Compressional Effects in the Capillary Flow
of Polycarbonate

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Synopsis

Recently, the characteristics for pressure corrections in capillary flow have been detailed. The apparent viscosity increases with increasing capillary shear rate for polystyrene and for poly(methyl methacrylate) have been previously explained using free volume theory. These general methods have been developed further in this work and applied to the non-Newtonian flow of a new system, the polycarbonate of bisphenol A. The pressure correction for up to 2 kilobars will be shown to linearize the capillary pressure drop versus the parameter L/D, capillary length over diameter. This correction eliminates the viscosity difference due to variations in L/D ratio. It is also observed that the zero-shear viscosity obtained by the extrapolation of the corrected capillary flow curves agrees well with new and independent data on the same polycarbonate obtained using a Weissenberg rheogoniometer. The flow data have been compared with theories and with earlier published data on the same polymer. The two sets of data are not concordant. These new and corrected shear-dependent data are, however, shown to be expressed qualitatively by the theory of Graessley, using the most probable molecular weight distribution.

INTRODUCTION

Pressure effects can be important in the capillary flow of polymer melts. Free volume is certainly decreased by the hydrostatic pressures used to achieve polymer extrusion.[1-5] The apparent viscosity can thus *increase* with increasing shear rate in the pressure extrusion of amorphous polymer. Such features have now been detailed in this laboratory for several polymers. Prior studies, however, have not been reported for the polycarbonate of bisphenol A, even though it is an engineering plastic of growing importance and a material commonly processed under pressure. Related studies on this polycarbonate have been published[6] and will be correlated with this new study where appropriate.

In this paper, we have evaluated possible compressional effects in the flow of a new system, the polycarbonate of bisphenol A. The plan is to relate shifts of free volume and T_g to the apparent viscosity change with pressure, using the well-known WLF equation which has foundation in free

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volume theory. In previous work, it has been shown that possible changes in T_g, caused by shifts with time, frequency, or shear rate, are not governing features in the pressure extrusion of poly(methyl methacrylate)[1] and polystyrene.[2,3] It is rather pressure effects on free volume that are controlling. This is consistent with results which show that the rheology is most affected as test temperature is lowered toward T_g.[3]

These concepts are herewith tested for rheological data developed in this paper for polycarbonate. It has been noted that the empirical WLF expression[7] is a consequence of the Doolittle's equation

$$\log a_t = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \tag{1}$$

where T, T_g = experimental and glass transition temperatures; C_1, C_2 = constants for a given polymer at constant pressure; and a_t = the shift factor.

The following relationship represents a good approximation:

$$\log a_t = \log \frac{\eta_0 T_g \rho_g}{\eta_g T \rho} \simeq \log \frac{\eta_0}{\eta_g} \tag{2}$$

where η_0 = Newtonian viscosity at T; η_g = viscosity at T_g; ρ, ρ_g = polymer density at T and T_g. Then

$$\log \eta_0/\eta_g = \frac{-C_1(T - T_g)}{C_2 + T - T_g}. \tag{3}$$

Ishida and Matsuoka[8] and O'Reilly[9] obtained a linear relationship between pressure and the glass transition for polycarbonate as given by the following empirical equation:

$$T_g = T_{g0} + A_1 p \tag{4}$$

where T_g, T_{g0} = glass transition temperatures at pressure p and atmospheric pressure; and A_1 = constant independent of pressure. Both papers[8,9] present almost the same values of A_1 and T_{g0}, 0.04°C/atm and 143–145°C, respectively.

