variety of conditions. Films annealed in various organic solvents exhibited enhanced permeability relative to untreated membranes. They postulate that this enhancement is caused by formation of more open or coarser spherulitic structures as a result of recrystallization during annealing. However, the same explanation is inapplicable to the PBLG films, since the formation of spherulites has been reported to occur only in aged solutions of PBLG.

To check whether the enhanced permeability of the benzene cast films was due to lower density of this film relative to the film cast from methylene chloride, densities of the membranes were measured at 25°. It was found that the densities were identical, 1.265 g cm^{-3}. This finding eliminates the possibilities of the "voids" left behind by the benzene molecule during casting, since if that were the case, one would expect a lower density for this film.

X-Ray scattering diagrams were taken from a sandwich of thin films with the incident beam normal to the surface (Figure 5). Films cast from methylene chloride show a more ordered pattern than the films cast from benzene, and this could account, in part, for the lower permeation rate of the former films. It appears that the two different morphological structures are reflected in the different path lengths of diffusion and therefore in the values of diffusion constants.

Pressure Coefficients for Newtonian Viscosity of Polymeric Liquids[1]

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ABSTRACT: Mathematical relationships between Newtonian viscosity and equilibrium p–v–T properties are reviewed and applied to published η–p–T data on polymeric liquids. It is shown empirically that at constant (*i.e.*, atmospheric) pressure the ratio of the compressibility, βv, and the isoviscosity term, $(\partial T/\partial p)_\eta$, is quite insensitive to temperature over a broad range down to the glass-transition temperature, *i.e.*, $\beta v/(\partial T/\partial p)_\eta = K$. From this, the variation of the viscosity–pressure coefficient, $(\partial \ln \eta/\partial p)_T$, with temperature can be predicted. For seven nonpolar polymeric liquids for which experimental data are available, $-10^4K = 17(\pm 1)$ cm^3/(g deg), apparently a "universal" constant for such liquids.

Relatively few measurements of pressure effects on the Newtonian viscosity of polymeric liquids have been reported. Somewhat more data are available on the pressure dependence of the glass-transition temperature, T_g, measured by a number of techniques. This paper discusses relationships between effects of pressure on T_g and viscosity, leading to methods for predicting the pressure coefficient of viscosity at various temperatures.

Although these relationships are focused on viscosity, it will become apparent that they should apply equally well to other relaxation processes which involve segmental mobility of the main polymer chain, such as the α process in dielectric relaxation.

Thermodynamic Equations

The following are exact relationships between the variables viscosity, volume, pressure, and temperature.

$$(\partial \ln \eta/\partial T)_v = (\partial \ln \eta/\partial T)_p + \alpha_0\gamma \qquad (1)$$

where $\gamma = (\partial p/\partial T)_v$, the thermal pressure coefficient, and $\alpha_0 = (\partial \ln \eta/\partial p)_T$, the pressure coefficient of viscosity. (The latter symbol is attributed to Hellwege and coworkers[2] and is not to be confused with α, the thermal expansion coefficient). Since

$$\alpha_0 = -(\partial \ln \eta/\partial T)_p(\partial T/\partial p)_\eta \qquad (2)$$

eq 1 can be rearranged to

$$(\partial \ln \eta/\partial T)_v/(\partial \ln \eta/\partial T)_p = E_v/E_p = 1 - \gamma(\partial T/\partial p)_\eta \qquad (3)$$

in which E_v and E_p are the flow "activation energies" at constant volume and pressure, respectively. The "activation volume" is given by

$$\Delta V^* = RT\alpha_0 = -RT(\partial \ln \eta/\partial T)_p(\partial T/\partial p)_\eta \qquad (4)$$

The following equation, explicit in volume, has already been reported[3] in an altered form

$$[(\partial v/\partial T)_\eta - (\partial v/\partial T)_p] = (\partial v/\partial p)_T/(\partial T/\partial p)_\eta \qquad (5)$$

$$= (\partial \ln \eta/\partial T)_p/(\partial \ln \eta/\partial v)_T \qquad (5a)$$

Henceforth in this paper, the term in the brackets will be designated as K. It will be shown that for a given liquid at constant (*i.e.*, atmospheric) pressure, K appears to be independent of temperature.

