Some Molecular Properties of Vinyl Polymers[1]

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ABSTRACT: The parameters in the Vogel viscosity equation, $\log \eta = \log A + B/(T - T_0)$, are evaluated for a number of vinyl-type polymers from literature data. Above the "chain-entanglement" molecular weight, $\log A = \log K + 3.4 \log Z_w$, where $\log K = -11$ to -12 and Z_w is the "weight-average" number of main-chain bonds per molecule. According to recent theories, T_0 is zero point for the configurational entropy and "free volume" extrapolated from the liquid state. On the basis of a "*trans-gauche*" rotational model for viscous flow (*i.e.*, segmental motion), evidence is presented that the parameter B is determined by the internal rotational barriers in the "isolated" polymer chain. Possible relationships between the intra- and the *inter*molecular rotational energetics, applying to the real polymer liquid, are suggested.

The equilibrium and dynamic properties of polymers must ultimately be related to a number of characteristic molecular parameters. One of these is T_0, the second-order transition temperature, lying below the experimental glass temperature, T_g. From a thermodynamic viewpoint, T_0 is the temperature at which the extrapolated conformational entropy[2] and free volume[3] of the polymer liquid become zero, and, from a kinetic viewpoint, it is the temperature at which the extrapolated segmental relaxation time becomes infinite. Thus, in principle, T_0 should be derivable from either equilibrium or dynamic measurements on the polymer liquid.

The Newtonian melt-viscosity of linear, vinyl polymers can be expressed by the Vogel equation[4,5]

$$\log \eta = \log A + B/(T - T_0) \tag{1}$$

Here, B is a kinetic parameter and there is some evidence[2b] that it is related to the internal barriers to rotation of main-chain bonds in the "isolated" polymer molecule. The temperature variation of the flow activation energy is obtained by differentiating eq 1 with respect to $1/T$

$$E_T = E_0[T/(T - T_0)]^2 \tag{2}$$

where $E_0 = 2.3RB$.

Above M_c, the "critical chain-entanglement" molecular weight, the preexponential term in eq 1 can be expressed as[6–8]

$$\log A = \log K + 3.4 \log Z_w \tag{3}$$

in which $Z_w = M_w/(m/2)$ is the "weight-average" number of main-chain bonds per molecule, m being the molecular weight of the repeating unit.

In this paper, eq 1–3 are used to evaluate T_0, E_0, and log K for a number of vinyl-type polymers from measurements reported in the literature. On the basis of a rotational model for segmental motion, intramolecular (isolated chain) energetics of bond rotation and possible relationships with intermolecular effects in bulk polymer liquids are presented.

Results

1. Poly(n-alkyl methacrylates). Table I lists the Vogel parameters for a number of vinyl polymers, reported by Berry and Fox in a recent review on polymer viscosity.[9] The first two polymers (PMA and PVAc) are simple isomers, having different arrangements of the carboxyl group with respect to the main chain. The T_0 (and T_g) values differ by 33°, with only a minor difference in E_0.

TABLE I
VISCOSITY PARAMETERS FOR VINYL POLYMERS[a]

	T_g, °K	T_0, °K	E_0,[b] kcal/mol
Poly(methyl acrylate)	275	215	4.60
Poly(vinyl acetate)	308	248	4.36
Poly(methyl methacrylate)[c]	381	301	5.44
Poly(methyl methacrylate)[d]	388	308	5.16
Poly(ethyl methacrylate)	335	265	5.76
Poly(n-butyl methacrylate)	300	220	6.16
Poly(n-hexyl methacrylate)	268	178	6.62

[a] See ref 9. [b] $E_0 = R/$"α". [c] Ideally atactic. [d] Conventional, 75% syndiotactic.

In the n-alkyl methacrylate series, T_0 decreases and E_0 increases regularly with the length of the n-alkyl group. It should be noted that the Vogel "α" parameter[9] bears no relationship to actual expansion coefficients for these methacrylates[10]: $\Delta\alpha = \alpha_l - \alpha_g = 2.5 \times 10^{-4}$ deg^{-1}, approximately constant, or α_l which increases in this series, while "α" decreases. This is further evidence[5] for the inadequacy of the simple "free volume" equation, $\ln \eta \propto b/\phi$, with $\phi = \Delta\alpha(T - T_0)$ or $\alpha_l(T - T_0)$, and with an *assumed* value of unity for b. This point will be discussed later.

