The spectral densities are obtained by Fourier transformation of either eq A10 or A11, and for eq A11 the results are

$$J_i = 2fK_i \sum_{k=1}^{s} \frac{A'\tau_{k0}}{1 + \omega_i^2\tau_{k0}^2} + \frac{B'\tau_{bk0}}{1 + \omega_i^2\tau_{bk0}^2} + \frac{C'\tau_{k0}}{1 + \omega_i^2\tau_{k0}^2}$$

$$\tau_{bk0}^{-1} = \tau_0^{-1} + \tau_k^{-1} + \tau_{ir}^{-1} \qquad \tau_{k0}^{-1} = \tau_0^{-1} + \tau_k^{-1}$$

$A' = (3 \cos^2 \Delta - 1)^2/4$; $B' = (3 \sin^2 2\Delta)/4$; $C' = (3 \sin^4 \Delta)/4$; $f = (3 \cos^2 \alpha - 1)^2/4 = 1/4$; $K_0 = 4/5$; $K_1 = 2/15$; $K_2 = 8/15$.

References and Notes

(1) A. Allerhand and R. K. Hailstone, *J. Chem. Phys.*, **56**, 3718 (1972).
(2) J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972).
(3) A. A. Jones, K. Matsuo, K. F. Kuhlmann, F. Geny, and W. H. Stockmayer, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **16**, 578 (1975).
(4) K. Matsuo, K. F. Kuhlmann, N. W.-H. Yang, W. H. Stockmayer, F. Geny, and A. A. Jones, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1347 (1977).
(5) G. Herman and G. Weil, *Macromolecules*, **8**, 171 (1975).
(6) W. P. Slichter and D. D. Davis, *Macromolecules*, **1**, 47 (1968).
(7) Y. Inoue, A. Nishioka, and R. Chujo, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 2237 (1973).
(8) F. Heatley, *Polymer*, **16**, 443 (1975).
(9) J. Spevacek and B. Schneider, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1789 (1976).
(10) A. E. Tonelli, *Macromolecules*, **5**, 558 (1972); **6**, 503 (1973).
(11) F. Laupretre and L. Monnerie, *Eur. Polym. J.*, **11**, 845 (1975).
(12) A. A. Jones and W. H. Stockmayer, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 847 (1977).
(13) G. C. Staffin and C. C. Price, *J. Am. Chem. Soc.*, **82**, 3632 (1960).
(14) J. M. Barrales-Rienda and D. C. Pepper, *J. Polym. Sci., Polym. Lett. Ed.*, **4**, 939 (1966).
(15) A. A. Brooks, J. D. Cutnell, E. O. Stejskal, and V. W. Weiss, *J. Chem. Phys.*, **49**, 1571 (1968).
(16) I. Solomon, *Phys. Rev.*, **99**, 559 (1955).
(17) L. G. Werbelow and A. G. Marshall, *J. Magn. Reson.*, **11**, 299 (1973).
(18) L. G. Werbelow and A. G. Marshall, *J. Am. Chem. Soc.*, **95**, 5132 (1973).
(19) L. G. Werbelow and D. M. Grant, *J. Chem. Phys.*, **63**, 544 (1975).
(20) L. G. Werbelow and D. M. Grant, *J. Chem. Phys.*, **63**, 4742 (1975).
(21) J. Riseman and J. G. Kirkwood, *J. Chem. Phys.*, **16**, 422 (1949).
(22) A. Isihara, *Adv. Polym. Sci.*, **5**, 531 (1968).
(23) A. A. Jones and W. H. Stockmayer, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15**, 16 (1974).
(24) A. A. Jones, W. H. Stockmayer, and R. J. Molinari, *J. Polym. Sci., Polym. Symp. Ed.*, **54**, 227 (1976).
(25) B. Valeur, J.-P. Jarry, F. Geny, and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 667 (1975).
(26) B. Valeur, L. Monnerie, and J.-P. Jarry, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 675 (1975).
(27) D. E. Woessner, *J. Chem. Phys.*, **36**, 1 (1962).
(28) A. A. Jones, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 863 (1977).
(29) R. Mattes and E. G. Rochow, *J. Polym. Sci., Part A-2*, **4**, 375 (1966).
(30) G. Allen, M. W. Coville, R. M. John, and R. F. Warren, *Polymer*, **11**, 490 (1970).
(31) A. G. Marshall, P. G. Schmidt, and B. D. Sykes, *Biochemistry*, **11**, 3875 (1972).
(32) J. Schaefer, *Macromolecules*, **6**, 882 (1974).
(33) R. P. Lubianez and A. A. Jones, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **17**, 138 (1976).
(34) D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, **56**, 3683 (1972).
(35) A. E. Tonelli, *Macromolecules*, **6**, 682 (1973).
(36) F. Laupretre and L. Monnerie, *Eur. Polym. J.*, **10**, 21 (1974).
(37) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **17**, 17 (1976).
(38) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **10**, 384 (1977).

