the specified conditions.

ment with that predicted from the extrapolated data of Scott[8] who studied partially vulcanized natural rubbers. Ten isotherms were described by a quadratic dependence of V on P and eight were cubic. There was no trend for these fits with temperature.

Representative values of α, k, $(dk/dT)_P$, and the averaged value to $k^{-2}(dk/dP)_T$ are presented in Table I. Corresponding quantities reported by Scott[8] are also displayed when applicable. The agreement is good, particularly in view of the fact that all of the values attributed to Scott are based on extrapolation of his observations on rubber with 3–31% (w/w) sulfur to the limit of no cross-linker.

The overall variation of the figure of merit, Υ, with T and P is reported in Figure 2. While indiscriminate averaging gives a mean value of $\Upsilon = -0.62 \pm 0.28$ (95% confidence), it is obvious that the variation is not random and the data at higher pressures contain all the smaller values. Larger uncertainties are associated with these high-pressure values, and it is doubtful that there is any real increase of Υ with pressure at higher pressures. As previously noted, $\Upsilon < 0$ is the most readily explicable range and natural rubber ($T_g \sim -60$ °C) lies within that range for $30 \leq T \leq 100$ °C.

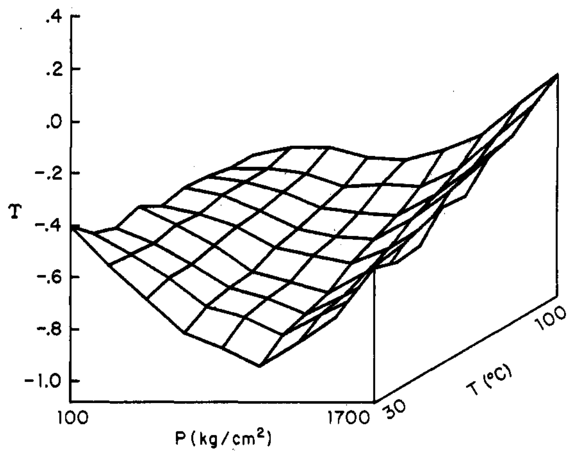

Figure 2. Quantity Υ plotted vs. both temperature and pressure for natural rubber. This is a perspective representation of the $\Upsilon(T,P)$ surface. The Υ value for any desired conditions can be read by translating the ordinate scale by the projected distance corresponding to $T - 30$ °C. For example, the value Υ(100 °C, 1700 kg/cm^2) is found to be approximately −0.22.

Reference to Table I reveals several features of natural rubber that may confidently be expected to pertain to all polymers above their T_g. The quantity $(dB/dP)_T$ is within experimental uncertainty of the conjectured[6] "universal" value of 10.2. As is obvious from $\Upsilon \sim -1$, the relative change of k with T is very small compared to $\sim 10\alpha$. Both dk/dT and α decrease with increasing pressure.

Polycarbonate. The original polycarbonate data have been previously published[4] so they are not reproduced here. Of particular importance is the observation by Zoller[4] that a minor anomoly (attributable to a low level of in situ crystallization) in the volume of the melt was detected in the data between 230 and 285 °C, depending on the pressure. The derivation of eq 1 for the form of Υ^1 is only valid in the absence of first- and second-order phase changes. Consequently, this temperature regime (230–285 °C) must be excluded from the present analysis, along with the isotherms which encompass the pressure-dependent T_g (150–230 °C). Table II displays the results from the remaining regions of interest, namely, the glass (30–150 °C) and the homogeneous melt (285–340 °C). Comparison is provided with the corresponding, derived quantities based on Zoller's published parameters for the Tait equation of state and the zero-pressure expansivity.

Since both the present analysis and Zoller's parameters are based on the identical data, it is to be expected that the agreement is generally excellent for polycarbonate glass. It is noteworthy that a serious discrepancy exists between the average value of $(dB/dP)_T$ and the constant value of −10.2 that this quantity should have when the Tait equation is employed with the "universal" value of c. Due to compensating effects, the final value of Υ does not strongly depend on the different but internally consistent ways of handling (dB/dP).