From eqs. (3) and (4), we have previously shown that viscosity changes with pressure can be expressed as

$$\eta_0 = \eta_g \exp \left[2.303 \frac{A_2 + A_3 p}{A_4 - A_1 p} \right] \tag{5}$$

where $A_2 = -C_1(T - T_{g0})$, $A_3 = C_1 A_1$, and $A_4 = C_2 + T - T_{g0}$.[3]

Equation (5) is strictly appropriate only for nonshear thinning. The success of this equation involves the apparently quantitatively separable effects of free volume and entanglement on viscosity. A treatment for the entanglement contribution to shear rheology has been developed by Bueche[10] and by Graessley.[11] They involve a general expression for shear thinning,

$$\eta = \eta_0 \cdot f(\dot{\gamma}\lambda) \tag{6}$$

where η = apparent viscosity, $\dot{\gamma}$ = shear rate, and λ = characteristic relaxation time, given as

$$\lambda = (12M/\pi^2\rho RT)\eta_0 \tag{7}$$

where M = molecular weight and R = gas constant. Equations (5), (6), and (7) may thus be combined to provide general expressions for the entanglement and pressure effects in polymer flow.

Any pressure effect on η_0 changes the relaxation time λ; but since the value of $12M/\pi^2\rho RT$ in this study is apparently small ($<2.5 \times 10^{-6}$), the change of entanglement relaxation time caused by pressure is negligible, compared to that of η_0, which means:

$$\eta(p + \Delta p) \simeq \eta_0(p + \Delta p) f(\dot{\gamma}\lambda). \tag{8}$$

It is possible that λ may change in proportion to the pressure-induced change in η.

The momentum equation in the capillary flow using cylindrical coordinates (y,o,z) is represented as

$$\rho \frac{D\bar{V}}{Dt} = -\nabla p - [\nabla \cdot \bar{\tau}] - p\bar{g} \tag{9}$$

where D/Dt is the material derivative; $\bar{V}$ is the velocity field; $\bar{\tau}$ is the stress tensor; and $\bar{g}$ is the gravitational field. The components of eq. (9) reduce to

$$\frac{\partial p}{\partial z} - \frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rz}) = 0. \tag{10}$$

The constitutive equation, also using cylindrical coordinates, is

$$\tau_{rz} = \eta \frac{\partial V_z}{\partial r}. \tag{11}$$

The substitution of eqs. (5), (8), and (11) into eq. (10) gives

$$(1/\eta_0) \exp\left[-2.303 \frac{A_2 + A_3p}{A_4 - A_1p}\right] \frac{\partial p}{\partial z} = c = \frac{1}{r}\frac{\partial}{\partial r}\left[\gamma f(\dot{\gamma}\lambda) \frac{\partial V_z}{\partial r}\right]. \tag{12}$$

The left-hand (top) side of eq. (12), on letting $x = 2.303 A_3/A_1 + A_2 + A_3p/A_4 - A_1p$, and considering atmospheric pressure to be the reference and the pressure drop to be Δp measured from $z = 0$, in order to set the c value, gives

$$z/L = 1 - \int_{x_0}^{x} \frac{e^x}{x^2}\,dx \bigg/ \int_{x_0}^{x_{\Delta p}} \frac{e^x}{x^2}\,dx \tag{13}$$

where x_0 = the value of x at zero pressure; $x_{\Delta p}$ = the value of x at pressure Δp; and L is capillary length.

The numerical integration of eq. (13) gives the axial pressure distribution in a capillary and also the average pressure as

$$\bar{p} = \int_0^1 p \frac{dz}{L}. \tag{14}$$

From eqs. (5), (8), and (14), the general equation is obtained for expressing both pressure and shear effects on polymer viscosity:

$$\eta_{0p} = \frac{\eta_0 \exp\left[2.303 \dfrac{A_2}{A_4}\right] f(\dot{\gamma}\lambda)}{\eta_0 \exp\left[2.303 \dfrac{A_2 + A_3\bar{p}}{A_4 - A_1\bar{p}}\right] f(\dot{\gamma}\lambda)} = \eta_p \exp\left[2.303 \frac{A_2}{A_4} - \frac{A_2 + A_3\bar{p}}{A_4 - A_1\bar{p}}\right]$$

(15)

where η_{0p} = viscosity at atmospheric pressure and η_p = viscosity at pressure p.

