Conformational Properties of Liquid Polyethylene

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ABSTRACT: The conformational entropy S_c of linear polyethylene liquid is calculated at $T_m = 414$ K for the three-state rotational model taking into account the "pentane interference". The volume contribution S_v is estimated using a volume-dependent $(\partial p/\partial T)_v$ which is derived via the Tait equation for liquid compressibility. The values are (cal deg^{-1} mol^{-1} CH$_2$) $S_c = 1.295$ and $S_v = 1.057$, and the sum is in excellent agreement with the experimental fusion entropy for extended-chain crystals: $\Delta S_m = 2.362$. Previous studies using isolated or unperturbed chain values for the rotational energy have over-estimated S_c and based on a volume-independent $(\partial p/\partial T)_v$ have under-estimated S_v. From a consideration of the pressure dependence of T_m up to 2000 bars, it is found that both S_c and f, the fraction of flexed bonds, remain constant at T_m while ΔS_m and S_v decrease. The "conformational volume" V_c associated with the rotational isomerization is estimated to be $V_c = 4.31$ cm^3/mol of flexed bonds. At T_m, V_c constitutes 30% of ΔV_m. For statistical mechanical calculations of the conformational properties, the simple rotational partition function due to Temperley is shown to be an adequate approximation to a more complex function derived later.

In an earlier paper,[1] relationships were developed between the conformational entropy S_c of polymer liquids and T_0, the constant in the Vogel equation for polymer liquid mobility. These were based on a modification of the Adam–Gibbs theory[2] for cooperative relaxation. In this new interpretation, the conformational entropy, S_c, arising from rotational isomerization about main-chain bonds, rather than the excess entropy $\Delta S = S(\text{liquid}) - S(\text{crystal})$, is the critical parameter in determining liquid mobility. In that work,[1] the simplest three-state rotational model with independent bond rotations was adopted.

In the present paper and with linear polyethylene (PE) as an example, we consider a physically more realistic model which takes into account the "pentane interference" and derive the conformational contribution to ΔS_m, the entropy of fusion. The volume contribution S_v is calculated on the basis of a volume-dependent thermal-pressure coefficient $(\partial p/\partial T)_v$, which in turn is derived via the Tait equation for liquid compressibility. The effects of pressure on ΔS_m and S_c are related to the pressure dependence of T_0(Vogel) and from the latter the "conformational volume" V_c, associated with the rotational isomerization, is estimated.

General Equations

We adopt the three-state rotational model (a trans state and two gauche states at a higher energy U) in which transitions between gauche bonds of opposite sign ($g^{\pm}g^{\mp}$) are excluded (the "pentane interference"). For this model the partition function is:[3,4]

$$Q = 0.5[1 + \sigma + (1 + 6\sigma + \sigma^2)^{1/2}] \tag{1A}$$

in which $\sigma = \exp(-U/RT)$.

This superseded the simpler function derived earlier by Temperley:[5]

$$Q' = [1 + 2^{1/2} \exp(-U/RT)] \tag{1B}$$

For a reason which will be given shortly, both of these functions will be developed in parallel. By standard statistical thermodynamics, the conformational (i.e., rotational) entropy is given by $S_c = R \ln Q + RT\,(\partial \ln Q/\partial T)$, which for the two partition functions being considered leads to:

$$S_c/R = \ln Q + \frac{(U/RT)(Q + 1)\sigma}{Q(2Q - 1 - \sigma)} \tag{2A}$$

or

$$S_c'/R = \ln Q' + (U/RT)(Q'-1)/Q' \tag{2B}$$

These are both plotted in Figure 1. By the indicated linear extrapolations and the arguments given previously,[1]

$$U = 4.4RT_0 \tag{3A}$$

or

$$U' = 4.0RT_0 \tag{3B}$$

As before,[1] the conformational entropy can also be expressed by the simple empirical equation:

$$S_c = 2.1(T - T_0)/T \tag{4A}$$

which applies between the limits $T_0/T \simeq 0.28$ to 0.68, the linear portion of curve A in Figure 1. For the alternate case,

$$S_c' = 2.0(T - T_0)/T \tag{4B}$$

which applies between the limits $T_0/T \simeq 0.19$ to 0.69 (curve B).

