

A Rheological Study of the Low Molecular Weight Butyl Polymer

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Synopsis

A rheological study has been performed to characterize the low molecular weight butyl polymers using a couette conical-cylindrical viscometer. The bulk viscosity was determined as a function of temperature, weight-average molecular weight, viscosity-average molecular weight, and shear rate. The temperature dependence of the viscosity, while adequately represented by the Williams, Landel, and Ferry equation, is best described by an Arrhenius equation for the temperature range investigated. The viscosity is shown to vary with the 3.5th power of the weight-average molecular weight above a critical molecular weight and to the 1st power below this molecular weight. Although the ratio of the weight-average molecular weight to the number-average molecular weight usually affects the flow properties of polymers, this was not true for the polymers investigated. The bulk viscosity was found to be independent of the molecular weight distribution for the temperature and shear rate range studied. It has been shown that a definite relationship exists between the bulk viscosity and the viscosity-average molecular weight as determined by dilute solution viscosity. A mathematical model has been developed to relate these two parameters as a function of temperature and shear rate.

INTRODUCTION

Understanding the rheological properties of the low molecular weight butyl (LM Butyl) polymer, which was recently introduced by the Enjay Chemical Company, is essential to the development of improved methods and procedures for polymer processing. Determination of the relationships between flow parameters and molecular structure can produce an insight and an understanding required in the development of improved polymers. These properties can also be used for process quality control.

The intention of this study was to determine whether or not a relationship exists between the bulk viscosity of the LM Butyl polymer and the viscosity-average molecular weight (i.e., dilute solution viscosity). If such a relationship could be found, it would not only yield a valuable method of monitoring the polymer process, but it would also help in obtaining essential information regarding the rheology of this polymer. The results of this experimental investigation have shown that a definite relationship does exist between the bulk viscosity and the dilute solution viscosity. By using a temperature-controlled conical-cylindrical viscometer, a mathematical

model has been developed which satisfactorily describes these two parameters and which can be used for process and product control.

EXPERIMENTAL

LM Butyl is a low molecular weight copolymer of isobutylene and isoprene, the same monomers that go into butyl rubber manufacture. During the course of development of this new low molecular weight grade of butyl, various materials were made in order to optimize the polymer. A group of these materials were selected for this study and are indicated in Table I.

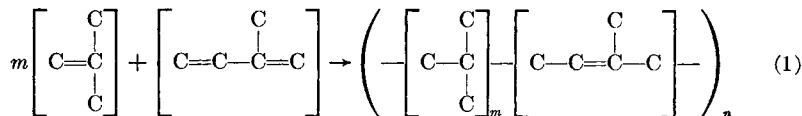
TABLE I
Polymer Properties

Polymer	\bar{M}_v	M_n^a	M_w^a/M_n	E^b
P-1	15,000	5,230	3.6	15,400
P-2	33,300	9,330	5.0	14,300
P-3	26,600	8,170	5.9	13,800
P-4	33,000	8,620	6.7	12,400
P-5	36,600	13,200	4.8	13,900
P-6	33,600	13,100	4.6	13,100
P-7	40,800	12,400	5.0	13,800

^a Obtained by gel permeation chromatography.

^b Activation energy.

The proprietary process to produce LM Butyl is a cationic polymerization which requires an entirely different catalytic system and higher operating temperatures than are used in the production of high molecular weight butyl. The copolymerization of the two monomers is represented in eq. (1). LM Butyl polymers are about $1/10$ the molecular weight of regular butyl; tensile strength is about $1/3$. Before using any of the polymers listed in Table I, each sample was vacuum-oven dried at 70°C for 24 hr. The viscosity-average molecular weight of each polymer was determined by gel permeation chromatography.



