A Molecular Interpretation of the Vogel Equation for Polymer Liquid Mobility

A. A. Miller

1070 Hickory Road, Schenectady, New York 12309. Received March 23, 1978

ABSTRACT: In the Adam–Gibbs equation for polymer liquid mobility, $-\ln \mu = C/TS_c$, the S_c is specified as the conformational entropy, associated with rotational isomerization about main-chain bonds, rather than the configurational (excess) entropy as has been usually assumed. The S_c, calculated for a three-state rotational model with independent bond rotations, is shown to change continuously with temperature, vanishing only at 0 K. Hence it appears that there is no "Kauzmann paradox", confirming the earlier conclusions by Smith with respect to the excess thermodynamic properties. In the Vogel equation, $-\ln \mu = B/(T - T_0)$, B is shown to be closely related to the rotational barrier(s) E_0, while T_0 is determined by the energy difference U between the rotational states. The glass transition temperature can then be defined in terms of E_0 and U only. The relatively small pressure dependence of $U(T_0)$, demonstrated for one case (poly(vinyl acetate)), suggests that the conformational properties are dominated by the intramolecular energy.

The temperature dependence of polymer liquid mobilities, as manifested by Newtonian viscosity or the α process in dielectric relaxation, can be expressed by the well-known Vogel equation:[1–4]

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

Following the earlier Gibbs–DiMarzio concepts,[5] Adam and Gibbs[6] (A–G) developed a theory for the cooperative relaxation of polymer liquids, which when applied to mobility led to:

$$-\ln \mu = Z^*E_0/RT \tag{2}$$

where Z^* is the number of monomer segments which must simultaneously overcome the individual barriers, E_0, to their rearrangement. Equations 1 and 2 are equivalent if $Z^* = T/(T - T_0)$ and $E_0 = RB$.

The A–G theory further derived an expression for the critical size of the cooperative unit:

$$Z^* = S_c^*/S \tag{3}$$

in which S is the molar "configurational" entropy of the liquid and S_c^* is a constant related to the number of available configurational states. Substitution in eq 2 leads to:

$$-\ln \mu = C/TS \tag{4}$$

where $C = S_c^*E_0/R$, a constant for a given polymer liquid.

By combining eq 1 and 4 we obtain:

$$S = k(T - T_0)/T \tag{5}$$

and

$$k = S_c^* = C/B \tag{5a}$$

The A–G theory assumed that the Vogel T_0 is identical with T_2, a "second-order transition" temperature at which the configurational entropy became zero.[6,7]

By extrapolation of calorimetric and viscosity data from the lower n-alkanes it was shown[8] that for linear polyethylene (PE) indeed, $T_2 = T_0 = 160$ K, apparently the first direct confirmation of the Adam–Gibbs concepts for polymers. However, soon thereafter it was found[13] that eq 4 with S as the configurational entropy could not represent the viscosity of PE between T_g and T_M with a constant value of C. Furthermore, for some polymers, notably polystyrene, T_2 (calorimetric) $\ll T_0$ (Vogel).[9–12]

To resolve these discrepancies we suggested[11–13] that the quantity applying in eq 4 was not the configurational entropy but the conformational contribution, S_c, associated specifically with rotational isomerization about main-chain bonds.[14] This is presumably the major mode of local motion involved in the mobility of polymer liquids. Thus, T_0(Vogel) becomes the temperature at which S_c extrapolates to zero. Since calorimetric or volumetric measurements give no direct information on the conformational properties, these must be estimated via molecular statistical mechanics. The model and the appropriate equations are given in Appendix A.