Isomobility States in Polymer Liquids

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ABSTRACT: A new universal constant, $-10^4K = 17\ (\pm 1)$ cm^3/(g deg), where $K = (\partial v/\partial T)_\eta - (\partial v/\partial T)_p$ and $(\partial v/\partial T)_\eta$ is an isoviscosity volume term, is demonstrated for vinyl-type polymer liquids from Newtonian η-p-T measurements in the literature. For viscosity, this value of K applies only up to the critical "entanglement" molecular weight, M_c, but from dielectric relaxation data and dT_g/dp data at the glass transition the same K is found for higher molecular weights as well. Results for the n-alkane series suggest that a main chain of about 15 carbon atoms is the minimum length for a temperature-independent K. Below this, $-K$ increases with temperature. A single nonvinyl polymer examined (bisphenol A polycarbonate), containing rigid aromatic groups in the main chain, gives $-10^4K = 10$ cm^3/(g deg). Implications for predicting polymer liquid mobilities at constant temperature and at constant volume are presented. All of the results support the view that the glass transition is an isomobility state which cannot be rigorously defined by thermodynamics alone.

Despite much experimental and theoretical effort over the past two decades the molecular parameters governing mobilities of polymer liquids have yet to be elucidated.

To rigorously test existing theories, or to provide a sound basis for any new ones, requires extensive data on mobilities for a variety of chemical structures over a broad range of p-v-T conditions down to the glass transition. Toward this end the present work continues the development of new quantitative relationships for Newtonian viscosity, applying also to the more localized motion of the polymer chain as manifested by dielectric relaxation.

Considering Newtonian viscosity as a function of p, v, and T the following exact relationship was derived by partial differentiation:[1,2]

$$-K = (\partial \ln \eta/\partial T)_p(\partial v/\partial p)_T/(\partial \ln \eta/\partial p)_T \tag{1}$$

where

$$K = (\partial v/\partial T)_\eta - (\partial v/\partial T)_p \tag{2}$$

Since $(\partial \ln \eta/\partial p)_T/(\partial \ln \eta/\partial T)_p = -(\partial T/\partial p)_\eta$, substitution in eq 1 gives

$$K = (\partial v/\partial p)_T/(\partial T/\partial p)_\eta \tag{3}$$

For a number of vinyl-type polymers it was found[2] that not only was K insensitive to temperature but it appeared to be a "universal" constant for these liquids, i.e., $-10^4K = 17\ (\pm 1)$ cm^3/(g deg). With K as a parameter and with polystyrene (PS) as an example, relationships were reported for estimating viscosities at constant volume and at constant temperature.[3] The latter calculations gave pressure coefficients, $(\partial \ln \eta/\partial p)_T$, which were independent of pressure up to at least 1000 bars in agreement with experimental observations, indicating that the v_η lines are parallel, as depicted in Figure 1. Preliminary calculations[2] with reported values of dT_g/dp in eq 3 suggested that the v_g line, representing the volume at the glass transition for elevated temperatures and pressures, is also parallel to v_η.