The temperature dependence of liquid viscosity at atmospheric pressure may be expressed by the Vogel equation

$$\ln \eta = A + 2.3B/(T - T_0)$$

from which

$$(\partial \ln \eta/\partial T)_p = -2.3B/(T - T_0)^2 \qquad (6)$$

Substitution of eq 6 in eq 4 gives

$$\Delta V^* = 2.3RTB/(T - T_0)^2(\partial T/\partial p)_\eta \qquad (7)$$

The preceding equations do not invoke any molecular model for viscous flow or the glass transition. By comparing the Vogel and the Adam–Gibbs viscosity equations at T_g for linear vinyl polymers, it was shown[4] that Z_g^*, the "co-

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(1) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; see *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 12, 517 (1971).

(2) K. H. Hellwege, W. Knappe, F. Paul, and V. Semjenow, *Rheol. Acta*, 6, 165 (1967).

(3) A. A. Miller, *J. Polym. Sci., Part A-2*, 6, 1161 (1968).

(4) A. A. Miller, *J. Chem. Phys.*, 49, 1393 (1968).

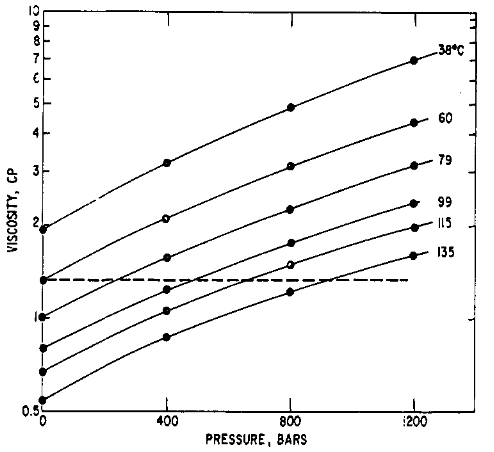

Figure 1. Viscosity-pressure isotherms for *n*-pentadecane; data of Hogenboom, *et al.*[5a]

operative unit" involved in segmental main-chain motion, is given by

$$Z_g^* = \Delta V_g^*/V_0 = T_g/(T_g - T_0) \qquad (8)$$

where V_0 is the "hard-core" volume of the repeating monomer unit. Combining eq 7 and 8 and rearranging, we obtain

$$(\partial T/\partial p)_\eta = \mathrm{d}\,T_g/\mathrm{d}p = (T_g - T_0)V_0/2.3RB \qquad (9)$$

which is identical with the empirical expression reported previously,[3] since "ϕ_g/b" = $(T_g - T_0)/2.3B$.

These relationships will now be applied to published viscosity and glass-transition data for two normal alkanes, polyisobutylene (PIB), polystyrene (PS), and other linear polymers.

Results

The η-p-T data of Hogenboom and coworkers[5a] for *n*-pentadecane and *n*-octadecane ($C_{15}H_{32}$ and $C_{18}H_{38}$) will be used. Figure 1 shows typical semilog plots of η-p isotherms for $C_{15}H_{32}$, up to 1200 bars of pressure in 400-bar increments. The broken horizontal line represents a constant viscosity. The intersections of such lines with each isotherm give the isoviscosity p-T conditions from which the isoviscosity volumes v_η can be calculated using the Tait equation with its appropriate constants.[5] The results for $C_{15}H_{32}$ are listed in Table I and displayed in Figure 2.