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In their review,[9] Berry and Fox give several examples of the effects of diluents (*i.e.*, plasticizers) on the viscosity parameters. Typically, up to about 50% concentration, the diluent causes an almost parallel decrease in T_g and T_0, with a relatively minor decrease in E_0. In the present case of the *n*-alkyl methacrylates the hydrocarbon group may be considered as a plasticizer, but one that is bound to the main chain, still lowering the thermodynamic T_0, while increasing the kinetic E_0 parameter.

2. Polypropylene. From calorimetric measurements on atactic and isotactic polypropylene, Passaglia and Kevorkian[11] found $T_m = 447°$, $T_g = 259°$, and estimated $T_0 = 206\ (\pm 20)$°K. Viscosity measurements on the high molecular weight polymer gave E_T = 9.3,[12] 10.1,[13] and 10.0[14] kcal/mol in the range 190–270°. Taking $T_0 = 206$°K and $E_T = 10.0$ kcal/mol at a mean temperature of 500°K, we find $E_0 \simeq 3.5$ kcal/mol by eq 2, and $(T_g - T_0)/2.3B \simeq 0.030$, the normal value for vinyl polymers.[7] For the Newtonian viscosity at 230°, Ouano and Mercier[15] reported $\log \eta = -13.8 + 3.4 \log M_w$ and thus by eq 1 ($B = 760°$, $T_0 = 206$°K) and eq 3, we find $\log K = -11.8$.

3. Poly(α-methylstyrene). Fujimoto and coworkers[16] reported stress-relaxation measurements in the range 433–501°K ($T_g = 438$°K). From their WLF constants, $T_S = 477°$, $C_1 = 8.86$, and $C_2 = 101.6°$, we derive $T_0 = T_S - C_2 = 376$°K and $B = C_1C_2 = 900$°K. Thus, $E_0 = 4.1$ kcal/mol. From Table III of that work,[16] $\log \eta = 8.29$ at 459°K for $M_w = 39{,}400$, giving by eq 1 and 3, $\log K = -12.1$. At $T_g = 438$°K, we compute $\log \eta_g = 12$, which is close to the normal value of 13 for $M \leqq M_c$,[5] and $(T_g - T_0)/2.3B = 0.03$, in common with other vinyl polymers.[5,7]

Fujimoto and coworkers estimated $(\mathrm{DP})_c = 102$ for the weight average degree of polymerization at the "critical entanglement" point and noted agreement with a value reported for polystyrene. However, the work of Allen and Fox[8] shows $(\mathrm{DP})_c \simeq 300$ for a number of vinyl polymers, including polystyrene. On this basis it would appear that M_c should be about 35,000 for poly(α-methylstyrene).

4. Polydimethylsiloxane. The viscosities of a series of linear PDMS fluids were measured by Barlow and coworkers[17] between −50 and +50°. For M_w = 32,000, which corresponds to M_c, their WLF constants are $T_S = 303$, $C_1 = 1.9$, and $C_2 = 222$, giving $T_0 = T_S - C_2 = 81$°K, $B = C_1C_2 = 420$°K, and hence E_0 = 1.9 kcal/mol. For the range 5–160°, $E_T = 3.5$ kcal/mol, as the limiting high molecular weight value.[18] At a mean temperature of 80°, eq 2 gives $E_T = 3.2$ kcal/mol, in good agreement with the observed value. By eq 1 and 3, using isothermal η–M_w data,[17,18] we find $\log K = -11.0$ for PDMS.

Barlow and coworkers extrapolated the viscosities to $\log \eta_g = 13$ and found T_g = 110–114°K, noting that these values were appreciably lower than the reported $T_g = 150$°K.[19] Actually, $\log \eta_g = 13$ only for $M \leqq M_c$[5] but for the 350 cSt fluid ($M_w \simeq M_c \simeq 32{,}000$), the extrapolated viscosity still gives $T_g = 110$°K. This should be close to the limiting high molecular weight value, since other properties (density, E_T, and WLF constants) for this fluid have also attained their limiting values.[17,18]

The discrepancy can be explained on the basis that the calculated value, $T_g = 110$°K, refers to the completely amorphous polymer, while the experimental value, $T_g = 150$°K, was measured on a semicrystalline material.[19] Similarly, for polymethylene, the estimate for the ideally amorphous polymer is $T_g = 200$°K,[2] while the experimental value for a 40–50% crystalline sample was found to be $T_g = 250$°K.[20] There is ample evidence that the segmental mobility of the amorphous portion is restricted by the crystalline phase, thereby increasing T_g for semicrystalline polymers.[21]

As has already been noted for PDMS,[17] and applying also to polymethylene, the lower, "ideal" T_g values conform very well with the empirical rule for symmetrically substituted polymers, $T_g/T_m = 0.5$.