At constant (atmospheric) pressure the temperature de-

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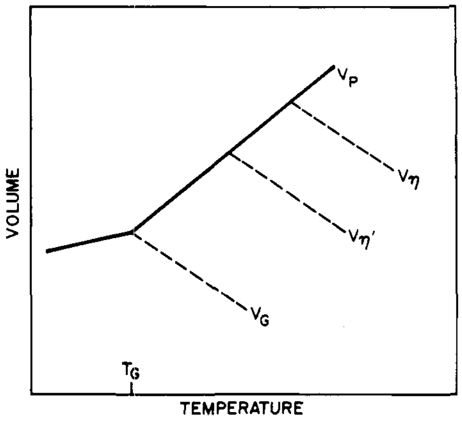

Figure 1. Generalized volume-temperature diagram. V_p is liquid volume at constant (atmospheric) pressure, V_η and $V_{\eta'}$ are isoviscosity volumes at viscosities η and η', and V_g is volume at the glass transition for elevated pressures.

Table I
Evaluation of *K* by Viscosity

	$10^3(\partial \ln \eta/\partial p)_T$, bar^{-1}	$-10^2(\partial \ln \eta/\partial T)_p$, deg^{-1}	$-10^4(\partial v/\partial p)_T$, cm^3/(g bar)	-10^4K, cm^3/(g deg)
PDMS (40 °C)	1.357[a]	1.798[b]	1.323[a]	17.5[c]
	1.295[a]	1.798[b]	1.291[a]	17.9[d]
PMMA[e] (155 °C)	4.10[f]	12.56[f]	0.525[g]	16.1

[a] E. Kuss and M. Taslimi, *Chem.-Ing.-Tech.*, **42,** 1073 (1970). [b] Equation 5b, $E = 3.5$ kcal/mol: T. Kataoka and S. Ueda, *Polym. Lett.*, **4,** 317 (1966). [c] $M = 8800$. [d] $M = 30\,500$. [e] $M_w = 13\,000$. [f] Reference 16. [g] O. Olabisi and R. Simha, *Macromolecules,* **8,** 206 (1975).

pendence of viscosity for vinyl polymers is best represented by the Vogel equation:[1,4-6]

$$\ln \eta = A + 2.3B/(T - T_0) \tag{4}$$

from which the temperature coefficient is:

$$(\partial \ln \eta/\partial T)_p = -2.3B/(T - T_0)^2 \tag{5a}$$

At high temperatures eq 4 approaches the Arrhenius form with a constant "activation energy" for viscous flow, E. Thus for this region,

$$(\partial \ln \eta/\partial T)_p = -E/RT^2 \tag{5b}$$

Equations 1-5 can also be applied to dielectric relaxation in the liquid by substituting $-\partial \ln f_{\max}$ for $\partial \ln \eta$, where $f_{\max}$ is the frequency at which the dielectric loss factor, ϵ'', goes through a maximum.

In this paper the universal character of K for vinyl-type polymers will be confirmed with a number of additional examples and contrasted with the value for a nonvinyl polymer. The effect of molecular weight and its distribution will be examined, with the linear alkane structure of very low and very high chain length as an example.

Results

Throughout this work, the initial compressibility is calculated by the Tait equation, $-(\partial v/\partial p)_T = cv/B$, with the Tait constants, c and B, from the literature as indicated in the references.

1. *K* by Viscosity. Table I lists the appropriate literature data from η-p-T measurements on poly(dimethylsiloxane) (PDMS) and poly(methyl methacrylate) (PMMA) with K calculated by eq 1.

2. *K* by Dielectric Relaxation. Table II gives the data from dielectric relaxation measurements on a high molecular weight poly(vinyl acetate) (PVAc) and data at 40 °C from measurements on poly(methyl acrylate) (PMA) with $M_w = 2 \times 10^6$.

Table II
***K* by Dielectric Relaxation**

t, °C	$-10^3(\partial \ln f_{\max}/\partial p)_T$, bar^{-1}	$(\partial \ln f_{\max}/\partial T)_p$, deg^{-1}	$-10^5 (\partial v/\partial p)_T$, cm^3/(g bar)	-10^4K, cm^3/(g deg)
PVAc 69.5	7.20[a]	0.244[b]	5.16[c]	17.5
79.5	6.30	0.200	5.38	17.1
89.5	5.98	0.166	5.61	15.6
	(5.6)[d]			(16.6)
98	5.23	0.144	5.81	16.0
	(5.0)[d]			(16.6)
108	4.52	0.123	6.05	16.5
118	4.07	0.107	6.31	16.5
PMA 40	5.91[e]	0.283[f]	3.80[g]	18.2