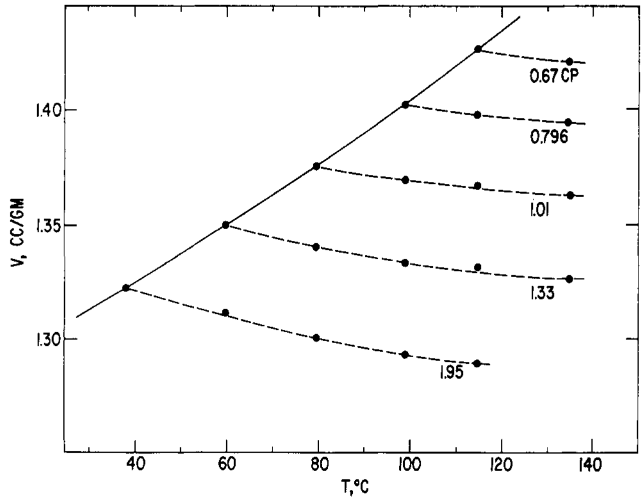

Figure 2. Isoviscosity volumes for *n*-pentadecane.

Table I

Isoviscosity p-v-T for $C_{15}H_{32}$

η, cP	Temp, °C	p, bars	v_η, cm^3/g
1.95	38	0	1.3224
	60	330	1.3114
	79	640	1.3003
	99	940	1.2925
	115	1180	1.2888
	135		
1.335	60	0	1.3499
	79	250	1.3403
	99	490	1.3334
	115	670	1.3317
	135	930	1.3258
1.01	79	0	1.3751
	99	200	1.3691
	115	360	1.3670
	135	570	1.3626
0.796	99	0	1.4015
	115	150	1.3982
	135	330	1.3947
0.67	115	0	1.4263
	135	170	1.4213

The changes in liquid volume, v, and in v_η near atmospheric pressure (*i.e.*, the first two temperatures for each viscosity in Table I) are given in Table II for the indicated temperature intervals. The numerical values of $(\partial v/\partial T)_\eta$ and $(\partial v/\partial T)_p$ change with temperature in opposite directions, but the difference, K, appears to remain constant.

The same conclusion can be derived from eq 5. The initial values of $(\partial T/\partial p)_\eta$ were calculated between $p = 0$ and the next higher η-p isotherm. The values of $(\partial v/\partial p)_T = \beta v$ were derived from the Tait equation at $p = 0$ and the lower temperature, as indicated in Table III. The last column shows agreement with the K values in Table II.

Allen and coworkers[6] reported η-p-T and γ measurements on a low molecular weight ($M_n \simeq 440$) sample of polyisobutylene. Interpolated values of γ, corresponding to the temperatures of the viscosity measurements, were derived from a smooth γ-T plot, and $(\partial T/\partial p)_\eta$ was calculated by eq 3. The v-T-M correlations of Fox and Loshaek[7] give $10^4(\mathrm{d}v/\mathrm{d}T)$

Table II

Evaluation of $K = (\partial v/\partial T)_\eta - (\partial v/\partial T)_p$[a]

Range, °C	$C_{15}H_{32}$ $(\partial v/\partial T)_p$	$(\partial v/\partial T)_\eta$	K	$C_{18}H_{38}$ $(\partial v/\partial T)_p$	$(\partial v/\partial T)_\eta$	K
36–60	12.4	−5.0	−17.4			
60–79	13.0	−5.0	−18.0	12.2	−5.3	−17.5
79–99	13.5	−3.1	−16.6	12.6	−3.1	−15.7
99–115	15.4	−2.1	−17.5	14.1	−2.7	−16.8
115–135	15.6	−2.0	−17.6	13.7	−3.3	−17.0
Mean			−17.4			−16.7

[a] All units 10^{-4} cm^3/(g deg).

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(5) (a) D. L. Hogenboom, W. Webb, and J. A. Dixon, *J. Chem. Phys.*, **46**, 2586 (1967); (b) W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Schiessler, *ibid.*, **29**, 727 (1958).

(6) G. Allen, G. Gee, H. A. Lanceley, and D. Mangaraj, *J. Polym. Sci.*, **34**, 349 (1959).

(7) T. G. Fox and S. Loshaek, *ibid.*, **15**, 371 (1955).