The variation of Υ with T and P for glassy polycarbonate is displayed in Figure 3. From decidedly positive values ca. 0.4 at low pressures, there is a smooth decrease as pressure increases. The cross-plotted isobars change sign between 900 and 1100 kg/cm^2 and reach $\Upsilon \sim -0.5$ at the highest pressures. The temperature dependence of Υ along each cross-plotted isobar is quite small except as $T \sim T_g$. Thus, when $P = 100$ kg/cm^2 (where the data approach

Table II
Representative Values of Derived Quantities for Data[4] on Polycarbonate Glass (29.1–144.3 °C, Inclusive) and Melt (291.3–336.7 °C, Inclusive)[a]

quantity	conditions	glass		T	melt	
		this work	Zoller[4]		this work	Zoller[4]
$\alpha \times 10^4$	$T = 87, P = 100$	2.5 ± 0.1	2.52	310.0	6.1 ± 1.0	5.13
	$T = 87, P = 500$	2.2 ± 0.1	2.27		4.8 ± 0.6	4.61
	$T = 87, P = 1000$	2.0 ± 0.1	2.01		4.2 ± 0.3	4.12
	$T = 87, P = 1800$	1.79 ± 0.04	1.71		3.5 ± 2.8	3.57
$k \times 10^5$	$P = 900, T = 29.1$	2.07 ± 0.03	2.00	291.3	5.2 ± 1.8	5.13
	$P = 900, T = 63.9$	2.17 ± 0.09	2.15	300.9	5.3 ± 2.1	5.21
	$P = 900, T = 98.9$	2.32 ± 0.08	2.31	318.7	5.5 ± 2.5	5.42
	$P = 900, T = 144.3$	2.57 ± 0.11	2.54	336.7	5.8 ± 3.0	5.64
$(\mathrm{d}k/\mathrm{d}T)_P \times 10^8$	$T = 87, P = 100$	7.4 ± 0.4	7.00	310.0	46.0 ± 3.0	33.7
	$T = 87, P = 500$	5.8 ± 0.3	5.67		19.3 ± 0.9	18.4
	$T = 87, P = 1000$	3.9 ± 0.7	4.50		11.0 ± 0.7	10.8
	$T = 87, P = 1500$	1.8 ± 0.3	3.74		2.2 ± 1.5	7.8
$k^{-2}(\mathrm{d}k/\mathrm{d}p)_T$	averaged	-8.0 ± 1.6	−10.2	av	-10.0 ± 6.0	−10.2

[a] Included for comparison are the corresponding values computed using Zoller's reported[4] parameters for the Tait equation assuming the "universal" value of $c = 0.0894$ and the zero-pressure expansivity. Same units and symbols as in Table I. Uncertainties again are 95% confidence limits.

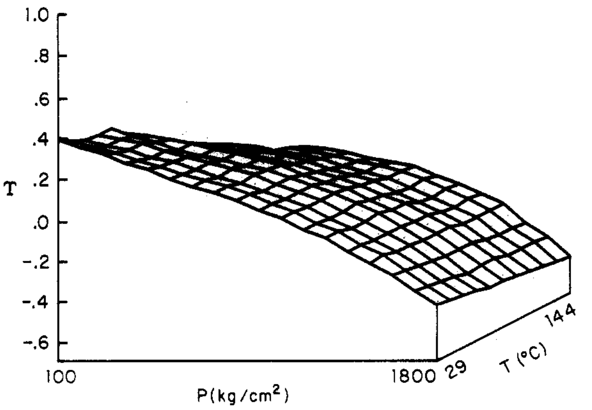

Figure 3. Υ plotted over the experimentally studied range of T and P for glassy polycarbonate.

right up to $T_g \sim 145$ °C) the data decrease monotonically from $\Upsilon = +0.42$ to -0.02 over the temperature range studied. As pressure increases this trend is suppressed; so much so that when $P \gtrsim 1000$ kg/cm^2 Υ is independent of temperature within experimental error. One plausible explanation of this is that only in the immediate region of T_g is there a substantial temperature dependence. Since $\mathrm{d}T_g/\mathrm{d}P = 0.052$ °C/(kg cm^{-2}) for polycarbonate,[4] increasing pressure means that the experimental temperature window is moving further below T_g.