A couette-type (i.e., conical-cylindrical) viscometer manufactured by Brookfield Engineering Laboratories, Inc., was used to measure the viscosities at low shear rates. The system consisted of a standard HBF Brookfield Synchro-Lectric Viscometer which held a modified cylindrical spindle. This spindle was inserted into a small jacketed sample chamber (see Fig. 1). Temperature control was accomplished by circulating a hot oil between a constant temperature bath and the sample chamber. Throughout this study, it was assumed that heat losses to the surroundings were negligible and that there was no viscous heat dissipation. As shown in Figure 1, the

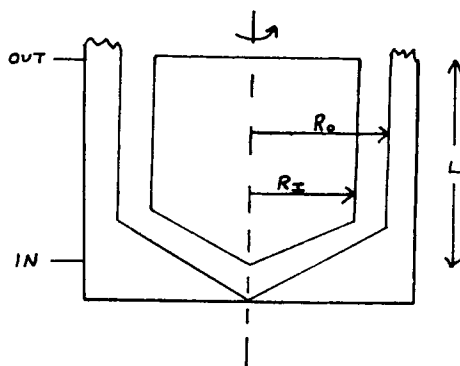


Fig. 1. Schematic diagram of viscometer. $R_1 = .1375$ in.; $R_0 = .2540$ in.; $L = .989$ in. Sample chamber, Brookfield #SC4-8, spindle, #SC4-16.

spindle and chamber are of conical-cylindrical shape. The reason for this combination of a conical and a coaxial cylinder viscometer is that the mean shear rate in the conical portion is nearly equal to that in the cylindrical annulus thereby minimizing end effects.⁷ The viscometer was calibrated against National Bureau of Standards calibrating oils.

The following relationships for the shear stress and shear rate were derived¹ for this couette assembly:

$$\tau_{r,\theta} = \frac{T}{2\pi R_1^2 L} \quad (2)$$

where $\tau_{r,\theta}$ = shear stress in dynes/cm² and T = torque in dyne cm, and

$$\dot{\gamma} = \frac{2WR_1^2 R_0^2}{(R_0^2 - R_1^2)r^2} \quad (3)$$

where $\dot{\gamma}$ = shear rate, r = distance from the axis of rotation, in cm, at which $\dot{\gamma}$ is being calculated, and W = angular velocity in radians per second.

Experimental

Viscosity-Temperature Dependence

The variation of viscosity with temperature for glass-forming polymers has been widely studied. It is believed by some (Gent² and Bueche³) that the relationship which best relates these two parameters is the WLF equation (Williams, Landel, and Ferry⁴), which states that

$$\ln \left(\frac{V_g}{V} \right) = \frac{A(T - T_g)}{B + (T - T_g)} \quad (4)$$

where g indicates properties at the glass transition and the constants A and B are 40 and 52, respectively, for most polymers (WLF-1 equation)

and 40 and 100 for polyisobutylene and butyl (WLF-2 equation). The glass transition temperature T_g was found by differential thermal analysis to be -70°C . If the WLF equation is correct for LM Butyl, a constant value for the viscosity at the glass transition temperature should be found.

The glass transition viscosity V_g was calculated for each polymer studied for both the WLF-1 and WLF-2 equations. The calculation was based on the experimental results of this investigation which covered a temperature range of 50° to 100°C . Table II lists the average values for

TABLE II
Variation of Viscosity with Temperature, According to Williams,
Landel, and Ferry Equation*

Polymer	$V_g(\text{WLF-1}) \times 10^{-10}$	$V_g(\text{WLF-2}) \times 10^{-17}$
P-1	$0.529 \pm 1.2\%$	$0.014 \pm 16.1\%$
P-2	$0.413 \pm 10.5\%$	$0.130 \pm 14.6\%$
P-3	$0.207 \pm 6.9\%$	$0.066 \pm 18.1\%$
P-4	$0.368 \pm 8.5\%$	$0.119 \pm 29.3\%$
P-5	$0.516 \pm 7.9\%$	$0.172 \pm 12.5\%$
P-6	$0.414 \pm 12.9\%$	$0.130 \pm 14.7\%$
P-7	$0.646 \pm 6.9\%$	$0.204 \pm 17.1\%$

* (General) WLF-1: $\ln\left(\frac{V_g}{V}\right) = 40(T - T_g)/[52 + (T - T_g)]$; (polyisobutylene)
WLF-2: $\ln\left(\frac{V_g}{V}\right) = 40(T - T_g)/[100 + (T - T_g)]$

the glass transition viscosity for the seven polymers investigated. Included in this table are the values (in per cent form) which indicate the spread of the calculated viscosity over this temperature range. These values indicate that the LM Butyl data correlate with the WLF-1 equation better than with the WLF-2 equation. This is important since the WLF-2 equation is specifically designed for polyisobutylene and butyl polymers. One reason for this situation is that the WLF viscosity-temperature relationship is only accurate within the range $T_g < T < (T_g + 120)$; its importance diminishes above this range.