TABLE III
EVALUATION OF K BY EQ 5

iso-η, cP	Δt, °C	Δp, bars	$(\partial T/\partial p)_\eta$, deg/bar	$-10^5\beta v$, cm³/(g bar)	-10^4K, cm³/(g deg)
			n-Pentadecane		
1.95	22.2	330	0.067_5	12.0 (38)[a]	17.8
1.335	19.4	250	0.077_5	13.7 (60)	17.7
1.01	19.4	200	0.097	16.1 (79)	16.6
0.796	16.1	150	0.107	18.8 (99)	17.6
0.67	20.0	170	0.118	21.0 (115)	17.8
			K(mean) -17.5×10^{-4} cm³/(g deg)		
			n-Octadecane		
2.06	19.4	270	0.072	12.8 (60)[a]	17.8
1.48	19.4	210	0.093	14.5 (79)	15.6
1.15	16.1	160	0.100	16.6 (99)	16.6
0.94	20.0	180	0.111	18.8 (115)	17.0
			K(mean) -16.8×10^{-4} cm³/(g deg)		

[a] Numbers in parentheses represent temperature, °C.

TABLE IV
EVALUATION OF K FOR PIB (M_n = 440)

Temp, °C	E_v/E_p	γ, atm/deg	$(\partial T/\partial p)_\eta$, deg/atm	$-10^5\beta v$, cm³/(g atm)	-10^4K, cm³/(g deg)
−14	0.517	12.04	0.040	6.9	17.2
−10	0.520	11.84	0.040_5	7.0	17.3
−4	0.515	11.56	0.042	7.2	17.1
15	0.482	10.64	0.0486	7.8	16.0
25	0.465	10.16	0.0526	8.2	15.5
35	0.513	9.70	0.0502	8.6	17.0
45	0.626	9.22	0.0405	9.0	22.2 (?)
55	0.860	8.80	0.0159	9.4	59.3 (?)

TABLE V
VISCOSITY–PRESSURE COEFFICIENTS FOR POLYSTYRENE[a]

Temp, °C	$-10^5\beta v$,[b] cm³/(g bar)	$(\partial T/\partial p)_\eta$, deg/bar	$2.3B/(T-T_0)^2$, deg⁻¹	$10^3\alpha_0$, bar⁻¹ Calcd	Obsd[c]
89 (t_g)	5.2	0.031	0.690	21.4	
130	6.5	0.039	0.198	7.7	7.3
165	7.8_5	0.046_5	0.101	4.7	5.1
200	9.5	0.056_5	0.063	3.6	

[a] t_g = 89°, t_0 = 42°, $2.3B$ = 1530°, $M \simeq 9100$. [b] Reference 3. [c] Reference 2, *via* Figure 3.

= 8.3 cm³/(g deg). Taking this to be independent of temperature[7] over the range under consideration (−14 to 55°), we obtain $(\partial v/\partial p)_T = (\partial v/\partial T)_P/\gamma$, to be used in eq 5. The results are listed in Table IV. Excluding the data at 45 and 55°, where errors in the measured temperature and pressure dependences of viscosity were expected to be the greatest,[6] it is seen that K is quite constant, with a mean value of -16.7×10^{-4} cm³/(g deg), giving $10^4 (\partial v/\partial T)_\eta = -8.4$ cm³/(g deg).

The p–v–T data of Hellwege and coworkers[8] for a polystyrene liquid with t_g = 89° have been discussed.[3,9] From the Fox and Loshaek T_g–$1/M$ relation,[7] we estimate $M \simeq 9100$ for this sample.

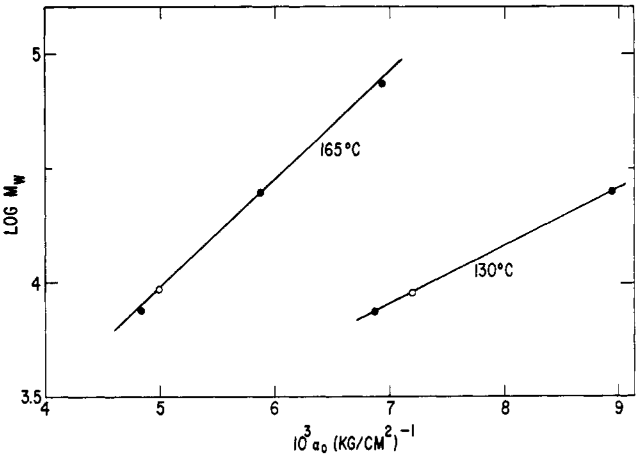

Figure 3. Viscosity–pressure coefficients for polystyrene: (●) measurements of Hellwege, *et al.*,[2] (○) interpolation for M = 9100.