5. Other Vinyl Polymers. For linear polyethylene[2b] $T_0 = 160°$ and $B = 640$°K. The latter value, which is for kinematic viscosity, is corrected to absolute viscosity by the factor $E_T(\text{absolute})/E_T(\text{kinematic})$ = 1.05 calculated[2b] at 200°, giving $E_0 = 3.1$ kcal/mol. From the η–M–T relation (eq 3) of Tung[22] and eq 1 and 3 of the present work, we obtain $\log K = -10.2$.

Tung[22] reported $E_T = 14.6$ kcal/mol over a temperature range centering around 200° for branched (low-density) polyethylene. *Assuming* $T_0 = 160$°K, the same as for the linear polymer, $E_0 = 6.4$ kcal/mol by eq 2. By Tung's η–M–T eq 4 and the present eq 1 and 3, $\log K = -11.8$.

The limiting high molecular weight values of T_0 and B for polystyrene[5] and the log A relationship[7] have been reported. By eq 1 and 3, $\log K = -11.5$. Finally, the T_0, B, and log A values for high molecular weight polyisobutylene[6] lead to $\log K = -12.0$. The viscosity parameters are summarized in Table II.

Table II

Viscosity Parameters (Equations 1 and 3)

	T_0, °K	E_0, kcal/mol	Log K
Polyethylene (linear)	160	3.1	−10.2
Polyethylene (branched)	(160)	6.4	−11.8
Polypropylene	206	3.5	−11.8
Polyisobutylene	123	5.7	−12.0
Polystyrene	323	3.1	−11.5
Poly-α-methylstyrene	376	4.1	−12.1
Polydimethylsiloxane	81	1.9	−11.0

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Discussion

1. The Preexponential Term, K. According to eq 1 and 3, K must measure the "inherent viscosity" per main-chain bond after the major effect of chemical structure has been eliminated, *i.e.*, $B/(T - T_0) = 0$. Indeed, the variation in log K between the different polymers is relatively small. For three cases (PS, PIB, and PDMS) the values are about the same as for log ζ_0 listed in Table II of the Berry and Fox review.[9] Interestingly, linear polyethylene, which has the highest value of K, also has an abnormally *low* Z_c compared to the other vinyl polymers.[8]

For molecular weights below Z_c, the preexponential term in eq 1 is $\log A' = \log K' + a \log Z_w$. But at Z_c, $\log A = \log A'$ and hence $\log (K'/K) = (3.4 - a) \log Z_c$. Considering the earlier polystyrene data,[7] for example, $a = 1.1$, $Z_c = 670$, and thus $\log (K'/K) = 6.5$ or $\log K' = -5.0$. Very approximately, to the extent that $Z_c \simeq 600$ and $a \simeq 1$ for vinyl polymers,[8,9] $\log (K'/K) \simeq 6.7$. Since K' does not involve complicating "chain entanglements," it is probably a truer measure of the "inherent viscosity" per bond than K.

2. Energetics of Bond Rotation. Considering first the *isolated* polymer chain, we adopt the simple three-state rotational model, with the *trans* conformation as the ground state and two equivalent *gauche* conformations (g_- and g_+) at a higher energy, ϵ_0. We assume that viscous flow involves a reversible rotation of the main-chain bonds, $t \rightleftarrows g$, and define the potential barriers in the forward and reverse directions as V_0 and $V_0 - \epsilon_0$, respectively. Finally, it is assumed that the experimental E_0 is the arithmetic mean of the two barriers. Thus

$$E_0 = V_0 - \epsilon_0/2 \tag{4}$$

For the rotation of the central C–C bond in the isolated butane molecule (the first member of the *n*-paraffin series in which *gauche* conformations occur), Hoyland[23] calculated two closely agreeing sets of values and cited favorable comparisons with earlier estimates. He found, for example, $V_0 = 3.54$ and $\epsilon_0 = 0.82$ kcal/mol, which in eq 4 give $E_0 = 3.1$ kcal/mol, identical with the value found for the "isolated" polyethylene chain (Table II).