A linear relationship was found when the data for a given shear rate were plotted in the form of log viscosity versus the reciprocal of the absolute temperature $1/T$, as shown in Figure 2. This type of relationship is best described by the Arrhenius equation

$$\eta = ke^{E/RT} \quad (5)$$

where E is the apparent activation energy of viscous flow. Using a linear regression program, the activation energy for each material studied was found and is listed in Table I.

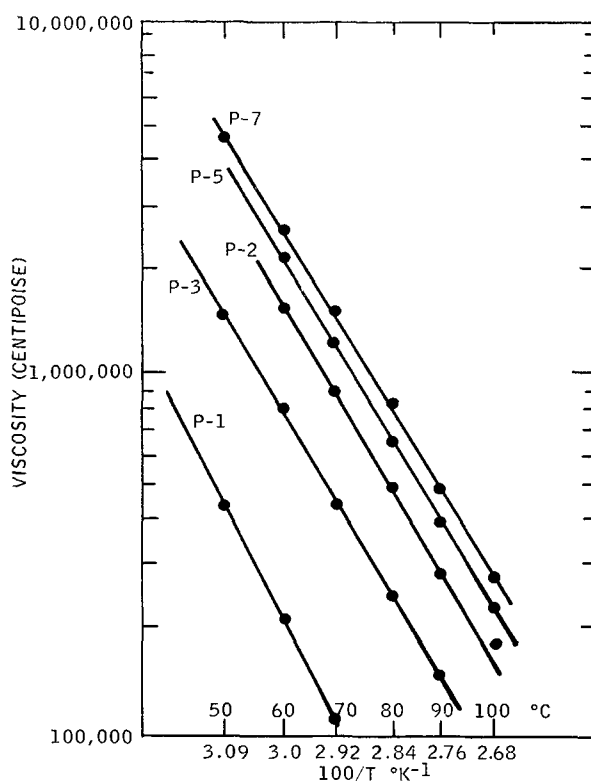


Fig. 2. Log viscosity vs. reciprocal of absolute temperature ($\dot{\gamma} = .589 \text{ sec}^{-1}$).

Viscosity-Molecular Weight Dependence

It is widely known that the molecular weight distribution and the range of molecular weights can have a marked influence on flow properties (i.e., viscosity). It is also known that the following relationship between molecular weight and viscosity is valid for most polymers:

$$\eta = KM_w^a \quad (6)$$

where a is unity for low molecular weights and 3.5 for high molecular weights. According to Bueche,³ this relationship applies only for narrow molecular weight distributions. A plot of log viscosity versus the log of the weight-average molecular weight for various temperatures is shown in Figures 3 and 4 at a shear rate of 0.589 sec^{-1} . These plots verify the viscosity-molecular weight relationship, eq. (6), since at high M_w the slope is 3.5. The slope of the line in the low M_w range was verified to be 1, even though only one data point was available. This was done by drawing a line with a slope of 1 through the data point and noting that it consistently crossed the high molecular weight range line at a constant value. From these figures, a value for the so-called critical molecular weight can be

