Viscosity of Polyisoprene

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Synopsis

The effects were studied of molecular weight, shear rate, and temperature on the viscous behavior of various linear, monodisperse polyisoprenes of about 90% *cis*-1,4 structure. Viscosities of from 10^{10}–10^{5} poise were measured on a double cone and plate viscometer while viscosities of 10^{4}–10^{-2} poise were measured on rotating cylinder viscometers. For such polyisoprenes the variation of Newtonian (zero shear) viscosity η with the weight-average molecular weight in the molecular weight range of 2×10^{4}–1×10^{6} may be represented as

$$\eta = A \bar{M}_w^{3.9_5}$$

where A is a temperature-dependent parameter given by

$$\log A = -101.14 + \frac{8.999 \times 10^4}{T} - \frac{3.19222 \times 10^7}{T^2} + \frac{3.816 \times 10^9}{T^3}$$

The variation of the apparent viscosity η_a with shear rate $\dot{\gamma}$ is also determined and a combined equation may be formulated as

$$\eta_a = A \bar{M}_w^{3.9_5}/[1 + 1.22 \, (A\gamma/T)^{0.58} \, \bar{M}_w^{2.87} \times 10^{-5}]$$

This equation is compared with other expressions for the variation of viscosity with molecular weight, temperature, and shear rate.

INTRODUCTION

The viscosities of solid polymers have been extensively studied. In particular much experimental work has been carried out on the variation of the melt viscosities with molecular weight and molecular weight distribution,[1a,2-9] shear rate (or shear stress),[1b,2,3,5,8,10-17] and temperature.[1c,3,4,7,8,12-18]

For example, Bueche has deduced theoretically[1a,19] that for polymeric materials above a certain critical chain length the relationship between the viscosity at zero shear rate η and the weight-average molecular weight $\bar{M}_w$ should be given by

$$\eta = A \bar{M}_w^{3.5} \tag{1}$$

and a considerable amount of experimental evidence supporting this equation has been obtained,[1,2-7] together with a smaller amount of evidence contradicting it.[5,8,9]

Three main theories have been developed to account for the variation in apparent viscosity η_a with shear rate $\dot{\gamma}$. That of Pao[20] requires a knowledge of the polymer relaxation spectrum and appears to predict a second Newtonian region at which the apparent viscosity η_a should be about one-quarter of the zero shear viscosity η (see Figure 2 in ref. 20). No good evidence of such behavior has been observed. On the other hand, the theories developed by Bueche[17] (see Appendix) and Rouse[21] show at least a qualitative agreement with experimental data[2,5,8,9,11,15] in that the predicted bulk viscosity decreases continuously with increasing shear rate. Bueche and Harding,[22] however, later considered Bueche's treatment to be quantitatively incorrect and proposed an empirical equation. As will be shown later, all the treatments (except that of Pao) may be represented roughly by equations of the form

$$\eta_a/\eta = 1/(1 + K\dot{\gamma}^n) \tag{2}$$

where K and n are adjustable parameters.

The variation of viscosity with temperature has also been studied, and the semiempirical proportionality

$$\ln \eta \propto 1/T \tag{3}$$

has been proposed for simple liquids. Theoretical justification has been given for its extension to polymers.[1d] Generally, this relationship seems to apply best to polymers fairly well above their glass transition temperature,[4,9,12–15,17] but at lower temperatures, deviations occur.[12,16]

The work presented in this paper describes the effect of each of these variables (molecular weight, shear rate, and temperature) upon the viscosity of polyisoprene. Polyisoprene has the advantages that it is easily prepared as an essentially monodisperse linear material,[23,24] and oxidative or shear degradation results in a decreased molecular weight which can easily be detected by a reduced intrinsic viscosity.

Viscosities were measured for a series of polyisoprene samples at temperatures of 27, 50, 75, and 100°C. Shear rates from 10^{-5} to 25 sec.$^{-1}$ were applied. Two separate types of viscometers were used, namely, a modified Mooney Plastometer (double cone and plate) and a modified Brookfield viscometer (coaxial cylinder). This equipment and its use is described in detail below.

EXPERIMENTAL

Modified Mooney Plastometer

The use of a variable-speed Mooney Plastometer fitted with a biconical rotor has already been described.[25] The apparatus used was similar except that gearing was provided so that a shear rate range of 10^{-5}–5 sec.$^{-1}$ could be covered.

