Rotational energetics in vinyl polymer liquids: 1. Poly(vinyl acetate)

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Mobilities of liquid poly(vinyl acetate) as expressed by the Vogel equation, $-\ln\mu = B/T - T_0)$, are extrapolated to negative pressure using previously determined pressure coefficients. The extrapolations are extended to $P^* = -b$ (Tait) where the liquid volume becomes 'infinite' and the polymer chains are in the hypothetical 'isolated' state. By an analysis of the rotational kinetics and relationships developed previously, this procedure leads to U^* and V^* for the 'isolated' chain, where U^* is the energy difference between the rotational states and V^* is an energy barrier between these states. It is found that the greatest increase occurs between U^* for the 'isolated' chain and U for the liquid at atmospheric pressure, with relatively little further increase up to 2000 bars. The energy barrier V, on the other hand, increases more uniformly over the entire pressure range from P^* to 2000 bars. On the basis of the analyses of the rotational energetics and kinetics, an approach to a unified molecular interpretation of shear-induced lowering of viscosity (non-Newtonian viscosity) and shear-induced crystallization in certain flowing polymer liquids is suggested.

INTRODUCTION

An earlier paper[1] presented a molecular interpretation of the T_0 and B parameters in the Vogel equation for polymer liquid mobility:

$$-\ln\mu = B/(T - T_0) \tag{1}$$

On the basis of a modification of the Adam—Gibbs theory[2] for the cooperative relaxation in polymer liquids in conjunction with a simple 3-state rotational model, it was shown that:

$$U = 4.2RT_0 \tag{2a}$$

and,

$$E_0 = RB \tag{2b}$$

in which U is the energy difference between the *trans* state and two equivalent *gauche* states (g^+ and g^-) and E_0 is related to the rotational barriers.

With poly(vinyl acetate) (PVAc) as an example a procedure for estimating the pressure dependences of T_0 and B had been reported earlier[3]. Between P_0 (atmospheric pressure) and $P = 1000$ bars T_0 and B increased by 5 and 15% respectively and these changes were attributed to *inter*molecular contributions to U and E_0 in equations 2a and 2b. It was suggested that the strictly internal contributions, U^* and E_0^*, characteristic of the 'isolated' chains, might be derived by appropriate extrapolations into the negative pressure region. This would permit comparisons between different polymers, uncomplicated by intermolecular effects in the bulk polymer liquid or polymer—solvent interactions in dilute solutions.

The present paper develops one such an extrapolation procedure in detail for PVAc. The rotational energetics thus derived for the 'isolated' chain are compared with those for the real polymer liquid at P_0 and above. The following paper applies this procedure to four additional vinyl-type polymers

RESULTS

Liquid volumes at negative pressures

For positive pressures, liquid $p-v-T$ properties are well represented by the Tait equation:

$$v = v_0[1 - c\ln(P + b)/b] \tag{3a}$$

in which the specific volumes are v at (P,T) and v_0 at (P_0, T) and c is a constant independent of P and T. The parameter b is independent of pressure and varies with temperature as:

$$b = b_0\exp(-b_1 t) \tag{3b}$$

where b_0 and b_1 are constants for a given liquid and t is the temperature, usually expressed in degrees C.

From equation 3a the isothermal compressibility is:

$$-(\partial v/\partial p)_T = cv_0/(P + b) \tag{3c}$$

Negative pressures have been applied to liquids by various means in attempts to measure their 'tensile strength', In the case of dodecane, for example, it was shown that the Tait equation applies at least in the initial part of the negative pressure region[4]. In the present work we shall extrapolate the Tait equation to negative pressures $P^* = -b$ where according to equation 3a the volume v becomes infinite and hence the polymer chains are in the hypothetical 'isolated' state. It is not necessarily implied here that the $p-v-T$ properties follow the Tait equation all the way down to P^* but rather that the Tait b is a reasonable parameter on the basis of which to compare 'isolated' chains of different polymers. With this proviso the $p-v-T$ properties for PVAc, calculated
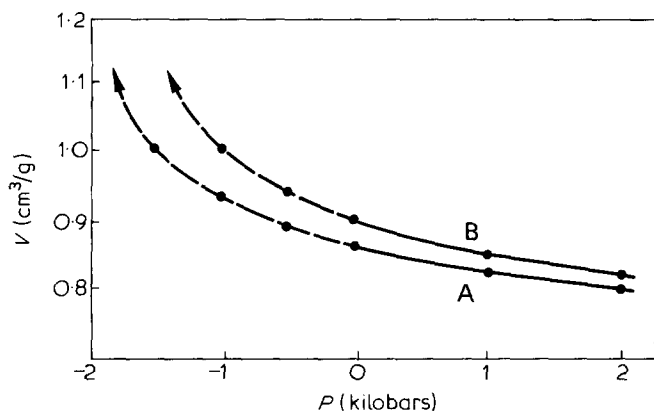
Figure 1 Liquid volumes as functions of pressure for PVAc, calculated with the Tait equation. A. 60°C; B, 120°C

by equation 3a with the previously reported Tait values[3,5a] and v_0 measurements[5b], are depicted in *Figure 1*.