[a] J. M. O'Reilly, *J. Polym. Sci.*, **57,** 429 (1962), Figure 7. [b] By eq 5a, with $2.3B = 2183°$ and $T_0 = -25$ °C (ref 5). [c] S. Beret and J. M. Prausnitz, *Macromolecules,* **8,** 536 (1975). [d] Estimated from a smooth plot against temperature. [e] G. Williams, *Trans. Faraday Soc.*, **60,** 1556 (1964). [f] Equation 5b, $E = 55$ kcal/mol at 40 °C[e] [g] $(\mathrm{d}p/\mathrm{d}T)_v = 14.7$ bars/deg,[e] $10^4\, \mathrm{d}v/\mathrm{d}T = 5.6$ cm^3/(g deg).

Table III
***K* at the Glass Transition**

	T_g, °C	$\mathrm{d}T_g/\mathrm{d}p$, deg/bar	$-10^5(\partial v/\partial p)_T$, cm^3/g bar)	-10^4K, cm^3/(g deg)
PS	89	0.0305[a]	5.17[b]	16.9
PS	101	0.0316[c]	5.58[c]	17.6
PMMA	103	0.0234[a]	4.00[b]	17.1
PVC	76	0.0138[a]	2.84[b]	21.0 (?)
		0.0163[d]		17.4
Po-MS[e]	131	0.0342[c]	5.88[c]	17.2
PVAc	31	0.0235[f]	4.21[f]	17.9

[a] K. H. Hellwege, W. Knappe, and P. Lehman, *Kolloid Z. Z. Polym.*, **183,** 110 (1962), Table 6. [b] R. Simha, P. S. Wilson, and O. Olabisi, *ibid.*, **251,** 402 (1973). [c] A. Quach and R. Simha, *J. Appl. Phys.*, **42,** 4592 (1972). [d] A. Zosel, *Kolloid Z. Z. Polym.*, **199,** 113 (1964). [e] Poly(*o*-methylstyrene). [f] Reference 7, Figure 7, and Table 9a.

Table IV
***K* for *n*-Decane**

t, °C	$10^3(\partial \ln \eta/\partial p)_T$, bar^{-1}	$-10^2(\partial \ln \eta/\partial T)_p$, deg^{-1}	$-10^4(\partial v/\partial p)_T$, cm^3/(g bar)	-10^4K, cm^3/(g deg)
37.8	1.122[a]	1.322[b]	1.65[c]	19.5
71.1	1.068	1.078	2.16	21.8
104.4	1.078	0.896	2.94	24.4
137.8	1.144	0.756	4.22	27.9

[a] A. L. Lee and R. T. Ellington, *J. Chem. Eng. Data,* **10,** 346 (1965), Figure 2. [b] Equation 5b; η-T data from "Selected Properties of Hydrocarbons", Part I, A. P. I. Project 44 Carnegie Press, 1953, Table 20c. [c] M. S. Benson, P. S. Snyder, and J. Winnick, *J. Chem. Thermodyn.*, **3,** 891 (1971).

3. *K* at the Glass Transition. Numerous measurements at the glass transition permit the evaluation of K by exact equations of the form of eq 2 and 3, i.e., $K = \mathrm{d}V_g/\mathrm{d}T - (\partial v/\partial T)_p$ and $K = (\partial v/\partial p)_T/(\mathrm{d}T_g/\mathrm{d}p)$. These results are given in Table III.