The fraction of flexed bonds in the g^+,g^- states is given by:

$$f = (Q + 1)\sigma/Q(2Q - 1 - \sigma) \tag{5A}$$

or

$$f' = (Q' - 1)/Q' \tag{5B}$$

Compared to eq 2A, the differentiation of eq 2B with respect to temperature is considerably more tractable. Fortunately, as will be shown later, both equations give very similar values for S_c and its temperature derivative, and hence, as a very good approximation, the conformational heat capacity can be derived from eq 2B:

$$C_{pc} = T(\partial S_c/\partial T)_p = R(U/RT)^2(Q' - 1)/Q'^2 \tag{6B}$$

Also[1]

$$-(\partial S_c/\partial p)_T = C_{pc}\,(\partial \ln U/\partial p)_T \tag{7B}$$

The volume entropy S_v is obtained from the thermodynamic identity,

$$(\partial S/\partial v)_T = (\partial p/\partial T)_v = \gamma \tag{8}$$

Contrary to the assumption that has often been adopted in estimates of S_v at the melting points of crystalline polymers,[6-8] it is now well established that γ is not constant but increases as the liquid is compressed isothermally.[9-11] Owing to the pressure-induced crystallization, the isothermal change in γ with liquid volume at T_m cannot be measured directly but has been estimated by a linear

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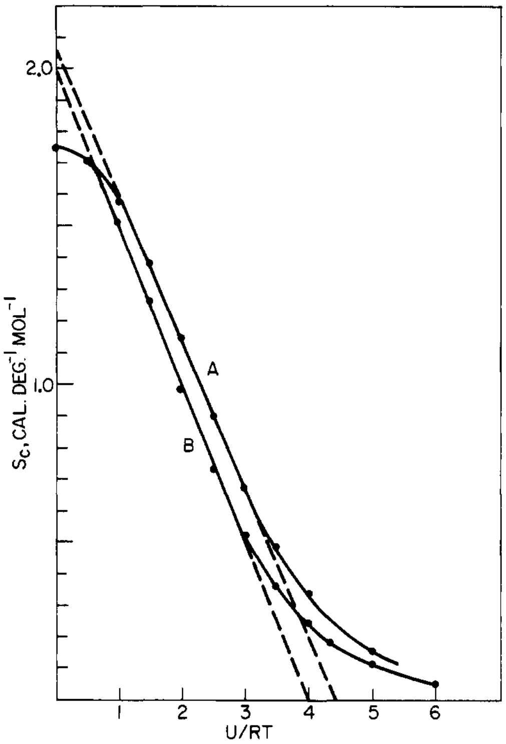

Figure 1. Conformational entropy for the three-state rotational model ($g^{\pm}g^{\mp}$ transitions excluded) with differing rotational partition functions: (A) eq 2A; (B) eq 2B.

extrapolation of γ measured in the melt above T_m.[10,11]

We have proposed a new method for deriving γ as a function of volume in the isothermal compression of a polymer liquid.[12] This is based on the Tait relationships for liquid compressibility:

$$V = V_0[1 - c \ln (P + b)/b] \qquad (9)$$

$$\beta = -(\partial \ln v/\partial p)_T = V_0C/V(P + b) \qquad (10)$$

in which V_0 and V are the liquid specific volumes at P_0 (atmospheric pressure) and pressure P, respectively, at the same temperature, and $C = 0.0894$, a universal constant which is independent of pressure and temperature.[13-15] The temperature dependence of b is:[15-17]

$$b = b_0 \exp(-b_1T) \qquad (11)$$

or $-\mathrm{d} \ln b/\mathrm{d}T = b_1$.

The thermal expansion coefficient, α, as a function of pressure is given by the temperature derivative of eq 9 at constant pressure:[15,17]

$$(\partial \ln v/\partial T)_p = \alpha = \alpha_0 - P\beta b_1 \qquad (12)$$

where α_0 is the value at P_0. Thus α and β can be calculated for a series of pressures (or volumes) from which $\gamma = (\alpha/\beta)$ is derived as a function of volume at constant temperature.

Results

Table I
Calculation of γ at T_m = 414 K

P, kbar	V, cm^3/g	$10^5\beta$, bar^{-1}	$10^4\alpha$, deg^{-1}	γ, bar/deg
0	1.268[a]	9.75[b]	7.81[c]	8.01[d]
0.5	1.219	6.57	6.27	9.55
1.0	1.184	5.00	5.48	10.96
2.0	1.137	3.42	4.62	13.50
3.0	1.103	2.62_5	4.14	15.76
4.0	1.077_5	2.14	3.81_5	17.82
5.0	1.056_5	1.81	3.58	19.72
6.3	1.034	1.52	3.34	22.00

[a] Equation 9, b = 916 bars. [b] Equation 10. [c] Equation 12. [d] $\gamma = \alpha/\beta$.