According to the Gibbs–DiMarzio theory,[2a] the *intra*molecular $t \rightarrow g$ flex energy is given by ϵ_0 (calories per mole) $\simeq 2RT_g$. (The constant 2 is consistent with $T_g = 200°\text{K}$ for $(CH_2)_\infty$[2] and the ϵ_0 value for butane.) In terms of the thermodynamic temperature, $T_0 = 160°\text{K}$ for $(CH_2)_\infty$,[2b] we have the relation

$$\epsilon_0 \simeq 2.5RT_0 \tag{5}$$

Table III lists E_0 from Tables I and II, ϵ_0 estimated by eq 5, and the intramolecular barrier, V_0, in the forward ($t \rightarrow g$) direction calculated by eq 4.

The effects of substituents on E_0 and V_0 differ somewhat, owing to differences in ϵ_0. While E_0 for PE and PS are the same, the phenyl substituent produces a 0.4-kcal increment in V_0. Both E_0 and V_0 are increased by about 1 kcal as the result of α-methyl substitution (PS → Pα-MS and PMA → PMMA). The introduction of a second methyl group (PP → PIB) has a much larger effect than the first (PE → PP). Also, a second methyl group produces a greater increment in both E_0 and V_0 than does a phenyl group (PIB *vs.* Pα-MS). Analysis of the polymethacrylates (Table I) by the same method shows the following regular trends between PMMA (atactic) and PHMA: $\epsilon_0 = 1.5$–0.9 and $V_0 = 6.2$–7.1 kcal/mol.

TABLE III
INTRAMOLECULAR ENERGETICS (KILOCALORIES PER MOLE) FOR BOND ROTATION

	E_0	ϵ_0	V_0
PE	3.1	0.80	3.5
PP	3.5	1.03	4.0
PIB	5.7	0.62	6.0
PS	3.1	1.61	3.9
Pα-MS	4.1	1.88	5.04
PMA	4.6	1.07	5.1
PMMA[a]	5.4	1.50	6.15
PVAc	4.4	1.24	5.0
PDMS	1.9	0.40	2.1

[a] Ideally atactic.

The rotational energetics discussed thus far are for the isolated polymer chain and hence are *intra*molecular. In the bulk polymer liquid, the flow activation energy, E_T, increases with decreasing temperature, according to eq 2. This behavior can be ascribed to the increasing *inter*molecular contribution to the rotational barriers. Following the same argument as for the isolated chain, E_T is taken to be the arithmetic mean of the barriers in the bulk polymer liquid, and if it is *assumed* that the intermolecular interactions produce the same relative enhancement in both directions, we have a relationship analogous to eq 4

$$E_T = V_T - \epsilon_T/2 \tag{6}$$

where V_T is barrier in the forward ($t \rightarrow g$) direction and ϵ_T is the $t \rightarrow g$ flex energy at temperature T. By eq 2, 4, 6

$$V_T = V_0(T/T - T_0)^2 \tag{7}$$

$$\epsilon_T = \epsilon_0(T/T - T_0)^2 \tag{8}$$

It may be noted that eq 8 behaves properly in the limits $\epsilon_T \rightarrow \epsilon_0$ as $T \rightarrow \infty$ (isolated chain) and $\epsilon_T \rightarrow \infty$ as $T \rightarrow T_0$. The latter is dictated by the requirement that the conformational entropy,[2] and hence the fraction of flexed bonds, must become zero at T_0. Obviously, the $(T/T - T_0)$ term to the *first* power would also give these same limiting values for ϵ_T.

On a molecular level, the rotation of a main-chain bond from its regular *trans* conformation to the more disordered *gauche* form requires additional volume and therefore work, ϵ', against the intermolecular cohesive forces, to produce this volume. Thus, for the bulk polymer liquid, the flex energy must contain both intra- and intermolecular contributions: $\epsilon_T = \epsilon_0 + \epsilon'$. Following an earlier argument, the temperature T_0 at which ϵ_T becomes infinite is governed by the relative magnitudes of ϵ_0 and ϵ', as well as the temperature dependence of the latter. This refutes a previous suggestion[24] that T_0 is determined solely by the cohesive energy of the polymer

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liquid, ϵ', in the present context. Also, it would seem that the temperature dependence of molecular conformations for the polymer liquid and for the "isolated" polymer chain (*i.e.*, in dilute solution under θ conditions) should be different, since the former depends upon ϵ_T and the latter upon ϵ_0.