By direct volume measurements on PVAc McKinney and Goldstein[7] found $10^4\, \mathrm{d}V_g/\mathrm{d}T = -10.8$ and $10^4(\mathrm{d}v/\mathrm{d}T) = 6.0$ giving $-10^4K = 16.8$ cm^3/(g deg). Similarly, volume measurements by Naoki and Nose[8] give -13.1 and 4.7, respec-

Table V
***K* for *n*-Pentane, Benzene, and Carbon Tetrachloride**

	t, °C	$10^3(\partial \ln \eta/\partial p)_T$, bar^{-1}	$-10^2(\partial \ln \eta/\partial T)_p$, deg^{-1}	$-10^4(\partial v/\partial p)_T$, cm^3/(g bar)	-10^4K, cm^3/(g deg)
n-C_5H_{12}	37.8	0.881[a]	9.70[b]	2.74[c]	30.2
	71.1	1.049	7.92	4.89	36.9
C_6H_6	30	0.813[d]	1.310[e]	1.16[d]	18.8
	75	0.890	0.996	1.79	20.0
CCl_4	30	0.974[d]	1.38[e]	0.709[d]	10.0
	75	1.00	1.05	1.103	11.6

[a] A. L. Lee and R. T. Ellington, *J. Chem. Eng. Data*, **10,** 101 (1965), Figure 1. [b] Equation 5b, η–T data at 100 psi (6.9 bars).[a] [c] $\Delta v/\Delta p$ for 100–200 psi interval.[a] [d] A. A. Miller, *J. Phys. Chem.*, **67,** 2809 (1963). [e] Equation 5b, η–T data from J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, 1950, pp 146 and 227.

Table VI
***K* for Linear Polyethylene (180 °C)**

Sample	$10^{-3} M_w$	M_w/M_n	$10^3(\partial \ln \eta/\partial p)_T$, bar^{-1}	$-10^2(\partial \ln \eta/\partial T)_p$, deg^{-1}	-10^4K, cm^3/(g deg)
1	62	5.2	0.892	1.87[a]	32.0
2	69	5.7	0.918	1.94	32.4
3	150	12.5	1.67	2.64	24.1
4	210	9.6	0.857	1.61	28.8
5	220	14.6	0.887	0.94	16.2
6	73	7.4	0.765	0.92	18.4
7	52	3.7	1.07	2.92	42.0
8	100	8.3	3.25	4.15	19.6
9	280	23.4	3.99	5.27	20.2

[a] Equation 5b at 180 °C; at this temperature $-10^5(dv/dp)_T$ = 15.3: O. Olabisi and R. Simha, *Macromolecules*, **8,** 206 (1975).

tively, leading to -10^4K = 17.8 cm^3/(g deg) for a chlorinated polyethylene.

4. Bisphenol A Polycarbonate. As an example of a nonvinyl polymer containing rigid automatic rings in the main chain, we present the results for this polycarbonate.

O'Reilly[9] reported dT_g/dp = 0.043°/bar (T_g = 150 °C) from dielectric measurements. With $-10^5(dv/dp)_T$ = 4.5 cm^3/(g bar) for the liquid at 150 °C[10] we find by eq 3, -10^4K = 10.4 cm^3/(g deg). By direct volume measurements on polycarbonate (M_w = 40 000), the results of Matsuoka and Ishida[11] give $10^4\, dV_g/dT$ = −5.4 and $10^4\, (dv/dT)$ = 4.9. Thus, -10^4K = 10.3 by eq 2, in agreement with the value derived by eq 3.

The η-p-T data of Cogswell and McGowan[12] lead to $10^3\,(\partial \ln \eta/\partial p)_T$ = 2.95 bars^{-1} at 237 °C and E = 27.4 kcal/mol for the range 237–297 °C. From a η–M relationship[13] at 302 °C we estimate $M_w \simeq$ 32 000 for this material. With $-10^5(dv/dp)_T$ = 5.4 cm^3/(g bar)[10] at 240 °C, we obtain -10^4K = 9.7 cm^3/(g deg) by eq 1 and 5b, agreeing with the value found above at the glass transition. Thus, while K for this polymer also appears to be relatively insensitive to temperature between T_g = 150 and 237 °C, it is significantly lower than the "universal" value for vinyl-type polymers.

5. Effect of Chain Length. Two normal alkanes, n-$C_{15}H_{32}$ and n-$C_{18}H_{38}$, gave[2] -10^4K = 17 cm^3/(g deg) (the "universal" value) in the temperature range 38 to 135 °C. It is of interest to examine the effect of decreasing chain length and to compare the results with two simple rigid molecules.

Table IV gives the data for n-$C_{10}H_{22}$ and Table V for n-C_5H_{12}, C_6H_6, and CCl_4. The K values for the n-alkanes are summarized in Figure 2.