Table II
Entropy Contributions[a] at T_m = 414 K (T_0 = 160 K)

U, cal/mol	1335[b]	1271[c]	1398[d]
S_c	1.573[b]	1.234[c]	1.295[d]
$(S_c + S_v)$[e]	2.630	2.291	2.352

[a] ΔS_m = 2.362 (±0.115);[18] all entropy units are cal deg^{-1} mol^{-1} CH$_2$. [b] $g^{\pm}g^{\mp}$ allowed, eq 7 and A3 in ref 1. [c] $g^{\pm}g^{\mp}$ excluded, eq 3B and 2B. [d] $g^{\pm}g^{\mp}$ excluded, eq 3A and 2A. [e] S_v = 1.057, this work.

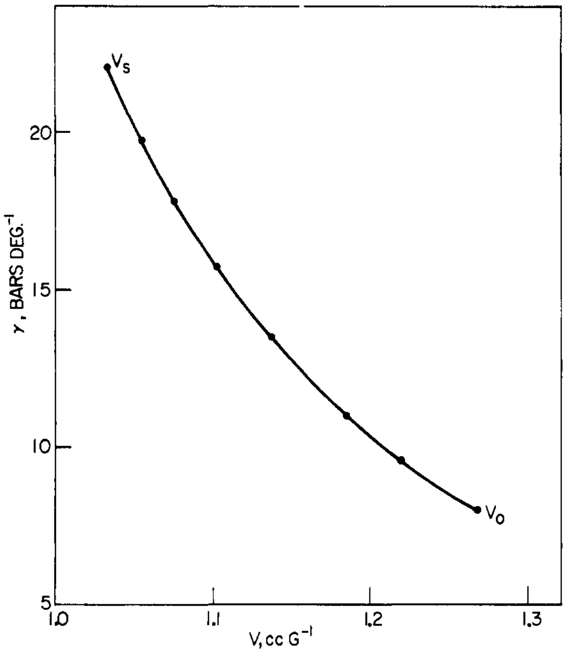

Figure 2. Volume dependence of the thermal pressure coefficient γ at T_m = 414 K.

S_v and S_c at T_M. Wunderlich and Czornyj have recently presented a critical review of the equilibrium melting of linear polyethylene.[18] For extended-chain crystals at T_m = 414 K, V_s = 1.034 cm^3/g for the crystal specific volume. For the liquid at T_M, we take the value measured by Olabisi and Simha,[16] V_0 = 1.268 cm^3/g. From the latter work and eq 11, b(Tait) = 916 bars. The calculations for γ as a function of volume are listed in Table I, and the results are plotted in Figure 2. A "graphical integration" of this nonlinear plot was performed by summation of the product of the average $\bar{\gamma}$ for each pressure interval in Table I and the volume increment dv over the same interval. Thus,

$$S_v = \sum_{V_s}^{V_0} \bar{\gamma}\, \mathrm{d}v = 3.160 \text{ cm}^3 \text{ bars deg}^{-1} \text{ g}^{-1} = 1.057 \text{ cal deg}^{-1} \text{ mol}^{-1} \text{ CH}_2$$

By an indirect method involving extrapolations from two lower n-alkanes, Robertson[9] derived an expression for γ_∞ (referring to the infinite chain) which was linear in V. For our values of T_m, V_0, and V_s, Robertson's eq 10 leads to S_v = 1.10 cal mol^{-1} deg^{-1}, a remarkable agreement considering the vastly different procedures. By a linear extrapolation of $\gamma - V$ from the melt in the vicinity of T_m, Tsujita and co-workers[10] reported S_v = 0.91 cal mol^{-1} deg^{-1}, but for the lower values, T_m = 407 K and ΔV_m = 0.212 cm^3/g, presumably referring to ordinary folded-chain rather than extended-chain crystals. A *linear* extrapolation