Similarly, the Vogel parameters, B and T_0, for a series of polystyrene fractions[3] give linear plots with $1/M$, from which $2.3B$ = 1530° and t_0 = 42° for the fraction with t_g = 89°.

For this liquid, $10^4(\mathrm{d}v/\mathrm{d}T)$ = 5.5 cm³/(g deg)[3] and at t_g, γ = 10.6 bars/deg,[3,9] leading to $10^5\beta v$ = −5.2 cm³/(g bar). Since $(\partial T/\partial P)_\eta = \mathrm{d}T_g/\mathrm{d}p$ = 0.031 deg/bar,[3,9] we obtain, by eq 5, 10^4K = −16.8 cm³/(g deg). Taking K to be independent of temperature at constant (*i.e.*, atmospheric) pressure, we can calculate the viscosity–pressure coefficient, α_0, at any temperature by eq 5, 6, and 2, giving the values listed in Table V. Hellwege and coworkers[2] measured α_0 for several molecular weights of polystyrene. At constant temperature (165°), α_0 is almost linear in log M_w for the three lowest molecular weight samples, as shown in Figure 3. The values for M = 9100 (t_g = 89°) at 130 and 165° were obtained by the indicated interpolations.

By eq 7 at T_g, ΔV_g^* = 635 cm³/mol; with V_0 = 84 cm³/mol as the hard-core volume per repeating monomer unit,[3] we obtain $\Delta V_g^*/V_0$ = 7.6, agreeing with $T_g/(T_g - T_0)$ = 7.7 by eq 8.

Sufficient data at T_g are accessible for the estimate of K by eq 5 for a number of other polymer liquids. Eichinger and Flory[10] have reported p–v–T measurements on a polyisobutylene (PIB) of high molecular weight (M = 40,000)

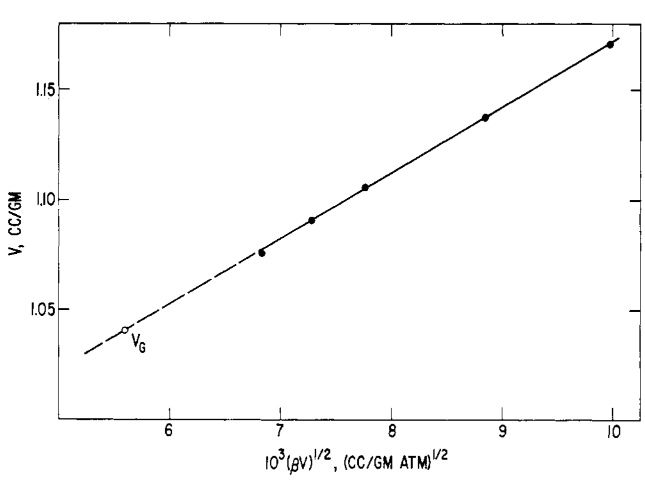

Figure 4. Extrapolated compressibility of polyisobutylene: (●) data of Eichinger and Flory.[10]

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(8) K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid-Z. Z. Polym.*, 183, 110 (1962).
(9) G. Gee, *Polymer*, 7, 177 (1966).
(10) B. E. Eichinger and P. J. Flory, *Macromolecules*, 1, 285 (1968).