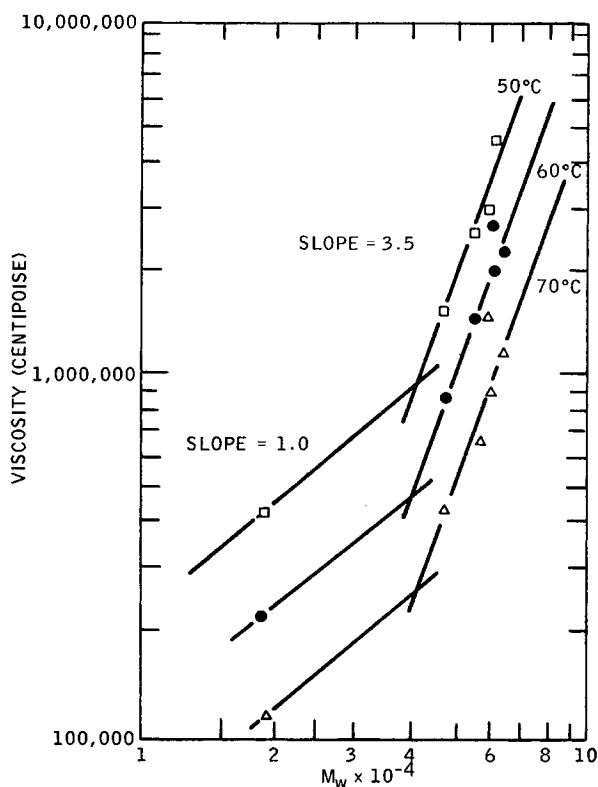


Fig. 3. Bulk viscosity vs. weight-average molecular weight for $\dot{\gamma} = .589 \text{ sec}^{-1}$.

found. This critical value is the molecular weight at which the slope changes from 1.0 to 3.5. The value obtained from these plots is 40,000, as compared to 17,000 for polyisobutylene. The reason for the large difference in critical M_w is due to the shear rate at which the measurements were taken. For polyisobutylene $\dot{\gamma}$ was much smaller than the 0.589 sec^{-1} used for LM Butyl measurements. While weight-average molecular weights are important parameters in characterizing a polymer, they are often difficult to obtain rapidly. Because of this, one usually resorts to the viscosity-average molecular weight measured by dilute solution viscosity.

A linear relationship was found to exist for a given temperature and shear rate when one plots the $\log \bar{M}_v$ versus the \log viscosity as indicated in Figure 5. It is of interest that the average slope of these straight lines is 2.6, as opposed to the results found when the weight-average molecular weight was used. The lack of agreement between these two plots is not understood at this time. The major result obtained from this figure is that if one measures the dilute solution viscosity of the polymer, for example, at the reactor effluent, the bulk viscosity of the finished polymer will be known. This is important since the bulk viscosity is a crucial

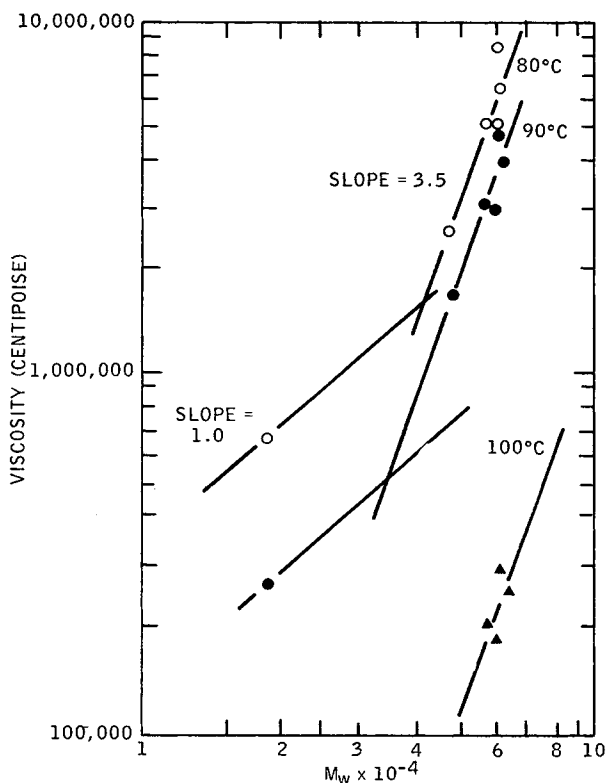


Fig. 4. Bulk viscosity vs. weight-average molecular weight for $\dot{\gamma} = .589 \text{ sec}^{-1}$.

product specification, and thus a critical point for process control has been found. Of course, this procedure could be used in reverse; measuring the polymer bulk viscosity will result in a value of the viscosity-average molecular weight.