Mobilities at negative pressures

There is ample evidence that for polymer liquids the pressure coefficients of mobility $(\partial \ln\mu/\partial p)_T$, based on measurements of either the α-process in dielectric relaxation[6,7] or of Newtonian viscosity[8,9], are independent of pressure up to at least 2000 bars, i.e. $-\ln\mu$ is linear in P. Thus:

$$-\ln\mu = B/(T - T_0) + (\partial \ln\mu/\partial p)_T \Delta P \qquad (4)$$

in which B and T_0 are the Vogel constants at P_0 (atmospheric pressure). Equation 4 with the previously reported[3] Vogel values and pressure coefficients for PVAc is plotted in *Figure 2* and the isotherms are extrapolated linearly down to $P^* = -b$. The extrapolated mobilities at P^*, designated henceforth as μ^*, can also be calculated by the relationship:

$$-\ln\mu^* = B/(T - T_0) \left[1 + cv_0/(T - T_0)K\right] \qquad (5)$$

where $-10^4 K = 17$ cm^3/g °C. This equation can be derived from equation 4 above together with equations 2, 5 and 8 of the previous work[3].

In *Figure 2* the value of $-\ln\mu^*$ depends upon the temperature of the extrapolated isotherm with a maximum appearing at the 80°C isotherm. (It turns out that there is also a maximum in the activation energy $E = RT^2 (d\ln\mu^*/dT)$ at this temperature.)

Calculations with equation 5 for all of the other polymers (following paper) also gave a maximum $-\ln\mu^*$ for a particular isotherm, which we designate as T_{max} and which turns out to be about 100 to 110°C above the respective T_0 values. For a rational comparison between the different polymers we shall restrict all subsequent calculations to the T_{max} isotherm.

Pressure dependence of Vogel T_0 and B

The pressure dependence of T_0 and B can be calculated by[3]:

$$[B/(T - T_0) - (\partial \ln\mu/\partial p)_T \Delta P]^{-1} = T/B' - T_0'/B' \qquad (6)$$

in which T_0, B apply at P_0 (atmospheric pressure) and T_0', B' apply at pressure P. In the previous work[3] this equation was used over a broad temperature range (60–120°C) but, for the reason mentioned in the preceding section, equation 6 will now be applied only in the immediate vicinity of T_{max}.

The standard procedure to be adopted for all of the polymers considered in these two papers is as follows.

T_{max} is determined to ±5° with equation 5, and the left term of equation calculated at each isobar for three temperatures: T_{max} and $T_{max} \pm 10°$C. The pressure coefficient appropriate for each temperature is derived from equation 2 of the earlier work[3]. The left term of equation 6 is linear in T leading to the value of $1/B'$ for the particular isobar and then, by re-substitution of B', giving the value of T_0'. For PVAc the temperatures chosen were 70°, 80° (T_{max}), and 90°C and the results, calculated with greater precision than previously[3], are listed in *Table 1*. The pressure dependence of T_0 follows a cubic equation:

$$T_0' = T_0 + a_1 P + a_2 P^2 + a_3 P^3 \qquad (7)$$

for which the constants are also listed in *Table 1*.

The T_0 values were extrapolated into the negative pressure region by use of equation 7 and $-\ln\mu$ similarly extrapo-
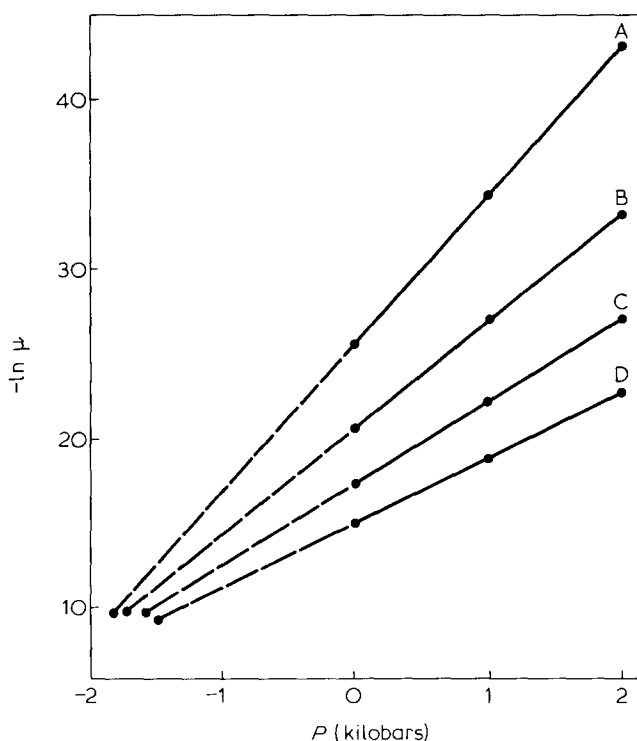