A physical interpretation of the Υ variation with T and P for polycarbonate glass is illuminating. The large, positive value of Υ must reflect the existance of significant intramolecular and/or free volume effects. As for the ideal gas, positional disorder leads to negative values of Υ, so that conformational and orientational degrees of freedom must account for $\Upsilon > 0$. As the glass is compressed, these degrees of freedom are less important and Υ decreases. However, temperature and pressure are not just alternatively effective variables for suppressing these degrees of freedom. The work of isothermal compression is given by

$$W = -\int P(\partial V/\partial P)_T \, \mathrm{d}P \tag{4a}$$

For purposes of crude estimation we may ignore the pressure dependence of compressibility and

$$W \approx Vk(\Delta p)^2/2 \tag{4b}$$

Polycarbonate (cf. Table II) has $k \approx 2.2 \times 10^{-5}$ (kg/cm^2)$^{-1}$ over the range studied so that for $\Delta p = 2000$ kg/cm^2, $W/V \approx 1$ cal/cm^3. Typically, $C_p \approx C_v \approx 0.34$ cal/kg for polymer glass specific heats and we deduce that application of the full 2000 kg/cm^2 would only lower the temperature of our samples by about 2 K if applied adiabatically. Yet as already observed, Υ depends markedly on pressure but hardly at all on temperature when well away from T_g. We conclude that the degrees of freedom responsible for $\Upsilon > 0$ require available volume that is *not* markedly dependent on the mean separation between molecules except as T_g is approached.

The high-temperature melt behavior of polycarbonate is similar to that exhibited by natural rubber. Details are recorded in Table II (columns 5 and 6). Again, the values at the extreme high-pressure end of the experimental range must be viewed with caution. Υ values are decidedly negative of order −1 and so featureless in T and P that a graph has been omitted. The quantity $(\mathrm{d}B/\mathrm{d}P)_T$ is again found to be within experimental error of its conjectured, universal value and sensibly constant. All uncertainties are larger than others in Tables I and II because only six isotherms were measured above 285 °C.

Summary

The pressure–volume–temperature behavior of natural rubber has been determined. Results are in excellent agreement with the extrapolated finding of Scott.[8] The data have been used to obtain the mechanical ratio Υ which indicates how important entropic factors are in the deformation of a material. For polymers in the melt state Υ is negative and very significant, of order unity. It does not depend strongly on temperature. While the pressure dependence is more pronounced, the increasing uncertainty at the highest pressures employed may be largely responsible for the sensitivity exhibited in this range. Observations on the melt state of polycarbonate are analogous to those on natural rubber. In these polymer melts the Tait parameter c maintains a constant, universal[6] value of 0.0894, within experimental error.

Glassy polycarbonate exhibits significantly large and positive values of Υ at low pressures. Entropic contributions to its bulk modulus cannot be ignored. With increasing pressure, Υ decreases and becomes large and negative for pressures in excess of about 1200 kg/cm^2. This indicates at least two kinds of mechanically significant entropy. The mean value of Υ is nearly zero over the experimental range, but this represents a fortuitous cancellation of the different entropic contributions.

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Zoller on the details of data acquisition. J. Dowell assisted with the three-dimensional plotting.

Registry No. Lexan 101 (SRU), 24936-68-3; Lexan 101 (homopolymer), 25037-45-0.