An alternate procedure would be to determine a pressure coefficient b experimentally and use the general empirical eq. (16) instead of eq. (5):

$$\eta = \eta_0 \exp(bp)$$

(16)

to correct for the viscosity increases. That is, the Penwell-Porter equation may or may not agree with η–p data, even at low pressure. Equation (16), however, with an experimental b would likely agree at low pressure, particularly if log η versus p is linear as is common at low pressure.

EXPERIMENTAL

Polymer

The sample investigated in this study is a bisphenol A polycarbonate (Lexan 141 obtained from General Electric Company). It was dried in the manner of Baumann and Steingiser.[6] When using the Weissenberg rheogoniometer, sheets were pressed from pellets and subsequently dried before insertion into the Rheogoniometer. The weight-average molecular weight of the sample was determined from viscosity data as part of this study. The molecular weight distribution in terms of weight-to-number average molecular weight is estimated indirectly here from rheology to be consistent with direct measurements on polymers from the same composition and series to be 2.4–3.0.

Capillary Measurements

In the study of pressure effect on viscosity, an Instron capillary rheometer (Type MCR) was used with a series of tungsten carbide capillaries described in Table I.

The data of O'Reilly, Karasz, and Bair[12] indicate the existence of a crystallization temperature of 230°C for this polycarbonate composition. The T_g may be near 150°C. The test temperatures were therefore 250°, 270°, and 290°C in order to avoid crystallization due to pressure. Among possible capillary corrections, the kinetic energy and the pressure losses were negligible for conditions used here, except for the capillary with an L/D of 4.27.

TABLE I
Dimensions of Tungsten Carbide Capillaries Used in the Instron Rheometer
for Studies of Pressure on the Flow of Polycarbonate[a]

Capillary diameter $\times 10^{-2}$, in.	Capillary ratio, length/diameter (L/D)
6.040	4.27
2.000	12.2
2.000	19.8
3.020	30.5
6.040	33.1
5.035	39.0

[a] All 90° entrance angle.

The Bagley corrections and the Rabinowich correction were applied, before and after pressure correction, respectively. Checks were also made to ensure that sufficient time was allowed for thermal and stress equilibrium. Checks of viscosity before and after pressure application confirmed polymer stability during the tests.[13-18]

Cone-and-Plate Measurements

For steady-shear viscosity measurement in the absence of pressure, a Weissenberg rheogoniometer (Model R-17) was used with a cone-and-plate diameter of 2.5 cm and a 4° cone angle. Test temperatures were 230°, 240°, 250°, 260°, and 270°C. The short time required for thermal equilibrium caused no appreciable sample degradation.

RESULTS AND DISCUSSION

Pressure Effects on Polymer Flow

The original capillary flow data are shown in Figure 1. They show that viscosities uncorrected for pressure can show an apparent viscosity *increase* with increasing shear (pressure).

The rheology of polycarbonate is generally expressed here in terms of correlations developed by Bagley. Figure 2 shows a Bagley plot at 250°C (pressure versus ratios of capillary L/D) after the elastic end correction has been made. Nonlinearity is evident especially at higher values of L/D, which is the direct result of pressure effects on apparent viscosity.[1-3] As expected for such effects, similar results with less pronounced curvature were obtained at 270° and 290°C. At the capillary exit, the capillary wall temperature rise due to viscous dissipation was calculated to be less than 4°C under all conditions used here. The Bagley correction was made on these data in the way described, by Penwell and Porter.[1-3] The end correction coefficient ν, defined as