Figure 2 Isothermal mobilities of PVAc liquid as functions of pressure. A, 60°C, $-\ln\mu^* = 9.67$; B, 80°C, $-\ln\mu^* = 10.15$; C, 100°C, $-\ln\mu^* = 9.84$; D, 120°C, $-\ln\mu^* = 9.32$

Table 1 Pressure dependence of Vogel T_0 and B for PVAc

P, bars	ΔT_0, degrees	ΔB, degrees
0	0	0
200	3.25	60
400	5.99	124
600	8.32	191
800	10.35	260
1000	12.09	332
2000	18.31	708
T_0, K	248	$B(P_0) = 2183°$
$10^2 a_1$	1.757	$(dB/dp)_0 = 0.296$ deg/bar
$10^6 a_2$	−6.753	
$10^9 a_3$	1.273	

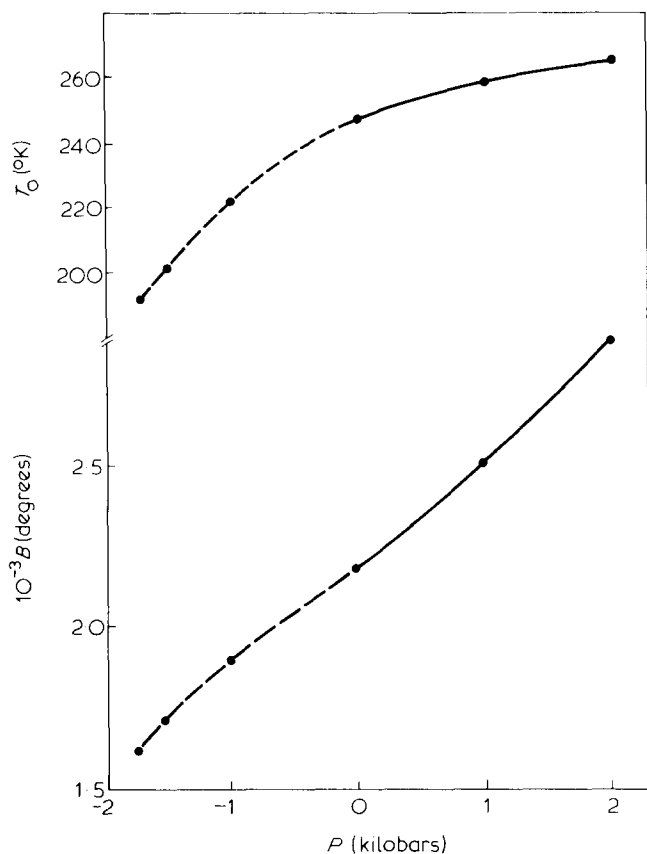*Figure 3* Vogel constants, T_0 and B, as functions of pressure for PVAc

lated by equation 4 for the $T_{max} = 80°C$ isotherm (cf *Figure 2*). The corresponding values of B were then calculated by the Vogel equation 1. *Figure 3* shows T_0 and B as functions of pressure between +2000 bars and $P^* = -b = -1695$ bars. At the latter negative pressure, $T_0^* = 192.6°C$, $-\ln\mu^* = 10.15$, and $B^* = 1628°$. Thus, by equations 2a and 2b respectively, $U^* = 1607$ and $E_0^* = 3234$ cal/mol, compared to $U = 2069$ and $E_0 = 4336$ cal/mol at P_0 (atmospheric pressure).

In *Figure 3* it may be noted that the relatively small change in T_0 (hence U) in the positive pressure region corresponds to a similarly small change in volume (*Figure 1*). Both T_0 and the volume change much more rapidly with pressure in the negative region.