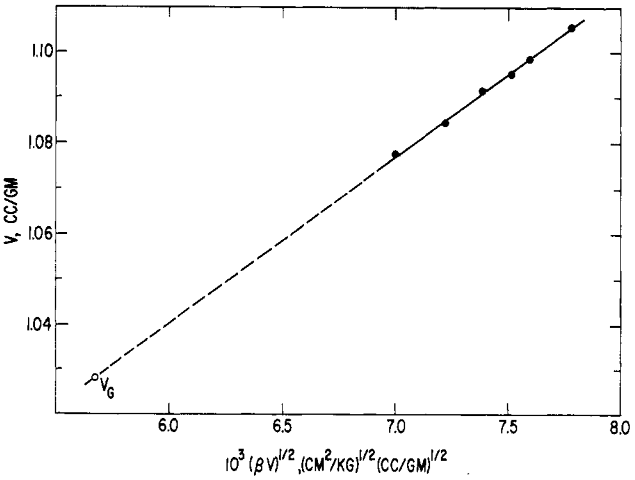

Figure 5. Extrapolated compressibility of natural rubber: (●) data of Wood and Martin.[11]

between 0 and 150°. Compressibilities were linearly extrapolated[3] as $(\beta v)^{1/2}$ *vs.* v to v_g (Figure 4), which, in turn, was estimated by a linear v–T extrapolation to T_g. The data of Wood and Martin[11] for unvulcanized natural rubber (NR) were treated similarly (Figure 5).

For PIB by eq 9, with $(T_g - T_0)/2.3B = 0.030$[12,13] and $V_0 = 55$ cm^3/mol,[14] we find $dT_g/dp = 0.020$ deg/atm. For NR, with $(T_g - T_0)/2.3B = 0.026$[13] and $V_0 = 55.5$ cm^3/mol,[14] $dT_g/dp = 0.018$ deg/atm. These computed dT_g/dp values are significantly lower than those previously reported in the literature, and the discrepancy will be explained later in the Discussion.

Table VI lists the results for PIB and NR, as well as for additional polymers for which the appropriate data at T_g are available directly from the literature: poly(vinyl acetate) (PVAc), poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA).

Considering the first three polymers in Tale VI, together with the two *n*-alkanes, the low molecular weight polyisobutylene, and the polystyrene discussed earlier, the K values fall within a narrow range: $-10^4K = 16$–18. It is difficult to judge, at this stage, whether or not the somewhat higher values for PMMA and PVC reflect a real trend due to increasing polarity.

The following summarizes the relationships for estimating the viscosity–pressure coefficient, α_0. By combining eq 2, 5, and 6, and substituting for K in terms of the parameters at T_g, we obtain for any temperature T

$$\alpha_0 = 2.3B/(T - T_0)^2(dT_g/dp)\beta v/(\beta v)_g \tag{10}$$

where $(\beta v)_g$ represents the compressibility of the liquid at the glass-transition temperature. Equation 10 differs from that given in the earlier work[3] by the factor $\beta v/(\beta v)_g$, which increases with temperature.

In terms of the expansion volume,[3] $v_E = v - v_0 = k(\beta v)^{1/2}$, so that $(\beta v)/(\beta v)_g = [(v - v_0)/(v_g - v_0)]^2$. For polymer liquids, v is linear in T over a broad temperature range.[3,4,7] To the extent that dv/dT is constant, $\beta v/(\beta v)_g = \gamma_g/\gamma$.

TABLE VI

EVALUATION OF K FOR MISCELLANEOUS POLYMERS

	PIB[a]	NR[a]	PVAc	PVC	PMMA
T_g, °K	210	200	298	348	370
v_g, cm^3/g	1.04	1.03	0.84[b]	0.73[d]	0.86[d]
$-10^5\beta$, atm^{-1}	3.0	3.1	4.0[b,c]	3.9[e]	5.1[e]
dT_g/dp, deg/atm	0.020	0.018	0.021[c]	0.014[e]	0.023[e]
-10^4K, cm^3/(g deg)	15.8	17.9	16.0	20.0	19.0

[a] See text. [b] G. Allen, D. Sims, and G. J. Wilson, *Polymer*, **2**, 375 (1961). [c] J. M. O'Reilly, *J. Polym. Sci.*, **57**, 429 (1962). [d] See ref 8. [e] See ref 9, Table 6.