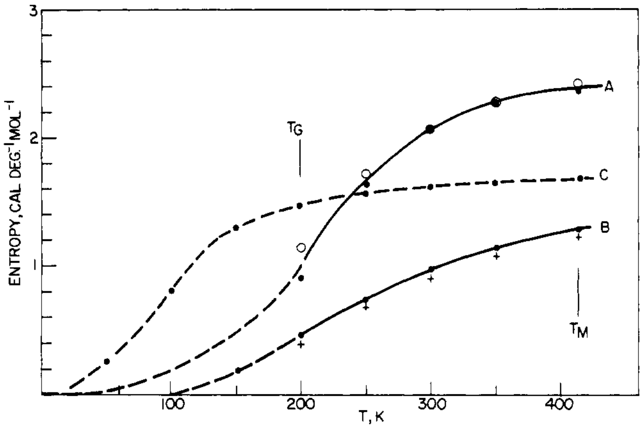

Figure 3. Temperature dependence of entropies. (A) Excess entropy, ΔS: (●) eq 13 and 14; (○) calculated by Broadhurst.[22] (B) Conformational entropy, S_c: (●) from eq 2A (U = 1398); (+) from eq 2B (U = 1271). (C) S_c from eq 2A with U = 500 cal/mol.

from V_0 in Figure 2 would give $\gamma \simeq 15$ bar/deg at V_s, from which $S_v \simeq 0.90$ cal deg^{-1} mol^{-1}.

Table II lists the calculation of the conformational entropy S_c for PE at T_m = 414 K, involving the two rotational models and the three partition functions with T_0(Vogel) = 160 K.[19,20]

In Table II, the sum ($S_v + S_c$) exceeds the experimental entropy of fusion ΔS_m for the model which allows $g^{\pm}g^{\mp}$ transitions while the exclusion of these transitions gives good agreement with ΔS_m, particularly as calculated with eq 2A. This is gratifying because the neglecting of the "pentane interference" is physically unrealistic in the first place.[3–5]

Lower values of U, applying to the "isolated" chain, would also give ($S_v + S_c$) exceeding ΔS_m with our value of S_v. For example, Smith[3] used U = 800 and 540 cal/mol in eq 2A and obtained S_c = 1.59 and 1.68, respectively, at T_m = 414 K. Also, Tonelli[8] has reported S_c = 1.76 and S_v = 0.46–0.52 cal mol^{-1} deg^{-1}, the latter values based on the assumption of a volume-independent γ, essentially the value at V_0 in Table I. It appears that past work[6–8] has over-estimated S_c while under-estimating S_v by about the same amount. Further evidence for this is the behavior of S_c over a broad temperature range as discussed next.

Effects of Temperature. The excess entropy is given by:

$$\Delta S = \int_{T_2}^{T} \Delta C_p \, d \ln T \tag{13}$$

in which $T_2 = T_0$ = 160 K for PE.[19,20] Heat capacities for the liquid and crystalline phases reported by Wunderlich[21] lead to:

$$\Delta C_p = 7.266 - 0.0178T \text{ cal deg}^{-1} \text{ mol}^{-1} \tag{14}$$

Figure 3 shows ΔS as a function of temperature between T_g = 200 K[19,20] and T_m = 414 K, calculated by eq 13 and 14. Shown also are the ΔS values calculated by Broadhurst[19,22] by extrapolation from lower n-alkanes. The asymptotic approach of ΔS toward zero has been demonstrated by Smith.[23]

The S_c values derived from eq 2B closely parallel those given by the more correct eq 2A with essentially the same slopes, $(\partial S_c/\partial T)_p = C_{pc}/T$. This justifies the use of the simpler eq 2B, leading to eq 6B and 7B. Curve C was calculated from eq 2A for a lower value, U = 500 cal/mol, generally accepted for the "isolated" or "unperturbed" chain.[4,8,24] It is seen that the lower U does not permit S_c to decrease rapidly enough with temperature, with the result that in the vicinity of 200 K and below S_c exceeds ΔS, which is clearly impossible. Furthermore, this curve is virtually identical with one calculated by Tonelli[25] with U_σ = 500 and U_ω = 2000 cal/mol, the latter energy referring to $g^{\pm}g^{\mp}$ transitions as against the complete exclusion of these transitions ($U_\omega = \infty$) adopted in the present work. This is because the statistical weight $\sigma = \exp(-U_\sigma/RT)$ overwhelms $\omega = \exp(-U_\omega/RT)$, especially at the lower temperatures. For example, at 414 K, σ = 0.54 and ω = 0.088, and at 200 K, σ = 0.28 and ω = 0.0065. A value of U = 800 cal/mol[3] also leads to a discrepancy in S_c vis-à-vis ΔS in the low-temperature region. We consider the results in Figure 3 to be conclusive evidence that U values appropriate for the isolated or unperturbed chain cannot be used in statistical mechanical estimates of S_c or other conformational properties for the real polymer liquid.