$$\tau_R = \Delta p / 4(L/D + \nu)$$

where τ_R = corrected shear stress and Δp = total pressure drop, was less than 6.0 under all shear rates and temperatures used here. The extrudate
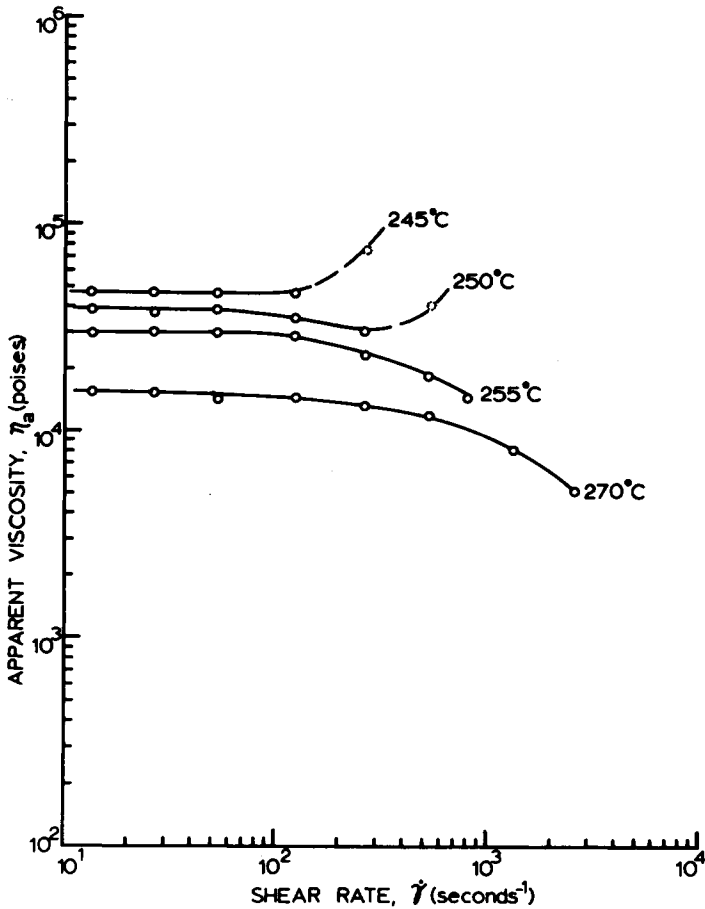
Fig. 1. Pressure effect on the capillary flow of polycarbonate.

expansion observed for this polymer was generally less than 10%, slightly exceeding this value at the highest shear rate and at the lowest test temperature, 250°C.

The L/D ratios where Bagley plots become nonlinear are plausibly a function of both temperature and shear rate. The lower the temperature and higher the shear rate, the lower the L/D where nonlinearity is observed.[2]

Figure 3 shows the viscosity curves obtained after the Bagley corrections for the several capillaries and test temperatures. The displacement of viscosity curves at the same temperature for different capillaries can be seen. This feature again is the result of a pressure-dependent viscosity. As expected, the lower temperatures and the higher L/D ratios yield the higher pressure dependence.

Using our equations, the axial pressure distributions were computed for several capillaries at a temperature of 250°C and a shear rate of 3.0×10^2 sec^{-1}. These are shown in Figure 4. The average drop deviates from
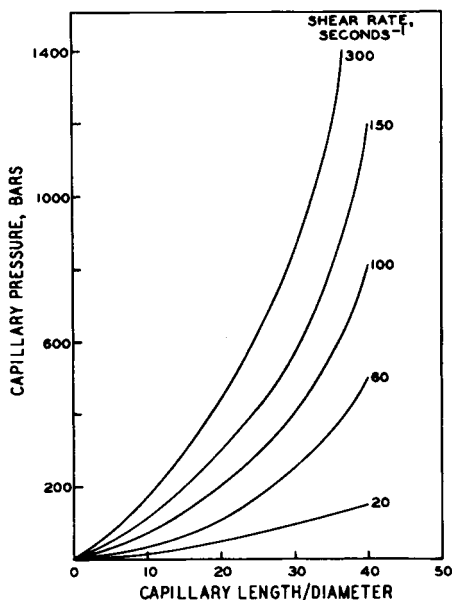
Fig. 2. Bagley plot after elastic energy correction and before pressure correction at 250°C.
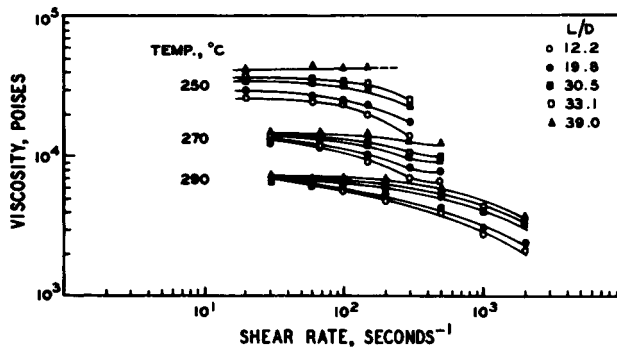