Results

Conformational Entropy. S_c calculated by eq A3 (Appendix A) is shown as a function of U/RT in Figure 1. The linear portion between $U/RT = 0.75$ and 3.0 can be represented by the empirical equation:

$$S_c = 2.5 - 0.595(U/RT) \tag{6}$$

From the indicated intercept, $U/RT = 4.2$ at $S_c = 0$, we obtain:

$$U = 4.2RT_0 \tag{7}$$

Combining eq 6 and 7 leads to eq 5 but now the latter is restricted to the limits $T_0/T = 0.18$ to 0.75, since $U/RT = 4.2T_0/T$. In eq 5, $k = S_c^* = 2.5$. This value should be independent of the polymer or its p–v–T state.[15]

In Figure 1 the indicated linear extrapolation to $S_c = 0$, with S_c becoming negative at lower temperatures (higher U/RT), corresponds to the well-known "Kauzmann paradox" which is thus simply the result of an improper extrapolation through the low-temperature region which is experimentally inaccessible to the liquid. This can also be readily demonstrated by plotting S_c as a function of T itself (i.e., RT/U) rather than its reciprocal. On the basis of a modified Hirai–Eyring equation of state for polymer liquids, Smith[16] revealed a similar fallacy in the extrapolations of *excess* thermodynamic quantities leading to $\Delta S = 0$ at a T_2 and $\Delta H = \Delta V = 0$ at a lower temperature, T_3.[11,16]

In at least two cases eq 7 gives agreement with U values estimated from other measurements. Saunders and coworkers[17] analyzed the photoelastic properties of cross-linked polyethylene (130–250 °C) by the same three-state model with independent bond rotations and found $U = 1.15$ kcal/mol, citing 1.35 kcal/mol by the same analysis of other work. With $T_0 = 160$ K for PE,[8,12] eq 7 gives $U = 1.33$ kcal/mol. By polarized Raman scattering, which can measure changes in populations of trans and gauche bonds, Maxfield and Shepard[18] derived by eq A1, $U = 1.00$ ($\pm$ 0.14) kcal/mol (20–100 °C) for polydimethylsiloxane (PDMS). For this polymer we estimate (Appendix B) $T_0 \simeq 136$ K and thus by eq 7, $U = 1.13$ kcal/mol.

Effects of Structure on $U(T_0)$. Table I lists the structures and other pertinent data for ten vinyl-type

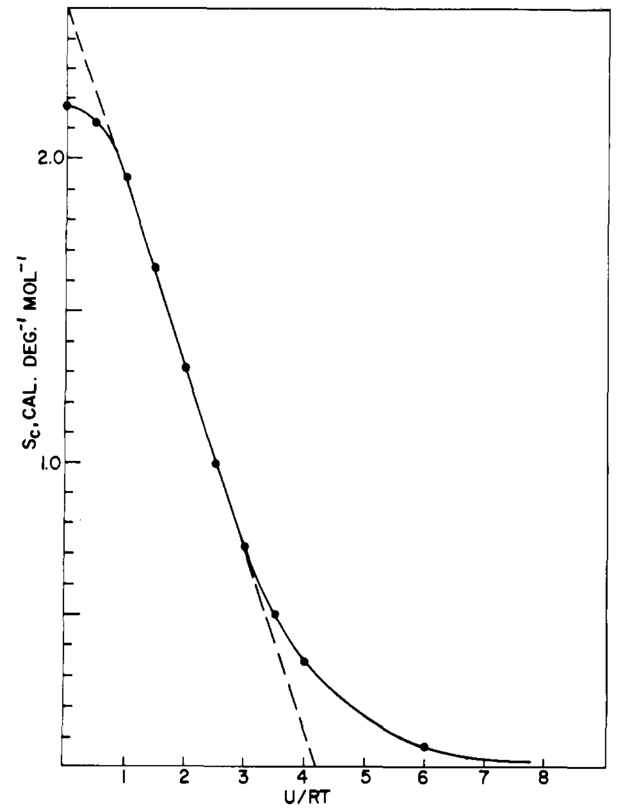

Figure 1. Conformational entropy for the three-state rotational model with independent bond rotations (eq A3).