Table III
Effects of Pressure on Entropies[a] at T_m

P, bars	0	1000	2000
T_m, K[28]	415	443	463
T_2 (=T_0), K	160	169[27]	174[27]
ΔS_m[b]	2.39 (2.4[c])	2.12 (2.1[c])	1.96
U, cal/mol[d]	1398	1479	1523
U/RT_m	1.694	1.682	1.665
S_c[e]	1.298	1.304	1.317
f[f]	0.221	0.222	0.223

[a] All entropy units are cal deg^{-1} mol^{-1} CH_2. [b] Equations 13 and 14. [c] Experimental values from ref 30. [d] $U = 4.4RT_0$ (eq 3A). [e] Equation 2A. [f] Fraction of flexed bonds by eq 5A.

Effects of Pressure. As pointed out by Naoki and Nose,[26] according to the thermodynamic relationship $[\partial(C_p/T)/\partial p]_T = -(\partial^2 v/\partial T^2)_p$ if the V–T isobars are linear, C_p will be independent of pressure. Examination of the isobars[16] for liquid PE, as well as for the solid below ~80 °C, where the crystallinity remains constant, showed no detectable curvature so we tentatively assume that ΔC_p (eq 14) is independent of pressure. Since $T_2 = T_0$ for PE, both will have the same pressure dependence. We have recently calculated T_0 as a function of pressure up to 2000 bars[27] and together with eq 13 and 14 can now calculate ΔS_m as a function of T_m, P_m for the extended-chain crystals.[28] As shown in Table III, ΔS_m decreases with increasing T_m, P_m in qualitative agreement with experiment.[29,30]

In Table III, the conformational entropy S_c and f, the fraction of flexed bonds in the g^+ and g^- states, were derived from eq 2A and 5A, respectively, recalling that $U = 4.4RT_0$ (eq 3A). Both S_c and f appear to remain constant at T_m, P_m (the alternate equations 2B, 5B, and 3B also give constant S_c and f but at very slightly different values). Hence the volume contribution $S_v = \Delta S_m - S_c$, as well as ΔS_m itself, decreases with increasing T_m, P_m.

Conformational Volume. The flexing of bonds in the melting transition from the ordered crystalline state to the more disordered liquid must involve a "conformational volume" V_c contribution to ΔV_m, analogous to the S_c contribution to ΔS_m. This can be estimated from the thermodynamic relation: $(\partial V_c/\partial T)_P = -(\partial S_c/\partial P)_T$ and eq 7B.

Since U by eq 3A or 3B is directly proportional to T_0, $(\partial \ln U/\partial P)_T = \partial \ln T_0/\partial P$. For PE liquid at atmospheric pressure, we have estimated[27] $10^5\, \partial \ln T_0/dP = 8.14$ bar^{-1}, which is independent of temperature at constant pressure. C_{pc} was calculated from eq 6B from 0 to 500 K and introduced into eq 7B, with the results shown in Figure 4.

At T_m = 414 K, $10^4\,(\partial V_c/\partial T) = 2.06$ cm^3 g^{-1} deg^{-1}. Taking $10^4\, dV_l/dT = 9.9$ and $10^4\, dV_s/dT \simeq 3.0$,[16] the temperature dependence of the excess volume is $10^4\, d\Delta V/dT \simeq 6.9$, of which 30% is contributed by $\partial V_c/\partial T$.

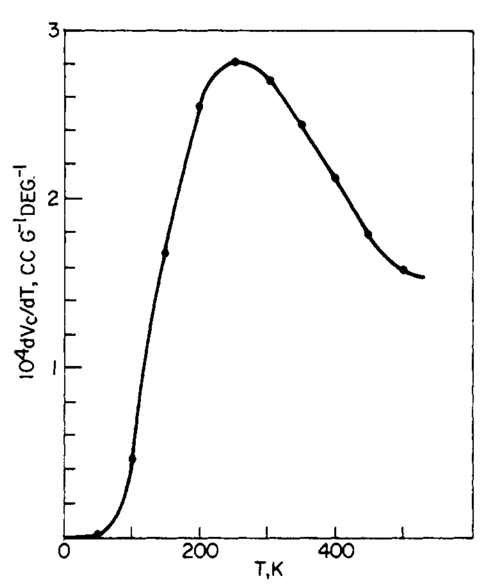

Figure 4. Temperature derivative of conformational volume as a function of temperature (eq 7B).