If α_0 is known at one temperature T, α_0' at another temperature T' will be given by

$$\alpha_0'/\alpha_0 = [(T - T_0)/(T' - T_0)]^2(\beta v)'/\beta v \tag{11}$$

The Vogel viscosity equation approaches the Arrhenius form at high temperatures, *i.e.*, $T \gg T_0$. Hence, for the Arrhenius region, $T_0 = 0$ in eq 11. Also, by eq 2 and 5

$$\alpha_0 = (E_p/RT^2)\beta v/K \tag{12}$$

According to eq 3 and 5, to the extent that dv/dT and K are independent of temperature, the ratio E_v/E_p will likewise remain constant. However, for simpler liquids dv/dT increases with temperature (*cf.* $C_{15}H_{32}$ and $C_{18}H_{38}$ in Table II) and E_v/E_p will decrease accordingly.

Discussion

Since eq 5 is an exact thermodynamic relationship, it will apply to any equilibrium p–v–T condition for the liquid down to the glass transition. On the other hand, it is emphasized that the temperature independence of $K = (\partial v/\partial T)_\eta - (\partial v/\partial Y)_p$ is an empirical observation for which an exact thermodynamic proof is not apparent.

The term $(\partial T/\partial p)_\eta$ decreases with decreasing temperature according to $(\partial T/\partial p)_\eta = \beta v/K$, down to its minimum value at T_g. The magnitude of this change may be seen in Tables III–V. Obviously, to apply in eq 9 and 10, experimental measurements of dT_g/dp must be made at, or corrected to, T_g. For example, on the basis of measurements at higher temperatures (and methods involving high frequencies), the following values have been reported as "dT_g/dp" (deg/atm): 0.025[15] and 0.036[16] for polyisobutylene and 0.024 for natural rubber.[17] It is suggested tht dT_g/dp values derived by eq 9, and cited in Table VI, are more nearly the correct values for these two polymers.

While low molecular weight liquids show a continuous change in the pressure coefficient of viscosity, α_0, with pressure (*cf.* Figure 1), experimental measurements on polymer liquids indicate that α_0 is independent of pressure over a broad pressure range.[2,18] Hence, for these liquids, α_0 values calculated near atmospheric pressure by the methods described in this paper may be reasonably applied up to at least 1000 atm.

The effect of chain "entanglements" on α_0 for polymer liquids has not yet been explored. For polystyrene at zero

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(11) L. A. Wood and G. M. Martin, *J. Res. Nat. Bur. Stand., Sect A*, **68**, 259 (1964).

(12) A. A. Miller, *J. Polym. Sci. Part A*, **1**, 1865 (1963).

(13) J. D. Ferry, "Viscoelastic Properties of Polymers," 2nd ed, Wiley, New York, N. Y., 1970, Table 11-II. The value reported here (0.026) leads to $dT_g/dp = 0.018$.

(14) W. Blitz, "Raumchemie der festen Stoffe," Leopold Voss, Leipzig, 1934.

(15) A. W. Nolle and J. J. Billings, *J. Chem. Phys.*, **30**, 84 (1959); H. Singh and A. W. Nolle, *J. Appl. Phys.*, **30**, 337 (1959).

(16) J. E. Anderson, D. D. Davis, and W. P. Slichter, *Macromolecules*, **2**, 166 (1969).

(17) J. E. McKinney, H. V. Belcher, and R. S. Marvin, *Trans. Soc. Rheol.*, **4**, 347 (1960).

(18) P. W. Bridgman, *Proc. Amer. Soc. Arts Sci.*, **77**, 115 (1949).

pressure, the critical entanglement molecular weight is about 30,000.[19] In Figure 3 the measured α_0 values were for the range M_w = 7500–74000. However, for M_w = 267,000 (log M_w = 5.43), which corresponds to an average of about eight entanglements per molecule, $10^3\alpha_0 = 4.4$ bar^{-1} at 165°, completely out of line with the trend of α_0 values in Figure 3. If this single datum is correct, it has important implications regarding the dynamics of chain entanglement–disentanglement in viscous flow. Presumably, also, processes involving only short segments of the polymer chains (*i.e.*, volume or dielectric relaxation) should not be complicated by entanglements, and α_0 for such processes should show a monotonic change with molecular weight, as does T_g, for example.[7]

(19) G. C. Berry and T. G. Fox, *Advan. Polym. Sci.*, **5**, 261 (1967).