Fig. 3. Instron capillary rheometer data with different capillaries for polycarbonate.

$\Delta p/2$ at higher L/D ratios, which indicates the necessity of using an average pressure drop obtained by the numerical integration of our last equations.

Figure 5 compares the Weissenberg data and the pressure-corrected viscosity curves after the Rabinowitch correction at 250°, 270°, and 290°C. Figures 6 and 7 show the Bagley plots after the pressure correction at 250° and 290°C. The Newtonian viscosity from the Weissenberg rheogoniometer are shown to agree well in Figure 5 with those obtained by extrapolation of the independent and pressure-corrected viscosity data obtained in the Instron capillary rheometer. The corrected capillary data in Figures 6 and 7 are shown to be essentially linear at all shear rates and
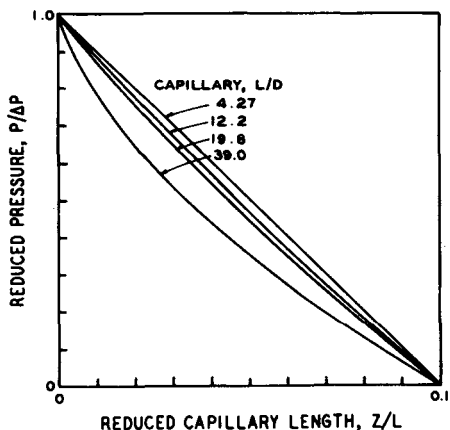
Fig. 4. Capillary pressure distribution for polycarbonate flow at 250°C and 300 sec^{-1}.
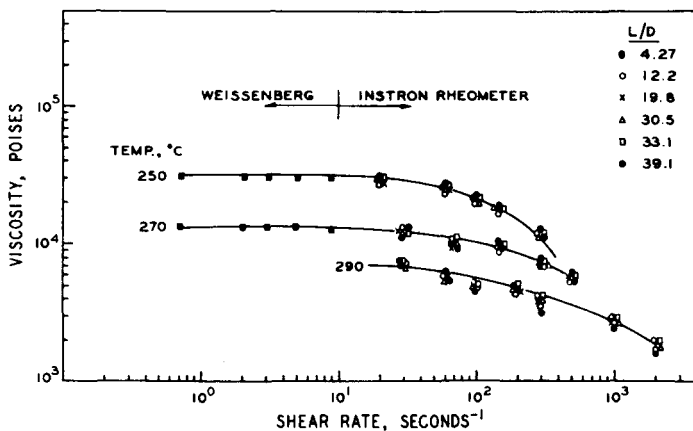

Fig. 5. Capillary flow curves for polycarbonate after rheometer pressure correction.

L/D ratios except for the highest L/D ratio 39.1 at 250°C. This small curvature is not experimentally certain nor explainable.

These results on polycarbonate are shown to be well defined by our equations for expressing the shear and pressure dependence of viscosity. Pressure corrections have not been previously discussed for the capillary flow of this polymer. Table II compares the apparent viscosities before and after pressure correction. As long as the shear rates and L/D ratios (≤ 12.2) are small, the pressure correction is small yet the Bagley correction is major. For example, the ratio of apparent viscosity before Bagley correction to that after correction are 1.5 and 1.02, at L/D ratios of 12.2 and 39.9, respectively.