Table I
Vogel T_0 and Derived U for Vinyl-Type Polymers

polymer	T_g, K	T_0, K	U, kcal/bond	4.2·T_0/T_g
PE, CH_2-CH_2	200[12,19]	160	1.33	3.36
PP, CH_2-$CH(CH_3)$	259[19]	206	1.72	3.34
PIB, CH_2-$C(CH_3)_2$	203[19]	123	1.03	2.54
PS, CH_2-CH(Ph)	371[19]	323	2.69	3.66
Pα-MS,[d] CH_2-$C(CH_3)$(Ph)	438[19]	376	3.14	3.60
PDMS, O-$Si(CH_3)_2$	150[a]	136	1.13	3.81
PPhMS, O-$Si(CH_3)$(Ph)	198[a]	183	1.53	3.88
PBD,[b] CH_2-CH=$CHCH_2$	161[20]	101	0.84	2.63
NR,[c] CH_2-$C(CH_3)$=$CHCH_2$	200[20]	146	1.22	3.07
PEO, CH_2-CH_2O	207[21]	180	1.19	3.65

[a] This work, Appendix B. [b] Cis/trans/vinyl = 96.5/1.9/1.6 (polybutadiene). [c] Natural rubber. [d] Poly(α-methylstyrene).

polymers, with U calculated by eq 7. It can be seen that while single methyl substitution (PE → PP) increases U, the *gem*-dimethyl grouping (PIB) causes a marked decrease, with about the same value for PDMS. The phenyl substituent in the two pairs, PE → PS and PP → PαMS, increases U by about the same amount, 1.4 kcal/mol.

In Table I the last column, which is equivalent to U/RT_g, shows that for these polymers Figure 1 deviates noticeably from linearity only near T_g. Thus by eq 4 and 5, no significant departure from Vogel behavior (eq 1) should be expected as the temperature is decreased down to T_g. Conversely, by this argument polymers with exceptionally high T_0/T_g ratios might show a noticeable deviation from Vogel behavior before T_g is reached; i.e., the true S_c would be greater than given by eq 5, making the actual mobility higher (eq 4) than predicted by the Vogel equation.

The Vogel B. By eq 1 and 2, B should be related to the barrier(s) to rotation about main-chain bonds: $E_0 = RB$.

Table II
Derived Rotational Barriers for Vinyl-Type Polymers

polymer	E_0,[a] kcal/mol	model	V_0, kcal/mol
PE	3.1	CH_3-CH_3	3.0[b]
		CH_3CH_2-CH_2CH_3	3.3-3.6[b]
PP	3.5	CH_3-$CH(CH_3)_2$	3.6-3.9[b]
PIB	5.7	CH_3-$C(CH_3)_3$	4.3[b]
PS	3.1, 2.9[c]	CH_3-$CH_2C_6H_5$	2.7[d]
		CH_3CH_2-C_6H_5	1.3[d]
Pα-MS	4.1		
PDMS	1.0	$(CH_3)_3$Si-$OSi(CH_3)_3$	~0[g]
PPhMS	1.0		
PBD	3.1, 2.8[e]	CH_3-CH=CH_2	1.98[f]
NR	4.1		
PEO	1.6		

[a] Same references as in Table I, unless otherwise specified. [b] Reference 22, Table 1, p 135. [c] D. J. Plazek, *J. Phys. Chem.*, **69**, 3480 (1965). [d] J. P. Lowe, *Prog. Phys. Org. Chem.*, **6**, 1 (1968). [e] Reference 3, Table II. [f] Reference 22, Table 1, p 52. [g] D. W. Scott et. al., *J. Phys. Chem.*, **65**, 1320 (1961).

Table III
Pressure Dependence of Vogel B and T_0 for Poly(vinyl acetate)[25]

P, bars	T_0, K	dT_0/dp, deg bar^{-1}	B, deg
0	248.0	0.0154	2183
200	251.2	0.0137	2246
400	253.8	0.0123	2311
600	256.1	0.0111	2380
800	258.2	0.0101	2448
1000	260.0	0.0092	2519

Table II compares E_0, for the same vinyl-type polymers as in the previous table, with the internal rotational barrier, V_0, for the indicated bond in some corresponding "model" molecules.