It is seen that below about C_{15} there is a sharply increasing divergence with temperature, an effect which is undoubtedly due to the increasing proportion of methyl end groups. A chain length of about 15 carbons as the lower limit for a temperature-independent, universal value of K is consistent with results reported previously,[2] based on η-p-T data for very low molecular weight polyisobutylene (M = 440, ~16 main-chain carbon atoms). Here it was found, also, that -10^4K = 17 cm^3/(g deg), independent of temperature over the range −14 to +35 °C.

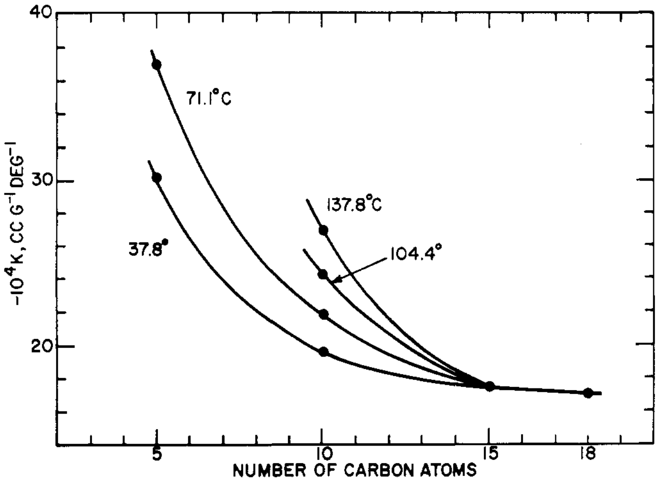

Figure 2. K as a function of the number of carbon atoms and temperature for normal alkanes.

With regard to the two simple molecules, C_6H_6 and CCl_4, in Table V it is noted that they have quite different values of K. Further η-p-T data are required to determine whether K for these two liquids is truly temperature independent.

6. Effects of High Molecular Weight and Dispersity. Figure 3 is a plot of the pressure coefficient of viscosity as a function of M_w for polystyrene at 165 °C from the measurements of Hellwege and co-workers.[14] The unexpectedly low value at the highest molecular weight (M_w = 267 000) previously mentioned[2] is now confirmed by two other independent studies.[12,15] It was suggested at the conclusion of the earlier work[2] that this effect may be caused by "entanglements" above a critical molecular weight, M_c, which for polystyrene is about 30 000 (log M_c = 4.48) at atmospheric pressure.[5]

For very high molecular weights the molecular weight dis-

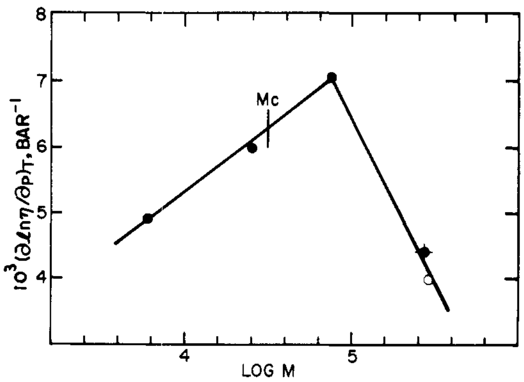

Figure 3. Pressure coefficient of viscosity for polystyrene at 165 °C: (●) Hellwege and co-workers,[14] (○) Raumsteiner[15] (+), Cogswell and McGowan.[12]

tribution also affects the viscosity pressure coefficient and hence the value of K. Table VI lists the K values computed by eq 1 for linear (high-density) polyethylene from the measurements of Christmann and Knappe.[16] All of the molecular weights are above M_c, which is reported to be about 4000.[5]

There is no obvious pattern in Table VI, except possibly for the limited correlation suggested by Christmann and Knappe that at about equal M_w (samples 1, 2, 6, and 7) the pressure coefficients (and K values) decrease as the molecular weight distribution, M_w/M_n, broadens. This applies also to samples 4 and 5 for K but not for the pressure coefficients.