Three separate samples of each material were tested. The first was tested both at 27 and at 50°C., while the other two were tested at 75 and

100°C., respectively. Before being tested the materials were pressed out into disks of $2^1/_2$ in. diameter and $^1/_4$ in. thick. The apparatus was brought to a temperature of about 100°C. and the rotor, sandwiched between the two disks, was inserted. The apparatus was closed sufficiently to allow the platens to come into contact with the disks (thus heating them). After an additional 2 min. the apparatus was completely closed and the rotor started at the lowest desired shear rate. The apparatus was then allowed to run overnight while cooling to ambient temperature and, when necessary, heated up to the desired temperature in the morning. Readings of the torque (the Mooney reading) and the time of revolution of one of the gear shafts driving the rotor were taken after the Mooney reading had varied by no more than $\pm^1/_2$ in a 30-min. period or the rotor had completed one-half revolution. The viscosity and shear rate were calculated by using eqs. (4) and (5):

$$\eta = 9850M/R \tag{4}$$

where η is the viscosity in poise. M is the Mooney reading (a reading of 100 corresponding to $73^1/_8$ in.-lb. torque),* and

$$\dot{\gamma} = 0.803R \tag{5}$$

where $\dot{\gamma}$ is the rate of shear on the polymer between the rotor surface and the platens (in sec.$^{-1}$) and R is the number of revolutions made by the rotor in 1 min. (calculated from the time of revolution of one of the gear shafts).

Modified Brookfield Viscometer

Polyisoprene of low molecular weight ($< \sim 2 \times 10^5$) is too fluid to be tested in the Mooney Plastometer. For this reason a Brookfield viscometer was used (Model HBT or LVF, obtained from Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts). On Model HBT a full-scale reading (100) represents a torque of 57,500 dyne-cm. whereas on Model LVF the corresponding torque is 674 dyne-cm. The viscometers were modified by the use of a nonstandard spindle (8 in. long and $^1/_8$ in. diameter) on which was fitted removable aluminum cylinders of various heights ($^1/_8$–2 in.) and the same diameter ($^3/_4$ in.). These were each rotated inside and concentric with a glass round-bottomed tube $1^1/_8$ in. in diameter which contained the polymer, with the top surface of the rotor adjusted to be 1 in. below the polymer surface. Oil from a thermostated bath (controlled to $\pm^1/_5$°C.) was circulated around this tube. Tests showed that the most viscous polymer used (polymer 5) attained the temperature of the bath in about 30 min., and all the materials were therefore allowed to stand for this time before the apparatus was started; readings were then taken after

* The factor 9850 contains an end effect correction[25] which is sensitive to the extent to which the polymer deviates from Newtonian behavior. Although this correction itself is significant, its variation with the degree of non-Newtonian behavior is small and in this case it has been calculated by assuming Newtonian behavior.

the rotor had run for 5 min. at some fixed speed. With the dimensions of this apparatus it can easily be shown that for Newtonian fluids

$$\eta = 105 \ \Delta B_{HBT}/[R(H - {}^1/_8)] = 1.23 \ \Delta B_{LVF}/[R(H - {}^1/_8)] \qquad (6)$$

and

$$\dot{\gamma} = 0.0251R \qquad (7)$$

where ΔB_{HBT} and ΔB_{LVF} are the differences in Brookfield readings (on the Model HBT or LVF, respectively) obtained by use of a cylinder of height H inches and one obtained with the cylinder of height $^1/_8$ in., R is the number of rotations made by the cylinder in 1 min., and $\dot{\gamma}$ is the mean rate of shear between the walls.

Limits of Accuracy and Repeatability

Mooney readings or values of ΔB less than 5 units were neglected. At a particular temperature, readings were continued until either full-scale torque or the highest available shear rate was reached (25.1 sec.$^{-1}$ on the Brookfield Model HBT, 15 sec.$^{-1}$ on the Brookfield Model LVF and 5.15 sec.$^{-1}$ on the modified Mooney plastometer), or until the polymer showed signs of rotor slip or polymer fracture. These were taken to be: (1) a sudden fall in the torque reading, (2) a gradual fall to a value below that previously obtained at a lower shear rate, (3) a prolonged oscillation of the torque reading. As a test of repeatability, a sample of polyisoprene (intrinsic viscosity [η] = 5.05 dl./g.) was tested on the Mooney apparatus at 27°C. with the shear rate first increasing and then decreasing. Although adequate time was allowed to reach equilibrium (at least 40 hr. at the lowest shear rate), no significant difference could be observed between the points obtained with the shear rate increasing and those obtained with the shear rate decreasing.

A variation in the Mooney reading of $\pm ^1/_2$ unit was observed when the apparatus was run under no load; this was due to irregularities in the torque measuring mechanism. If we assume that the Brookfield viscometer can be read to $\pm ^1/_2$ unit, then for torque measurement the maximum possible error (at a Mooney reading or value of ΔB of 5) is $\pm 10\%$. Since the speed of the rotor may be obtained much more precisely, then the torque measurement also is the limit of repeatability of the viscosity measurement.

As a check of the accuracy of the modified Brookfield viscometer a National Bureau of Standards standard oil (Type P) was tested. Its viscosities at 40° and 50°C. were found to be 208 $\pm$ 5 and 102 $\pm$ 3 poise, respectively. The correct values are 206 and 96 poise, respectively. From this it would appear that the accuracy of the measurements made in the modified Brookfield viscometer is about $\pm 5\%$.

Materials Tested

In all, seven polyisoprene samples were tested. Details of their intrinsic viscosities, viscosity-average molecular weights, and structure (*cis*-1,4 content as determined by infrared analysis) are given in Table I.