In general, E_0 closely parallels V_0. We note in particular that the introduction of a phenyl group (PE → PS) may actually produce a slight decrease in E_0 and V_0, in contrast to the effect of this substituent on U. The much lower V_0 for the rotation CH_3CH_2–C_6H_5 would correspond to a "nonconformational" rotation of the phenyl group in polystyrene. The E_0 for PS is consistent with the range 2.9–3.8 kcal/mol estimated indirectly from dilute solution studies.[23] Usually, α-methyl substitution in vinyl polymers increases E_0 by about 1 kcal/mol[19] while the *gem*-dimethyl grouping (PIB) produces by far the greatest increase. The lowering of V_0 for C–C rotation adjacent to a double bond, as evidenced by CH_3–CH=CH_2, may be partially obscured in PBD by rotations about the CH_2–CH_2 bonds between the repeating units, requiring a higher E_0. In contrast to PIB, the polysiloxane PDMS, in which hindrance has been relieved by the longer Si–O bond, has the lowest E_0. Substitution by phenyl (PPhMS), while it increases U, apparently has no effect on E_0 in polysiloxanes.

Effects of Pressure.[24] In eq A3 the only way that S_c can be changed isothermally is by allowing U to depend on pressure, which leads to eq A5. But by eq 7,

$$(\partial \ln U/\partial p)_T = (\partial \ln T_0/\partial p)_T \qquad (8)$$

We suggest that the pressure coefficient of T_0 reflects an *inter*molecular effect on U and since the two *gauche* states are considered equivalent in the model, the intermolecular energy can be included in U of the Boltzmann term (eq A1 and A2).

The pressure dependencies of the Vogel T_0 and B have already been derived[25] for one case, poly(vinyl acetate) (PVAc), with the results listed in Table III.

For this polymer U by eq 7 increases by only 5% between P_0 (atmospheric pressure) and P = 1000 bars, suggesting that even in the real polymer liquid U (and hence S_c) is dominated by the *intra*molecular rotational energy with only a minor perturbation by the p–v–T conditions. The rotational barrier $E_0(B)$ increases by 15% over the same pressure range.

The U and E_0 in Tables I and II have all been derived for the polymer liquids at P_0 and it is likely that these polymers will have differing pressure dependencies for both U and E_0 (i.e., $\mathrm{d}T_0/\mathrm{d}p$ and $\mathrm{d}B/\mathrm{d}p$). For a comparison of the strictly *intra*molecular contributions, characteristic of the "isolated" chains, the B and T_0 might be extrapolated by an appropriate method into the "negative pressure" region. This approach remains to be explored.

Mobility and the Glass Transition. By substituting $B = E_0/R$ and $T_0 = U/4.2R$ in the Vogel eq 1, we obtain for the mobility:

$$-\ln \mu = E_0/(RT - U/4.2) \qquad (9)$$

The glass transition is considered to be an isomobility state.[13,26] Indeed, it has been shown[25] that in the formation of PVAc glass at elevated pressures, the transition is characterized by a constant value of the Vogel term, $B/(T_g - T_0)$. This is the same as $2.3C_1{}^g$ in the W.L.F. context and the reciprocal is the well-known W.L.F. value, about 0.025 with some variation between different polymers.[20,27] Thus,

$$T_g = [U + (4.2/C_1{}^g)E_0]/4.2R \simeq (U + 0.1E_0)/4.2R \qquad (10)$$

The relative contributions of the thermodynamic U and the kinetic E_0 in determining the mobility and the T_g become apparent in eq 9 and 10.