Conclusions

The present work provides a further insight into the origin of the WLF "iso-free volume" at the glass transition.[25] By eq 1 and 3, at T_g, log η_g = log K + 3.4 log $Z + B/(T_g - T_0)$, applying at and above Z_c. But log $\eta_g = 13$ at Z_c[5] and for vinyl polymers, log $K \simeq -11.7$ (mean value from Table II) and approximately, $Z_c \simeq 600$.[8,9] Thus, $B/(T_g - T_0) \simeq 15$ and "ϕ_g/b" = $(T_g - T_0)/2.3B \simeq 0.029$, the WLF "free-volume." Even a ± 1 variation in the $B/(T_g - T_0)$ term, arising from a ± 1 variation in log K, produces only a ± 0.002 variation in "ϕ_g/b." In short, the WLF "iso-free volume" constant follows directly from purely kinetic (viscosity) considerations.

Simha and Boyer[26] derived a different "iso-free volume" at the glass transition based on $\Delta\alpha T_g \simeq 0.11$ and shown to be quite constant for a variety of vinyl polymers. However, their definition conflicts with another by which T_0, rather than 0°K, is the zero point for the "free-volume:" $\phi_g' = \Delta\alpha(T_g - T_0) \simeq 0.11 - \Delta\alpha T_0$. Certainly, the last term is not a constant for different vinyl polymers.

We conclude that for vinyl polymers, the Vogel viscosity equation (eq 1) applies and there is no need to invoke a 'hybrid" equation,[8] containing both Arrhenius and "free-volume" terms. Indeed, the "hybrid" equation leads to erratic and, in some cases, unreasonable values for the rotational barriers.[8]

Finally, we offer the following suggestions for extending the Vogel viscosity equation (eq 1) into the non-Newtonian region. Here, both the viscosity and E_T (determined at constant shear rate) decrease with increasing shear rate and approach a second Newtonian region.[27] By restricting the analysis to molecular weights somewhat below M_c, the added complication of "chain entanglements" could be avoided and the effect of shear rate on the rotational energetics (V_0, V_T, ϵ_0, ϵ_T) more readily isolated. High shear rates induce a change in molecular conformation toward a more extended form, as evidenced by (a) the normal stresses produced (*i.e.*, perpendicular to the shear direction) and (b) the "die-swell" effect, *i.e.*, the radical expansion of a polymer melt when rapidly extruded from a capillary die. This change in molecular conformation at the higher shear rates must undoubtedly be associated with a change in the rotational energetics from their normal values at zero shear rate.

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Internal Energy Contribution to the Elasticity of Natural Rubber

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ABSTRACT: It has recently been noted by a number of workers that the relative energy contribution, f_e/f, to the elastic stress of rubberlike materials appears to depend on the extension ratio at which thermoelastic measurements were carried out. This apparent strain dependence is in contradiction to the free energy additivity principle of the statistical theory of rubber elasticity. In this paper we resolve this problem by determining f_e/f from the temperature coefficient of shear moduli. The shear moduli were not directly determined from measurements of shear, but calculated from tensile elongation data. This method circumvents the difficulty encountered in directly obtaining the relative energy contribution from stress–temperature data. Both constant length and constant stress thermoelastic measurements were used to obtain f_e/f. A series of natural rubber samples, cross-linked in the presence of various amounts of *n*-hexadecane, were investigated. It is found that the relative energy contribution to the elasticity of natural rubber is 0.18. Changes in intermolecular interactions, brought about by the incorporation of diluents, produce no variation in the value of f_e/f. This observation supports the hypothesis that the energetic stress in rubber elasticity is wholly attributable to intrachain energies of the network chains.

The employment of thermoelastic studies has been instrumental in the development of a molecular interpretation of polymer behavior in the rubbery state. The observation that the stress–temperature coefficient of natural rubber is positive led to the postulate that the elastic force in this material is entropic in origin.[2] Earlier works tended to confirm this postulate, although the possibility that some of the force arose from internal energy change during deformation was considered.[3]

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