The Vogel B in *Figure 3* shows a slight upward curvature at positive pressures, which was undetected in the earlier, less precise calculations up to only 1000 bars[3]. There is a similar curvature at the negative pressures but in the opposite direction.

Rotational kinetics

A rotational energy diagram for the simple 3-state model which has been adopted here[1] is shown in *Figure 4*. At equilibrium, let f be the fraction of *gauche* (g^+ and g^-) bonds and $(1 - f)$ be the fraction of *trans* (t) bonds. The rate of isomerization in the 'forward' direction ($t \to g^+$ and $t \to g^-$) is:

$$r_f = 2(1 - f)e^{-V^*/RT} \tag{8}$$

and in the 'reverse' direction ($g^+, g^- \to t$),

$$r_r = fe^{-(V^* - U^*)/RT} \tag{9}$$

Since at equilibrium $r_f = r_r$, we obtain:

$$f/(1 - f) = 2e^{-U^*/RT} \tag{10}$$

which, of course, is the *gauche/trans* ratio derived also from statistical mechanics. The *overall* rate of isomerization, involving all transitions anywhere along the polymer chain, is $r_0 = r_f + r_r = 2r_f$ and hence from equation 8:

$$r_0 = 4(1 - f)e^{-V^*/RT} \tag{11}$$

and,

$$\partial \ln r_0/\partial T = \partial \ln(1 - f)/\partial T + V^*/RT^2 \tag{12}$$

But $\partial \ln r_0/\partial T = E_0^*/RT^2$ and from equation 10, $\partial \ln(1 - f)/\partial T = -fU^*/RT^2$. Thus:

$$E_0^* = V^* - fU^* \tag{13}$$

in which,

$$f = 2e^{-U^*/RT}/(1 + 2e^{-U^*/RT}) \tag{14}$$

According to equation 13 the value of the 'overall' activation energy E_0^* for the transitions lies between the barriers in the 'forward' and 'reverse' directions. In the limit of $f = 0$, corresponding to all *trans* bonds, $E_0^* = V^*$, and in the limit $f = 1$ (all *gauche* bonds), $E_0^* = V^* - U^*$.

There is no apparent reason that equation 13, which by implication was derived for the 'isolated' chain, cannot be applied to the real polymer liquid. Hence,

$$E_0 = V - fU \tag{15}$$

in which each of the parameters is now pressure-dependent. The results of such calculations for PVAc over the pressure range $P^* = -b$ to $P = 2000$ bars are given in *Table 2*. The V and U are shown schematically in *Figure 5*, which is a symmetrical bisection of *Figure 4* with the *trans* state as the reference at zero energy. It is seen that by far the largest change in U occurs between P^* and P_0 (atmospheric pressure) while V continues to increase by relatively large increments, the behaviour of both being consistent with the T_0 and B plots in *Figure 3*.
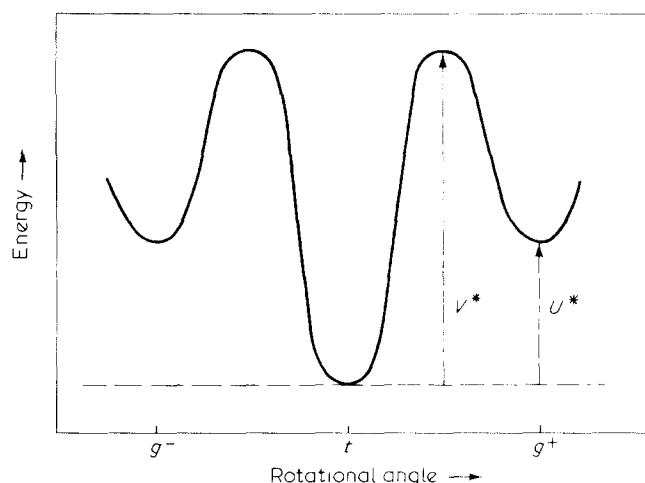

Figure 4 Schematic rotational energy diagram for 3-state rotational isomeric model

Table 2 Derived rotational energetics of PVAC

P bars	T_0 °C	U cal/mol	B deg.	E_0 cal/mol	f	V cal/mol
−1695*	192.6	1607	1630	3238	0.168	3508
0	248	2069	2183	4336	0.0947	4532
1000	260	2170	2515	4996	0.0831	5176
2000	266	2222	2891	5743	0.0776	5912

* 'Isolated' chain

DISCUSSION

This paper has presented an approach to the rotational energetics of the 'isolated' polymer chain *via* the dynamics of the real polymer liquid, as manifested by the α-process in dielectric relaxation or by Newtonian viscosity[1,3]. While these extrapolational procedures and hence the absolute values derived for U^* and V^* for the 'isolated' chain may be vulnerable to criticism, we believe that the method should be useful for comparing the relative effects of chemical structure on the strictly *intra*molecular energetics between different polymers. Also, the information generated in this and the following paper on the pressure dependence of the Vogel T_0 and B in the positive pressure region should be applicable to other extrapolational methods and/or to other rotational models.