By differentiating the Vogel term at T_g with respect to pressure we obtain:

$$\mathrm{d}T_g/\mathrm{d}p = \mathrm{d}T_0/\mathrm{d}p + [(T_g - T_0)/B]\,\mathrm{d}B/\mathrm{d}p \simeq (\mathrm{d}U/\mathrm{d}p + 0.1\,\mathrm{d}E_0/\mathrm{d}p)/4.2R \qquad (11)$$

Discussion

Any agreement between E_0 and V_0 in Table II is indeed unexpected as even a cursory examination of the rotational kinetics will show. For the *isolated* "model" molecule V_0 is the rotational barrier in the forward direction only (t→g,g′). But there is a barrier in the reverse direction (g,g′→t) which must be $V_0' = V_0 - U_0$ where U_0 is the t-g,g′ energy difference. It would appear that the experimental E_0 for the real polymer liquid should be somewhere between V_0 and V_0' but not necessarily coincide with V_0 itself. Two opposing factors may be involved here: (1) the E_0 for the real polymer liquid has already been increased by intermolecular interactions, as indicated in the earlier discussion on pressure effects; and (2) in viscous flow or dipole orientation the rotational barrier corresponding to V_0 may be lowered to an undetermined extent by the shear or electric fields.

With regard to U, more detailed models involving *inter*dependent bond rotations specify more than one rotational energy.[22] For example, in the case of linear polyethylene Tonelli[28] cites U_σ = 0.5–0.8 and U_ω = 1.5–2.0 kcal/mol. The simple three-state model with independent bond rotations gives an intermediate value, U = 1.33 kcal/mol, which is perhaps not surprising.

We have recently calculated[29] the volume and conformational contributions, S_v and S_c, to the entropy of fusion, ΔS_f, for polyethylene, polypropylene, poly(ethylene oxide), and polystyrene, using a volume-dependent $(\partial p/\partial T)_v$ in the thermodynamic identity: $(\partial S/\partial v)_T = (\partial p/\partial T)_v$ to determine S_v, and eq 5 for S_c. For these polymers S_v turns out to be 0.2 to 0.3 eu per main-chain bond higher than by previous estimates based on a volume-independent $(\partial p/\partial T)_v$, while S_c by eq 5 is correspondingly lower than by previous calculations for the isolated chains with interdependent bond rotations. Consequently, the agreement in $S_c + S_v = \Delta S_f$ at T_m is at least as good as by the earlier estimates.[30]

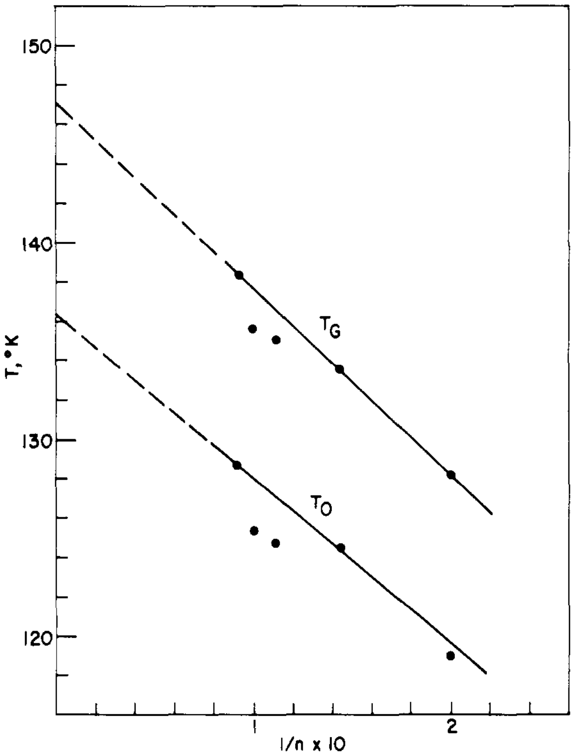

Figure 2. T_g and Vogel T_0 for dimethylsiloxane oligomers; n is the number of silicon atoms in the main chain.