By graphical integration of Figure 4, V_c itself can be derived as a function of temperature. This is shown in Figure 5A. At T_m = 414 K, V_c = 0.0715 cm^3 g^{-1}, which is again 30% of ΔV_m = 0.234 cm^3 g^{-1}. In Figure 5B, V_c is plotted against f, the fraction of flexed bonds calculated by eq 5B. The relationship is now linear with a slope of 0.308 cm^3 g^{-1} or 4.31 cm^3 per mol of flexed bonds. As a cross-check, f = 0.232 at T_m and V_c = $(4.31/14)f$ = 0.0713 cm^3 g^{-1}, in agreement with V_c derived above. The value V_c = 4.31 cm^3 mol^{-1} is to be compared with the van der Waals volume[31] of 10.13 cm^3 mol^{-1} and the "hard-core" volume[31] at 0 K of 13.40 cm^3 per mol of CH_2. At the molecular level the flexing of a bond produces a volume increment of $4.31/(6.02 \times 10^{23}) = 7.16 \times 10^{-24}$ cm^3.

Discussion

Karasz and co-workers[32] recently have questioned the entire concept of the separation of ΔS_m into S_v and S_c components. In rebuttal, we point out that neither S_c nor S_v alone can account for ΔS_m, but the two combined give a satisfactory entropy balance, as shown in the present work. Furthermore, their arguments do not apply to the general case of noncrystallizing or supercooled systems. For example, Figure 3 represents ΔS and S_c for a hypothetical supercooled PE liquid, which is difficult to obtain experimentally owing to its very rapid crystallization rate. Over the entire temperature range, S_c accounts for only a portion (~50%) of ΔS, and the remainder must be S_v. This could be demonstrated in other systems (polystyrene or polypropylene, for example) by comparing the atactic, noncrystallizing polymer with its isotactic, crystallizing form.

Since in the present context T_2(calorimetric) and T_0-(Vogel) are important parameters for estimating ΔS and S_c, it is appropriate to review the arguments regarding their relationship to each other. Although both of these have now been shown to be fictive temperatures,[1,23] they may still give qualitative information on molecular motions in polymer liquids. We have suggested that vinyl-type polymer chains that have substituents whose internal motions can contribute measurably to ΔC_p (hence to ΔS) in going into the liquid state will always show $T_2 < T_0$ since these substituent motions are not directly related to rotation about main-chain bonds, and it is the latter that determines S_c. Thus $T_2 < T_0$ for polystyrene[33] but $T_2 \simeq T_0$ for linear polyethylene,[19] poly(ethylene oxide),[20] polypropylene,[33] and poly(propylene oxide).[20] In the latter two polymers, motion (i.e., rotation) of the methyl substituent apparently does not noticeably enhance ΔC_p in going to the liquid state.

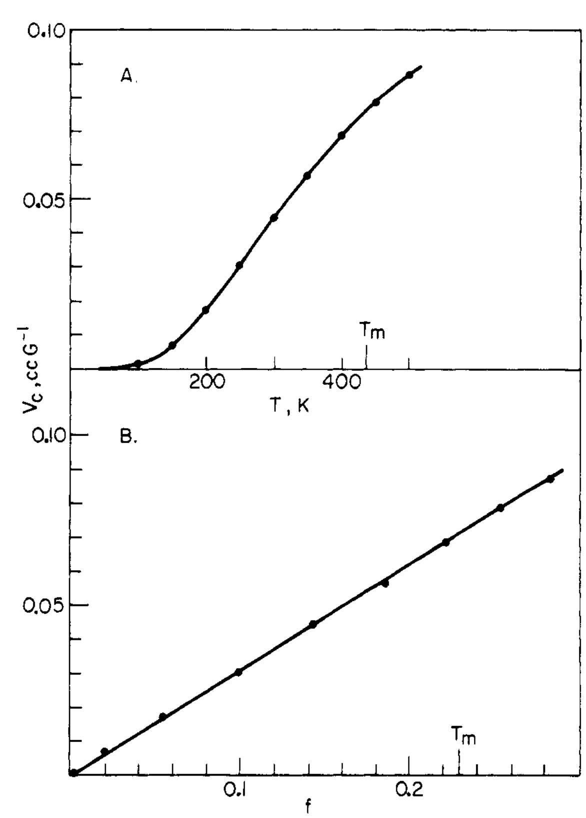

Figure 5. (A) Conformational volume as a function of temperature. (B) Conformational volume as a function of f, the fraction of flexed bonds by eq 5B.