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Excess Free Energies in Solutions of Isotopic Isomers. 3. Solutions of Deuteriated and Protiated Polymers

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ABSTRACT: Excess free energies and phase separation in mixtures of protio- and deuterio-substituted polymers are discussed in the context of the theory of isotope effects in condensed phases. In large molecules the internal degrees of freedom make the most important contributions to A^{ex}, which is obtained by considering the volume dependence of the free energy and integrating over the concentration-weighted molar volume isotope effect but along a congruent path. Agreement with experiment is demonstrated for the poly(perprotio-1,4-butadiene)/poly(perdeuterio-1,4-butadiene) and poly(perprotiostyrene/poly(perdeuteriostyrene) systems.

Introduction

Recently Bates, Wignall, and Koehler[1] (BWK), Bates, Dierker, and Wignall,[2] and Bates and Wignall[3] (BW) made measurements of critical behavior and incipient phase separation in solutions of deuteriated and protiated polybutadiene[1,2] and of deuteriated and protiated polystyrene.[3] In related experiments Atkin et al.[4] and Yang et al.[5] have studied the effect of deuteriation on phase separation in polymer blends. These studies owe their origin to questions arising in the interpretation of neutron diffraction studies of polymer blends and mixtures. Since the scattering intensity from neutrons and protons is so different, measurements of differential scattering cross sections from protio/deuterio solutions can be employed to answer questions concerning confirmation and shape, monomer–monomer pair distribution functions, chain tangling, etc.[6] The method is straightforward, however, only if the properties of the protio/deuterio solution are independent of isotopic label or if the isotope dependence is well understood in terms of the more fundamental potential energy surface (PES) describing the system. It is in this context that the experiments of Bates et al.[1–3] and others[4,5] are of interest. They unequivocally establish that substantial excess free energies exist in protio/deuterio solutions of polymers. Standard theories of solution[7] immediately lead to the prediction of phase separation of the upper consolute type. It is the purpose of this paper to demonstrate that this behavior is consistent with the theory of isotope effects in condensed phases[8] as recently applied by us to mixtures of isotopes.[9] The upper consolute solution temperatures (UCST's) calculated on the assumption of an isotope-independent PES are in good agreement with experiment. It is thus reasonable to assume that nonthermodynamic results, like neutron diffraction data, can also be interpreted with an isotope-independent PES. This is a useful and reassuring conclusion. In the present paper we restrict attention to solutions of isotopic isomers, one in the other.

Excess Free Energies of Solutions of Isotopes

Singh and Van Hook[9] (SVH) have recently presented a theory of nonideality in solutions of isotopes. Following the lead of earlier authors including Prigogine, Bingen, and Bellemans,[10] Bigeleisen,[11] and Jancso and Van Hook,[12] they expanded the Helmholtz free energy about the respective equilibrium volumes of the separated samples. This time, however, a careful distinction between the contributions of intermolecular and intramolecular degrees of freedom was maintained. In the original Prigogine approach each separated isotope was compressed or dilated to the molar volume of the isotopic mixture and then mixed isochorically. The free energy of mixing was taken as the sum of the free energies of compression and dilation and of isochoric mixing (which was assumed to be zero). The result is a well-known expression relating the difference in molar volumes of the separated isotopes, $\Delta V = V_1{}^0 - V_2{}^0$, (subscript 1 refers to the lighter isotope), to the excess free energy of mixing

$$A^e = x_1 x_2 (\Delta V)^2 / (2\kappa V^0) \qquad (1)$$

κ is the isothermal compressibility. Equation 1 is presented in the approximation that neglects isotope effects on κ and V^0 in the denominator. Buckingham and Hentschel[13] have presented an analysis that is similarly based.

We have criticized[9] the development leading to eq 1 on two counts. The first is on logical grounds. The theory of isotope effects assumes the PES's (appropriately expressed in reduced coordinates) are identical at the Born–Oppenheimer level for each of the separated isotopes and for the solutions formed from them. This straightforwardly leads to the conclusion that the distribution functions describing atom–atom correlations in the liquids, such as the two-particle correlation functions, $n^2(r^*,\theta,\phi)$, and the rotationally averaged radial distribution functions, $g(r^*)$, are also isotope independent. We use the term "congruent" to describe this situation. Here $r^* = r/\sigma$ is a reduced distance, and σ is a length parameter specified