Conclusions

The original Adam–Gibbs theory can be advanced closer to the experimental Vogel equation for polymer liquid mobility by using conformational entropy, associated with rotational isomerization about main-chain bonds, rather than configurational (excess) entropy. Both the configurational and the conformational properties have now been shown to vanish only at 0 K, thus dispelling the "Kauzmann paradoxes" and the need for any "second-order" thermodynamic transition temperature.

Our conceptual modification of the Adam–Gibbs theory has led to a molecular interpretation of the B and T_0 parameters in the Vogel equation and to new expressions for the glass transition temperature and the pressure dependence thereof.

The relatively small pressure dependence of $U(T_0)$, found for PVAc and attributed to intermolecular effects, suggests that the conformational properties are governed largely by the intramolecular energy even in the real polymer liquid.

Acknowledgment. We gratefully acknowledge support for this work by the National Science Foundation (Grant No. DMR76-20090, Polymers Program).

Appendix A. Rotational Properties

The simple three-state rotational model (i.e., a trans state and two equivalent gauche states at a higher energy U) with independent bond rotations will be adopted here. The ratio of gauche to trans bonds is given by:

$$g/t = 2e^{-U/RT} \qquad \text{(A1)}$$

and the rotational partition function is:

$$Q = (1 + 2e^{-U/RT}) \tag{A2}$$

Since $S_c/R = \ln Q + T\,(\partial \ln Q/\partial T)$, we have:

$$S_c = R \ln Q + (U/T)(Q - 1)/Q \tag{A3}$$

Also, for the conformational heat capacity:

$$C_{pc} = T(\partial S_c/\partial T)_p = R(U/RT)^2(Q - 1)/Q^2 \tag{A4}$$

From eq A3:

$$-(\partial S_c/\partial p)_T = (U/RT^2)(Q - 1)/Q^2\,(\partial U/\partial p)_T = C_{pc}\,(\partial \ln U/\partial p)_T \tag{A5}$$

Appendix B. Vogel Constants for Polysiloxanes

For polydimethylsiloxane (PDMS) the value of the Vogel term at the glass transition temperature, $B/(T_g - T_0)$, has been a long standing discrepancy in the polymer literature. For other vinyl-type polymers the reciprocal lies in the relatively narrow range 0.025 to 0.032, while for PDMS values of 0.071[20] and 0.085[31] are listed.

More recently, Barlow and Erginsav[32] reported the Vogel constants from viscosity measurements on five PDMS oligomers in the range $n = 5$ to 11 silicon atoms ($M = 384$ to 828). They calculated T_g by the Vogel equation on the basis that $\eta_g = 10^{13}$ P, a valid procedure[8] for molecular weights below M_c, the "critical entanglement" value. Figure 2 shows T_0 and T_g as a function of $1/n$. Despite some scatter, reasonable extrapolations to $1/n = 0$ can be made leading to $T_0 = 136$ K and $T_g = 147$ K, the latter being close to the accepted value (150 K) for the high polymer. The values for B were much too scattered to permit any extrapolation to the high polymer. However, in the region of room temperature, where $T \gg T_0$ and the viscosity shows Arrhenius behavior, the flow activation energy for the higher polymers (but still below M_c) is $E_T = 3.5$ kcal/mol.[33] Hence by the equation:

$$E_T = RB[T/(T - T_0)]^2$$

with $T = 298$ and $T_0 = 136$ K we obtain $B \simeq 530°$. Now $(T_g - T_0)/B = 0.026$ ($T_g = 150$ K), in harmony with other vinyl-type polymers.

The Vogel constants for a polyphenylmethylsiloxane (PPhMS), in which 25% of the methyls in PDMS had been replaced by phenyl groups, were determined by Kim[34] from viscosity measurements. The molecular weight was about 4000 ($n \simeq 45$) and well below M_c. The values reported were $T_0 = 182.9$ K and $B = 512.4°$. By the complete Vogel equation[34] and with $\eta_g = 10^{13}$ P we obtain $T_g = 198$ K, and thus $(T_g - T_0)/B = 0.029$, again within the range for other vinyl-type polymers.