Baumann and Steingiser[6] measured the melt behavior of various commercial polycarbonates, including a Lexan, using a capillary 14.7 mm in length and 1.62 mm in diameter ($L/D \sim 9.1$). Their pressures, on the

TABLE II
Capillary Flow Data for the Polycarbonate of Bisphenol A. Comparison of
Viscosities Before and After Pressure Correction

Lower temperatures			Higher temperatures		
Capillary L/D	$\dot{\gamma}$, sec^{-1}	$\eta_a/\eta_a{}^a$	Capillary L/D	$\dot{\gamma}$, sec^{-1}	$\eta_a/\eta_a{}^a$
12.2	20	~1.1	12.2	30	~1.0
	300	~1.2		2000	~1.1
39.0	20	~1.4	39.0	30	~1.1
	300	~3.5		2000	~2.0

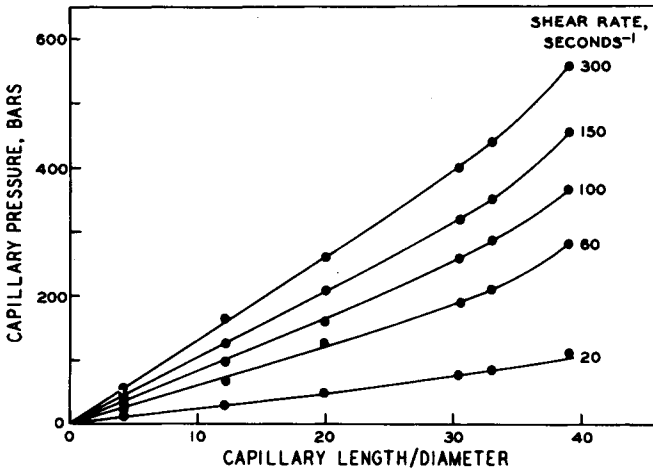a Pressure-corrected viscosities.

Fig. 6. Capillary flow of polycarbonate. Bagley plot after pressure correction at 250°C.
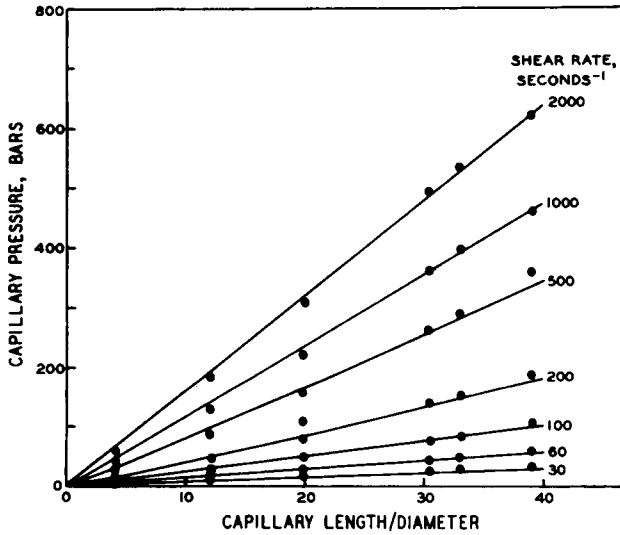

Fig. 7. Capillary flow of polycarbonate. Bagley plot after pressure correction at 290°C.
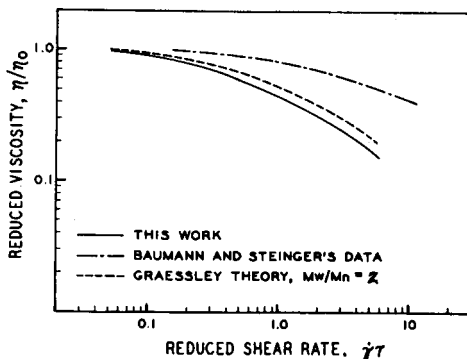
Fig. 8. Comparison of flow data and theory.