Dynamic Mechanical Properties of Transcrystalline Regions in Two Polyamides

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ABSTRACT: The influence of a surface transcrystalline region on the viscoelastic properties of nylon 6 and nylon 6-6 films was investigated. For thin films, an upper limit of E appears to exist when the thickness of the transcrystalline region equals the thickness of the entire film. The modulus of the transcrystalline region is higher than that of the bulk phase.

This work is a continuation of the study investigating the correlation between morphology and the physical characteristics of crystalline polymers. The earlier paper by Kwei, *et al.*,[1] reported on two polyolefins—high density polyethylene and isotactic polypropylene. The results established that oriented lamellae existed near the surfaces, and the viscoelastic properties of these polymer films are influenced by the relative amount of oriented surface region to the bulk phase.

The oriented surface structure which can be produced in crystalline polymers has been observed by many previous investigators.[2–6] It has also been noted that this phenomenon is highly dependent upon thermal history.[1–6] The application of proper cooling techniques during crystallization from the melt can induce the development of lamellae from nuclei to propagate normal to the polymer film surface. The result is an overall columnar surface alignment of spherulite sectors or transcrystalline region that has been observed in polyamides,[2,3] polyurethanes,[2] and polyolefins.[1,4–6] The purpose of this study is to describe an evaluation of the mechanical properties of the oriented surface regions of two polyamides—nylon 6 and nylon 6-6.

Experimental Section

Materials. Unmodified nylon 6 and nylon 6-6 were used. The nylon 6, Du Pont Zytel Type 211, was used from a newly opened air-tight container. The nylon 6-6, Du Pont Zytel Type 101, was oven dried for 4 days at 60° before compression molding.

Film Preparation. Polymer films were prepared by compression molding between two sheets of copper which had been oxidized in an oven for 7 min at 350°. The weak cohesive properties of the resulting copper oxide facilitated the removal of the polymer film from the copper substrate. Any residual copper oxide which adhered to the surface of the film was easily removed by a dilute solution of hydrochloric acid. This method of film preparation was useful for avoiding possible film distortion during the peeling process.

A second method for preparing compression-molded polymer films was also used. It was found that molding between two sheets of 0.003-in. thick, hard aluminum also gave easy release characteristics. Inspection showed that peeling of the aluminum substrate from the polymer film had little or no damaging effect on the morphology pattern of the film. Because of the relative ease with which compression molded films could be prepared, this method was ultimately used throughout the remainder of the program.

Thermal History. Nylon 6 was compression molded by keeping it in the melt state at 250° for 2 min. The film–substrate assembly was removed, while hot, from the press and cooled in air to room temperature. Nylon 6-6 was treated in the same manner except the melt temperature was at 300° prior to crystallization. All film specimens were tested immediately after preconditioning for a minimum of 16 hr at 23° and 50% relative humidity.

Dynamic Modulus. The dynamic Young's modulus E was measured by the use of the Vibron dynamic viscoelastometer, Model DDV-II, of Toyo Measuring Instrument Co. The description of the instrument was given by Takayanagi.[7] In the present study, all the experiments were carried out at 23° and a frequency of 110 Hz.

Results

Figure 1 is a photomicrograph of a transverse microtome section cut from a 7-mil thick nylon 6 film. The thickness of each oriented surface is estimated to be 1.2 mils. The combined surface thickness constitutes roughly 33% of the total film thickness. Films used in this study were prepared with the transcrystalline zone thickness relatively constant regardless of the film thickness.

The dynamic Young's modulus (E) of both polyamides was found to decrease with increasing thickness (t), as shown in Figure 2. A projected extension of the curves in Figure 2

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