Discussion and Conclusions

This and earlier papers[2,3] have demonstrated a new "universal" constant, $-10^4K = 17\ (\pm 1)\ \mathrm{cm^3/(g\ deg)}$, which applies to dielectric relaxation and to Newtonian viscosity of vinyl-type polymers of moderate molecular weight. Presumably, the same local motion (i.e., rotation about main-chain bonds) is involved in dipole orientation as in viscous flow. As seen in Figure 1, K is a measure of how much the liquid volume must be compressed to maintain an isomobility condition for a given increment of temperature. As listed previously[3] the range of $10^4(\partial v/\partial T)_p$ values extends from about 14 for n-$C_{15}H_{32}$ down to 4.0 for PVC.

By eq 1 the pressure coefficient of mobility can be predicted over a broad range of temperature down to T_g from the Vogel constants and compressibilities alone. Considering that for polymer liquids this pressure coefficient is independent of pressure up to at least 1000 bars, one can thus estimate the isothermal mobilities[3] as a function of pressure (or volume). Furthermore, it was shown earlier[3] that isochoric mobilities may be estimated from the Vogel constants and $(\mathrm{d}v/\mathrm{d}T)_p$ at zero pressure with K as a parameter. Thus the temperature and volume variables can be separated for these vinyl-type polymers with no new experimental measurements.

The single nonvinyl polymer, polycarbonate, reported here gave a K value that was significantly lower than the "universal" value. This may be related to the rigid aromatic groups in the main chain and suggests that other such structures (i.e., poly(ethylene terephthalate)) should be examined.

The results for polystyrene in Figure 3 indicate that M_c, the critical "entanglement" molecular weight, may increase with pressure, but further isothermal η–p measurements on the monodisperse polymer as a function of M_w are needed to test this. Such measurements might also provide an insight into the M_c phenomenon itself, as to whether it is the onset of "entanglements" or a transition from an extended chain to a folded chain conformation in the polymer liquid, as suggested recently by Privalko and Lipatov.[17]

In the present work, the glass transition has been approached via the properties of the liquid well above T_g and without invoking quasithermodynamic concepts involving properties of the glass itself. All of the present results are consistent with the idea that the glass transition is an isomobility state which cannot be rigorously defined by thermodynamics alone.[18]

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References and Notes

(1) A. A. Miller, *J. Polym.Sci., Part A-2*, **6**, 1161 (1968), Appendix.
(2) A. A. Miller, *Macromolecules*, **4**, 757 (1971).
(3) A. A. Miller, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15**, 412 (1974).
(4) H. Vogel, *Phys. Z*, **22**, 645 (1921).
(5) G. C. Berry and T. G. Fox, *Adv. Polym. Sci.* **5**, 261 (1967).
(6) A. A. Miller, *Macromolecules*, **2**, 355 (1969).
(7) J. E. McKinney and M. Goldstein, *J. Res. Natl. Bur. Stand., Ser A*, **78**, 331 (1974), Figure 4, Table 9a.
(8) M. Naoki and T. Nose, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1747 (1975), Table I, eq 14.
(9) J. M. O'Reilly, *J. Polym. Sci.*, **57**, 429 (1962), Table I.
(10) M. M. Martynuk and V. K. Semenchenko, *Colloid J. USSR (Engl. Transl.)*, **26**, 68 (1964), Figure 1.
(11) S. Matsuoka and Y. Ishida, *J. Polym. Sci., Part C*, **No. 14**, 247 (1966), Figure 2.
(12) F. N. Cogswell and J. C. McGowan, *Br. Polym. J.*, **4**, 183 (1972).
(13) G. F. Baumann and S. Steingiser, *J. Polym. Sci., Part A*, 3395 (1963).
(14) K. H. Hellwege, W. Knappe, F. Paul, and V. Semjenow, *Rheol. Acta*, **6**, 165 (1967).
(15) F. Raumsteiner, *Rheol. Acta*, **9**, 374 (1970).
(16) L. Christmann and W. Knappe, *Colloid Polym. Sci.*, **252**, 705 (1974).
(17) V. P. Privalko and Y. S. Lipatov, *Makromol. Chem.*, **175**, 641 (1974).
(18) A. A. Miller, *J. Chem. Phys.*, **49**, 1393 (1968).