Nonvinyl polymers with aromatic rings as part of the main chain show especially large differences between T_2 and T_0. For poly(ethylene terephthalate),[20] $T_0 - T_2 \simeq$ 100°, and for bisphenol-A polycarbonate[20] with a greater aromatic content, $T_0 - T_2 \simeq$ 140°. These results imply that the enhanced motions of these aromatic rings in the liquid state, while they may contribute to ΔS, do not contribute significantly to the overall *mobility* (i.e., S_c) of the polymer liquid which presumably involves rotations about the more flexible bonds in the chain.

These observations are consistent with a quantitative correlation which we have reported[34] for the glass transition: $K = dV_g/dT - (dV/dT)_p$, where V_g is the specific volume at the glass-liquid boundary and V is the liquid specific volume at atmospheric pressure. The same value, $-10^4K = 17 \pm 1$ cm^3 g^{-1} deg^{-1}, was found for a number of vinyl-type polymers while the polycarbonate gave a lower value, $-10^4K = 10.3$. Recent measurements by Zoller[35] on a highly aromatic polysulfone lead to an even lower value, $-10^4K = 6.6$ cm^3 g^{-1} deg^{-1}. Apparently the magnitude of K is related to the weight fraction of rotating segments of the main chain, with a maximum value for vinyl-type polymers where this weight fraction is uniformly unity.

The present work has demonstrated the fallacy in using isolated or unperturbed chain values for the rotational energy U in statistical mechanical calculations of S_c or other conformational properties of the real polymer liquid. In the previous paper,[1] a relatively small (5%) change in T_0 was reported for poly(vinyl acetate) liquid between atmospheric pressure and 1000 bars, indicating a correspondingly small perturbation on U by pressure. However, by extrapolating into the "negative pressure" region and approaching the conditions of the isolated chain, we have since demonstrated[27] a far greater decrease in T_0 (hence in U) for a number of vinyl polymers including PE. It is now apparent that our value of U is not the "average" between U_σ and U_ω, as suggested earlier,[1] but rather it is U_σ, which has been appreciably increased by intermolecular interactions.

The fraction of flexed bonds f is more sensitive to the value of U than is S_c and might be more amenable to experimental test or direct measurement. For example, in PE at $T_m = 414$ K by eq 5B, our treatment gives $f = 0.23$, but with $U = 500$ cal/mol (the isolated chain value), $f = 0.45$, about twice as large. In this connection, it should be noted that measurements of the molecular dimensions of liquid n-alkanes by small-angle neutron scattering when interpreted by the rotational isomeric state model require that $U \simeq 500$–600 cal/mol, agreeing with the unperturbed value for linear polyethylene.[24] However, there may still be uncertainties in the relationship between molecular dimensions and U, or more specifically, the fraction of flexed bonds. Preliminary calculations by Cook and Moon[36] have shown that variations in the rotational angle about the t, g^+, g^- minima could alter the end-to-end distance beyond what the rotational isomeric model would predict, tending to shorten an extended chain or lengthen a compacted one. This "flexibility" would make a low value of f *appear* to be higher when the end-to-end distance is interpreted by the unmodified rotational isomeric state model. Further calculations are required to determine the magnitude of this effect and whether the differing U and f values can thus be reconciled.

In conclusion, it is emphasized that our entire treatment has been based on a *three*-state rotational model including the "pentane interference". While apparently quite correct for linear polyethylene, this model may be more of an approximation when applied to other polymers (cf. discussions in ref 3 and 4). However, the conformational properties of the bulk polymer liquid may still be dominated by a single value of U, which in the present context is uniquely defined by the Vogel T_0. This in turn can be derived from the liquid mobility as manifested, for example, by the Newtonian viscosity or the α process in dielectric relaxation.

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