Room Temperature Bulk Viscosity

Owing to an experimental limitation, the bulk viscosity could not be measured at temperatures lower than 50°C . It is, however, important to know what the bulk viscosity is at room temperature, since many of the proposed applications for LM Butyl will be at this temperature. While it is not a recommended engineering practice, an approximate value for the bulk viscosity at 20°C can be found by extrapolating the bulk viscosity versus the reciprocal temperature curves. The results of the operation are shown in Figure 6. This is a plot of the extrapolated bulk viscosity versus the viscosity-average molecular weight at 20°C for a shear rate of 0.589 sec^{-1} . The ratio of the weight-average to the number-average molecular weight usually affects the bulk viscosity; however, this was not true in this case for the LM Butyl polymers studied. This is shown in Figure 6 where these various ratios are indicated; the ratio range investigated (3.6

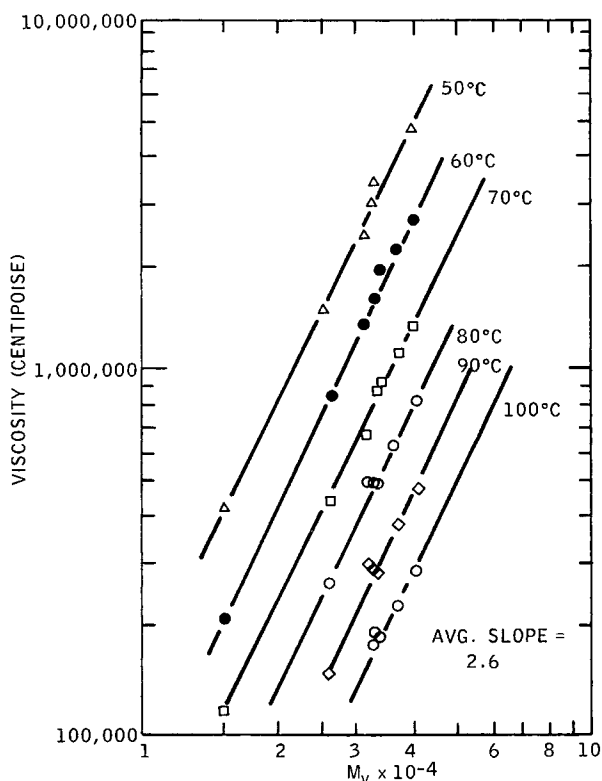


Fig. 5. Viscosity vs. viscosity-average molecular weight for $\dot{\gamma} = .589 \text{ sec}^{-1}$.

to 6.7) showed no effect on bulk viscosity. Recent work by Roper⁵ has shown that when the above polymers are fractionated into narrow M_w/M_n fractions, the above generalization holds. That is, the bulk viscosity to viscosity-average molecular weight relationship is independent of distribution for the temperature and shear rate range studied.

mathematical model: $\text{viscosity} = f(M_v, 1/T)$

Since the log of the bulk viscosity varies linearly with both the log of the viscosity-average molecular weight and the reciprocal of the absolute temperature, a mathematic model of the system can be developed. The purpose of this model is to bring the three variables involved in the experimental analysis into one general equation. The technique used to find this correlation is called the "Method of Composition" outlined by Ames and Behn.⁶ A summary of the method as it applies to this investigation follows.

One desires to relate the bulk viscosity V as a function of the viscosity-average molecular weight M and the reciprocal of the absolute temperature, $1/T = R$, as follows:

$$V = f(M, R).$$

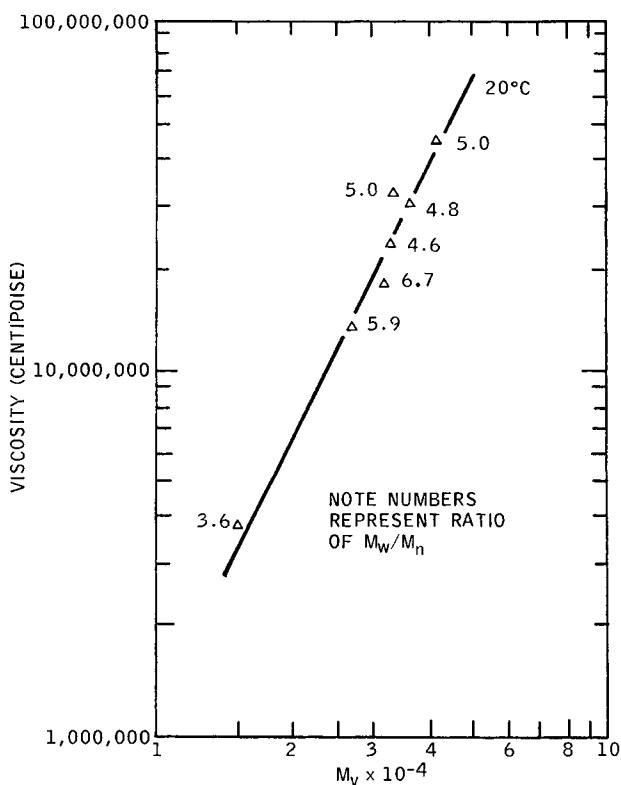


Fig. 6. Viscosity vs. viscosity-average molecular weight. Numbers represent M_w/M_n ratios.

Two basic relationships are required in order to develop a specific relationship between the variables of interest. They are

$$\frac{\partial (\ln V)}{\partial (\ln M)} = C(R) \quad (8)$$

$$\frac{\partial (\ln V)}{\partial (R)} = -A(M) \quad (9)$$

which are merely a mathematical restatement of Figures 5 and 2. In other words, the slope of the $\ln V$ -versus- $\ln M$ curve was constant for any given temperature and that the slope of the $\ln V$ -versus- $\ln 1/T$ curve was constant for any fixed molecular weight. Integration of eq. (8) with respect to $\ln M$ yields

$$\ln V = C(R) \ln M + E(R) \quad (10)$$

while the integration of eq. (9) with respect to R yields

$$\ln V = -A(M)R + B(M). \quad (11)$$

TABLE III
Regression Analysis Results (Mathematical Model)

Variable	Mean	Std. deviation	Correlation X vs. Y	Regression coefficient	Std. error of reg. coeff.	Computed T-value
γ	0.0297	.00157	0.9827	-751.	412.9	-1.829
δ	10.31	.2946	0.5765	4.87	1.202	4.050
α	.00288	.00014	0.7387	14752.	4265.2	3.459
β				-57.17		

Multiple correlation coefficient, 0.996884

Standard error of estimate, 0.0963

Sum of squares attributable to regression (SSAR), 53.4

Degrees of freedom associated with SSAR, 3

Mean square of SSAR, 17.78

Sum of squares of deviations from regression (SSDR), 0.3339

Degrees of freedom associated with SSDR, 36

Mean square of SSDR, 0.009276

F-Value, 1916.8

Note that $E(R)$ and $B(M)$ are constants of the partial integration. Equating eqs. (10) and (11) results in

$$-A(M)R + B(M) = C(R) \ln M + E(R). \quad (12)$$

Differentiation with respect to R yields

$$-A(M) = \frac{dC(R)}{dR} \ln M + \frac{dE(R)}{dR}. \quad (13)$$

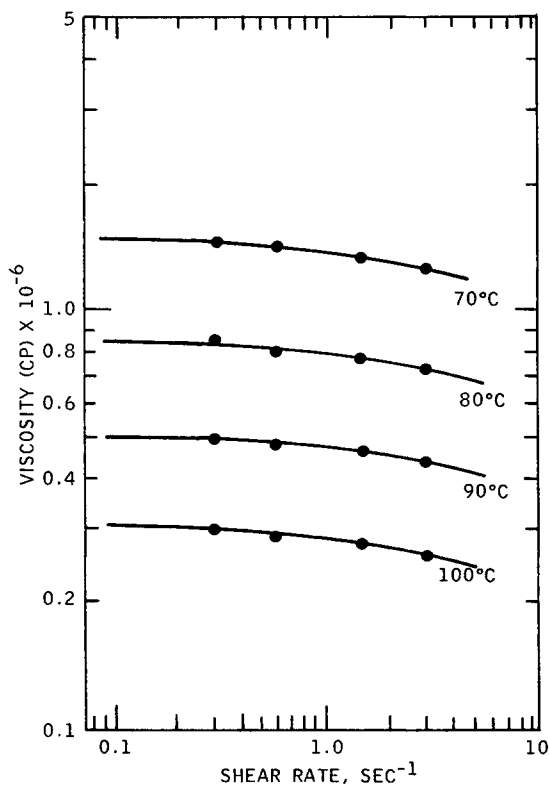


Fig. 7. Viscosity vs. shear rate, sample P-7.