basis of these data and calculations, should cause only minor effects on viscosity. Significantly, however, these early data indicate that polycarbonate is almost Newtonian at temperature over 288°C and at shear rate less than 150 sec^{-1}. These authors themselves commented on the lack of shear thinning for polycarbonates. Further, their earlier results differ significantly from these new data which exhibit non-Newtonian effects already at a shear rate of about 60 sec^{-1} at 290°C (see Fig. 5).

The viscosity–shear curves obtained here have also been compared with the theoretical viscosity curves of Bueche as modified by Middleman[19] and of Graessley[11] and involving terms for molecular weight and distribution.

An expression for weight-average molecular weight for this polymer at a constant shear stress of 2.63×10^3 dynes/cm^2 and at 302°C has been given[6] as

$$\log \eta_0 = 3.23 \log \bar{M}_w - 10.73.$$

The viscosity value at 302°C calculated from the Weissenberg data is 2.78×10^3 poises. Therefore, the molecular weight of our polycarbonate is calculated to be $\bar{M}_w = 2.9 \times 10^4$.

Figure 8 shows the comparison of our data with viscosity theory and with the data of Baumann and Steingiser. According to data of the General Electric Company, the $\bar{M}_w/\bar{M}_n$ of the polycarbonate used here is presumed to be 2.4–3.0. Therefore, the results in Figure 8 indicate that the shear dependence for polycarbonate agrees quite well with the theory of Graessley. The results deviate unaccountably from the expectancy of the modified Bueche theory.[19] This means that chemical composition, in contrast to distribution, plays a minor role in shear thinning. The deviation, however, is real and in the direction not expected for molecular weight distribution since the distribution is likely somewhat broader than calculated for most probable, and the shear curve of Graessley gives the expectancy of a yet broader distribution. We thus find that this polycarbonate is more shear thinning than expected, particularly on comparison with earlier data.[6]
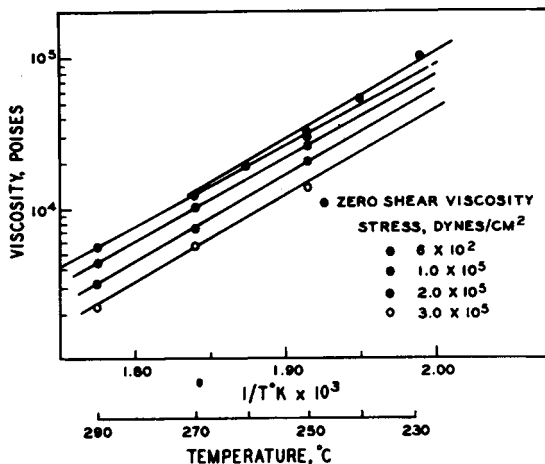
Fig. 9. Flow activation energy at constant shear stress and zero shear for polycarbonate.

The reason is not completely known for anomalously small shear dependence of viscosity presented by Baumann and Steingiser.[6] It is due in part to the fact that they made no Bagley end correction. An unduly broad molecular weight distribution is not likely a cause. The pressure and Rabinowitch corrections are also expected from this work to have only an insignificant effect on their data.

An Arrhenius plot of log η_0 versus $1/T°\mathrm{K}$ is shown in Figure 9. The Weissenberg data in Figure 9 are linear within experimental error over the measured temperature range as might be expected for studies over 100°C above T_g. An activation energy of 26 kcal/mole obtained from the slope in Figure 9 agrees well with published data of other workers.[6,20] This temperature-independent E provides an estimate of η_0 over a broad temperature range when η_0 is known only at one temperature. Baumann and Steingiser[6] have mentioned that the relatively high activation energy for polycarbonate is an indication of its polarity and stiffness or, alternately, the greater length of the independently moving statistical segments. Actually, the E is only modestly high, being similar to that for polystyrene and consistent with general chain "stiffness" criteria.[21]

The same E was obtained from the non-Newtonian region using corrected data from the Instron capillary rheometer for correlations at constant stress (Fig. 9). Values in Table III indicate that E at constant stress is independent of shear. This concept of a shear stress-independent E has been illustrated for many polymers by Proter and Johnson.[21] An E independent of shear stress is also an indirect proof that the pressure dependence of viscosity is well described by our equations.