The simplest 3-state rotational model with independent bond rotations has been adopted here, partly for convenience in the treatment. An alternate 3-state model in which transitions between *gauche* states of opposite sign are excluded ('pentane interference') may be physically more realistic. By the analysis reported previously[1] it will be shown[10] that for such a model the numerical coefficient in equation 2a is 4.4, making all U values in *Table 2* higher, but by less than 5%. This difference in U is partially cancelled by slightly lower values of f (equations 13 and 15) and causing a negligible change in V in *Table 2*.

One of the salient conclusions to be derived from this work is that intermolecular interactions, arising when the hypothetical 'isolated' chains are condensed to the real polymer liquid, cannot be neglected particularly when the conformational properties based on U are calculated. In PVAc at 80°C, for example, the increase from $U^* = 1607$ to $U(P_0) = 2069$ cal/mol (*Table 2*) changes the Boltzmann factor, $\exp{-U/RT}$, from 0.10 to 0.052, which in turn decreases f (equation 14) from 0.17 to 0.095 and the calculated conformational entropy S_c from 1.15 to 0.75 e.u. (*Ref 1, Figure 1 or equation A3*).

When the rotational kinetics (discussed earlier) are applied to viscous flow, the possibility of a shear-induced biasing of the rotational energetics must be considered. While this effect may be negligible at the low shear rate involved in Newtonian viscosity, this may no longer be the case at the high shear rates in non-Newtonian flow. Indeed, such biasing of the energy barriers at high shear rates has often been suggested and discussed in the literature, the most recent example being the work of Christmann and Weber[11], based on a different molecular model. In the present context, this isothermal decrease in viscosity and concomitant changes in the rotational energies would be equivalent to an isothermal extrapolation into the negative pressure region (*Figure 2*).

In addition, the well-known phenomenon of shear-induced crystallization, occurring isothermally, implies a decrease not only in the excess entropy ΔS but also in the conforma-
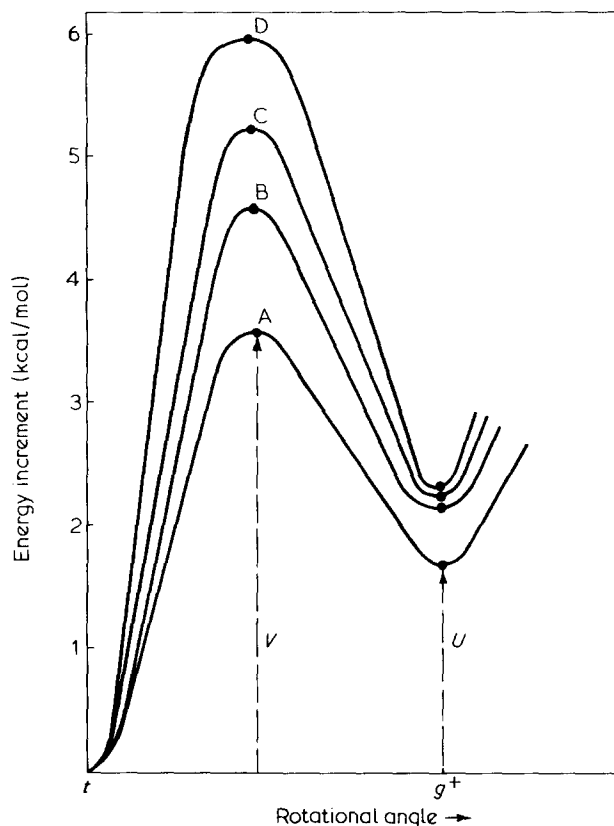

Figure 5 Derived rotational energy diagram for PVAc (bisection of *Figure 4*). A, $P = P^*$ ('isolated' chain); B, $P = P_0$ (atmospheric pressure); C, $P = 1000$ bars; D, $P = 2000$ bars

tional entropy S_c, which in turn implies an increase in the thermodynamic quantity U. In reporting another type of phase change in flowing polymer solutions VerStrate and Philippoff[12] have commented on these interactions between the dynamics and thermodynamics in polymer liquid systems. Such interactions should be amenable to a unified explanation at a molecular level by considering, among other factors, shear induced changes in the rotational energetics.

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