Since the left hand side of eq. (13) is a function of M only, the right-hand side must also be a function of M only. Therefore,

$$\frac{dE(R)}{dR} = \alpha \quad (14a)$$

$$\frac{dC(R)}{dR} = \gamma \quad (14b)$$

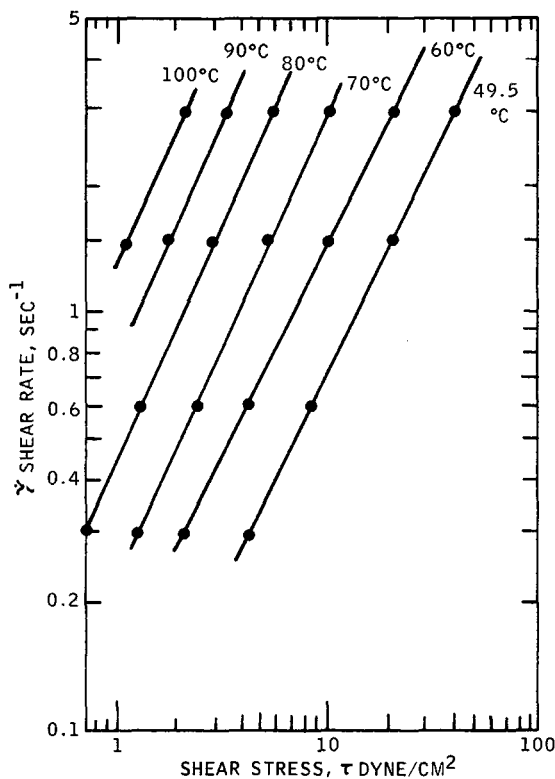


Fig. 8. Shear rate vs. shear stress, sample P-1.

where α and γ are absolute constants. One obtains upon integration of Equation (14 a & b).

$$E(R) = \alpha R + \beta \quad (15)$$

$$C(R) = \gamma R + \delta \quad (16)$$

Substitution of eqs. (15) and (16) into eq. (10) results in our desired expression for the viscosity:

$$\ln V = (\gamma R + \delta) \ln M + (\alpha R + \beta) \quad (17)$$

or

$$V = M^{(\gamma R + \delta)} \cdot \exp(\alpha R + \beta). \quad (18)$$

In order to determine the coefficient (γ , δ , α , β) and validate the mathematical model, a multiple-regression analysis has been performed. It should be pointed out that the experimental investigation gave conclusive results; however, it was felt that the above model would better serve to correlate the data. The results of the regression analysis are given in Table III. The only point in question is the computed T value for the variable γ ;

while it is not significant at the 95% confidence level, it is significant at the 90% confidence level. However, since the F -test was high and the multiple-regression coefficient was so excellent (0.997), the model as a whole gives a most adequate prediction of the system. Based on the results of this regression analysis, the mathematical model becomes

$$\ln V = \gamma R \ln M + \delta \ln M + \alpha R + \beta \quad (19)$$

where $\gamma = -751.$, $\delta = 4.87$, $\alpha = 14,752$, $\beta = -57.17$, $R = 1/T$ °K, $M = M_n$, and $V =$ bulk viscosity in centipoise.

Additional Rheological Properties

The basic reason one studies the rheological properties of polymers is so that one can predict the rate of flow of a fluid for a given stress. One is normally interested in how the shear rate varies with the shear stress and also how the viscosity varies with the shear rate. If one is to use data of this type for engineering applications, it should cover a wide range of shear rates (at least 3 decades). Information of this type was collected in this study. However, because of equipment limitations only a very small range of shear rates could be investigated. Thus, these data could not be used in the formulation of a general equation to describe the rheological properties of LM Butyl; however, the data is of some interest. Figure 8 shows the relation of shear stress to shear rate. Figure 7 shows the effect of viscosity on shear rate. From these graphs it can be seen that the LM Butyl polymer conforms to the class of fluids called pseudoplastics. While the data are limited, they can be used in conjunction with other data that could be obtained under high shear rates. High shear rate data can be found with a capillary viscometer. If such data were available, the more desirable general equation to describe the rheological properties could be realized.

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