One of the WLF constants, C_2, will vary somewhat with pressure since the thermal expansion coefficient is pressure dependent. Table IV lists the WLF constants obtained from these and previously published data.[9] Equivalent results, within experimental error, were obtained when the

TABLE III
Flow Activation Energy at Constant Shear Stress from Pressure
Capillary Viscometer

Shear stress $\times 10^{-5}$, dynes/cm^2	E_τ, kcal/mole
Newtonian[a]	*26*
0.6	26
1.0	26
2.0	26
3.0	25

[a] Data from Weissenberg rheogoniometer.

TABLE IV
WLF Constants for Polycarbonate of Bisphenol A

	C_1	C_2
This work	16.3	23.3
Ishida and Matsuoka[a]	15.0	72.0

[a] Calculated here from original data.

pressure-corrected viscosity was computed from these new or from published data. Therefore, variations of C_2 with pressure are expected to make no change in the final results. A yet more detailed explanation on the applicability of the WLF equation for pressure corrections are discussed by Penwell and Porter.[1-3]

The pressure dependence of T_g can be evaluated using isofree volume theory[22] or an isoconfigurational theory[23] if adequate P-V-T data are available. The experimental basis for this shift is given by eq. (4).

In eq. (5), A_1p will be a small percentage of A_4 at lower temperatures. Thus, eq. (5) becomes

$$\eta = \eta_0 e^{bp}$$

where $\eta_0 = \eta_g \exp 2.303\, A_2/A_4$ and $b = 2.303\, A_3/A_4$.

This pressure–viscosity model derived by Penwell, Middleman, and Porter[3] has also been obtained independently from the Eyring hole theory for viscosity.[24] Since $A_1p \simeq 40$ (if $p = 1000$ kg/cm^2), this term is not negligible, and therefore the pressure viscosity model $\eta = \eta_0 e^{bp}$ would be expected to fail at higher pressure. This is the reason eq. (5) was used directly.

CONCLUSIONS

The effects of pressure, up to 2 kilobars, have been evaluated for both the Newtonian and shear-thinning regions in the flow of the polycarbonate of bisphenol A. Equations for the pressure effects have been derived from the momentum equation, the WLF (Doolittle) equation, and the Bueche and Graessley theories. The equations quantitatively interpret the data

and confirm that apparently anomalous flow data can be explained by pressure reduction of free volume.

The resulting flow data show that:

1. Differences in flow data obtained with different capillaries are quantitatively due to pressure effects.

2. Definitive and linear Bagley plots have been obtained for the first time on this polymer. Minor residual and yet unexplained positive deviations are found at the highest shear rates and lowest temperatures.

3. Corrected viscosity–shear rate curves obtained using an Instron capillary rheometer agree well with data from a Weissenberg rheogoniometer which extends the available data over additional decades.

4. The magnitude of the shear dependence of apparent viscosity is qualitatively the same as that expected by the theory of Graessley and considerably more pronounced than previously published for this polymer. The original and modified Bueche theory for shear thinning inadequately interprets these data.

5. A constant activation energy for viscous flow at constant shear stress has been observed. This is the first demonstration of this feature for polycarbonate. The result also means that viscosity data as a function of shear will superimpose on master curves of fractional viscosity change with shear in terms of either $\eta_0 \dot{\gamma}/T^\circ \mathrm{K}$ or $\tau/T^\circ \mathrm{K}$.

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