References and Notes

(1) H. Vogel, *Phys. Z.*, **22**, 645 (1921).
(2) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).
(3) G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261 (1967).
(4) The pre-exponential constant μ_0, taken to be temperature and pressure independent, is included in μ.
(5) J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, **28**, 373, 807 (1958).
(6) G. Adam and J. H. Gibbs, *J. Chem. Phys.*, **43**, 139 (1965).
(7) J. M. Gordon, G. B. Rouse, J. H. Gibbs, and W. M. Risen, Jr., *J. Chem. Phys.*, **66**, 4971 (1977).
(8) A. A. Miller, *J. Polym. Sci., Part A-2*, **6**, 249 (1968).
(9) F. E. Karasz, H. E. Bair, and J. M. O'Reilly, *J. Phys. Chem.*, **69**, 2657 (1965).
(10) I. Abu-Isa and M. Dole, *J. Phys. Chem.*, **69**, 2668 (1965).
(11) A. A. Miller, *Macromolecules*, **3**, 674 (1970).
(12) A. A. Miller, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **18** (2), 485 (1977).
(13) A. A. Miller, *J. Chem. Phys.*, **49**, 1393 (1968).
(14) To avoid ambiguity we define "configurational" thermodynamic properties as the "excess" properties: $\Delta X = X(\text{liquid}) - X(\text{crystal})$, and designate the corresponding "conformational" properties as X_c.
(15) This follows from the original Adam–Gibbs[6] argument regarding S_c^* for their two-state "configurational" model.
(16) R. P. Smith, *J. Polym. Sci., Part A-2*, **8**, 1337 (1970).
(17) D. W. Saunders, D. R. Lightfoot, and D. A. Parsons, *J. Polym. Sci., Part A-2*, **6**, 1183 (1968).
(18) J. Maxfield and I. W. Shepard, *Chem. Phys. Lett.*, **19**, 541 (1973).
(19) A. A. Miller, *Macromolecules*, **2**, 355 (1969).
(20) J. D. Ferry, "Viscoelastic Properties of Polymers", 2nd ed., Wiley, New York, N.Y., 1970, Table 11-II.
(21) V. P. Privalko, Y. S. Lipatov, A. P. Lobodina, and V. F. Shumskii, *Polym. Sci.* USSR (*Engl. Transl.*), **16**, 3229 (1974).
(22) P. J. Flory, "Statistical Mechanics of Polymer Chains", Interscience, New York, N.Y., 1969.
(23) W. H. Stockmayer, *Pure Appl. Chem., Suppl.* **8**, (1973).
(24) For an alternate treatment of pressure effects, see E. A. Di Marzio, J. H. Gibbs, P. D. Fleming III, and I. C. Sanchez, *Macromolecules* **9**, 763 (1976).
(25) A. A. Miller, *Polymer*, in press.
(26) A. A. Miller, *Macromolecules*, **11**, 134 (1978).
(27) In the strictest sense, the glass transition is an isochronal state with a constant relaxation time, T. The relationship between T and mobility as defined here by the Vogel equation is beyond the scope of this work. See, for example, D. J. Plazek and V. M. O'Rourke in ref 31.
(28) A. E. Tonelli, *J. Chem. Phys.*, **53**, 4339 (1970).
(29) A. A. Miller, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **19** (2), in press.
(30) See B. Wunderlich and G. Czornyj, *Macromolecules*, **10**, 906 (1977), for a discussion of this problem with regard to polyethylene.
(31) D. J. Plazek and V. M. O'Rourke, *J. Polym. Sci., Part A-2*, **9**, 209 (1971), Table VI.
(32) A. J. Barlow and A. Erginsav, *J. Acoust. Soc. Am.*, **56**, 83 (1974).
(33) T. Kataoka and S. Ueda, *Polym. Lett.*, **4**, 317 (1966).
(34) M. G. Kim, *J. Chem. Soc., Faraday Trans. 2*, **71**, 426 (1975).