TABLE I
Materials Tested

Polymer no.	$[\eta]$, dl./g.	Molecular weight $\bar{M}_v$	*cis*-1,4 structure, %
1	7.4	1.87×10^6	92
2	4.7	1.00×10^6	—
3	3.4	6.4×10^5	85
4	1.84	2.78×10^5	94
5	0.80	8.9×10^4	83
6	0.50	4.65×10^4	83
7	0.30	2.30×10^4	—
8	0.11	5.8×10^3	—
Squalene	—	4.11×10^2	—

The molecular weights quoted were obtained from intrinsic viscosity measurements by using the relationship[26]

$$[\eta] = 2.0 \times 10^{-4} \bar{M}_v^{0.728} \qquad (8)$$

Intrinsic viscosities were measured in toluene solution with the use of Desreux-Bischoff[27] viscometers. Corrections to zero shear rate were applied where significant (at $[\eta] > 2$ dl./g.).

The samples were protected against oxidative degradation during testing by the addition of about 1 phr Antioxidant 2246 [2,2-methylene bis(4-methyl-6-*tert*-butyl phenol) from American Cyanamid Company] and 0.1 phr NaHS. These materials were dispersed in a toluene–methanol mixture and swollen into the polymers, which were then dried in vacuum for at least one week.

Two intrinsic viscosities were obtained on each material. The first was obtained on the unsheared sample and the second on a sample which had been sheared at 100°C. Differences were less than 3% and the values given in Table I represent the mean.

The polyisoprenes used were polymerized in the laboratory by use of butyllithium initiator in an aliphatic hydrocarbon solvent under an inert atmosphere as described by Morton[23] and Diem.[24] The polymerizations were taken to high conversion and the products were completely soluble in toluene. Such polymers have been reported to be linear and almost mono-disperse, with a little low molecular weight polymer.[26] For materials of high molecular weight (polymers 1–4, Table I), this was removed by reprecipitating the samples from toluene solution by the addition of methanol followed by slow cooling until about 50% of polymer was precipitated. This precipitate was washed and dried.

   Two other materials (polymers 5 and 6) were obtained by degrading
higher molecular weight polyisoprene. The product in each case was frac-
tionated by the addition of methanol to a toluene solution followed by slow
cooling. After about 40% of the original material had been precipitated,
the solution was filtered and cooling continued. When a further 20% of
the material was precipitated this was retained.
   No attempt was made to fractionate the lowest molecular weight ma-
terials (polymers 7 and 8 and squalene).

RESULTS

   Values of the apparent viscosities of a typical higher molecular weight
polyisoprene (polymer 3) at various shear rates are shown in Figure 1.
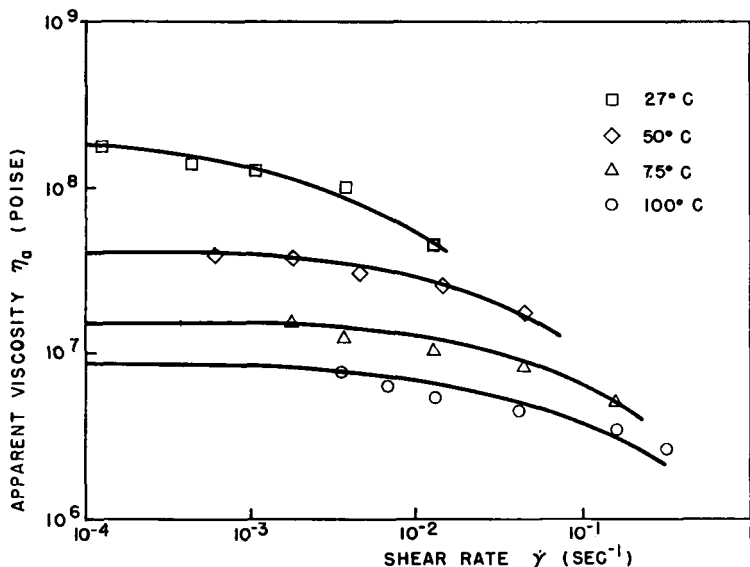Values of the zero shear viscosities for this and other polymers were es-

Fig. 1. Viscosities of polymer 3.

timated* and are given in Table II. Lower molecular weight polyiso-
prenes gave constant viscosities at various shear rates (i.e., the materials
were Newtonian under the conditions of test). Values of their viscosities
are given in Table III.

   * The estimation was performed visually, by using a French curve. It is realized that
the values quoted in Table II may have a random error of up to 50%, but this is not very
significant when compared with the range (about 8 decades) of the bulk viscosity meas-
urement.

TABLE II
Estimated Values at Zero Shear Viscosities for Polyisoprenes at Various Temperatures

Polymer no.	$\bar{M}_v$	Viscosities, poise			
		27°C.	50°C.	57°C.	100°C.
1	1.87×10^6	—	5×10^9	1.5×10^9	1×10^9
2	1.00×10^6	1×10^9	2×10^8	—	—
3	6.42×10^5	2.5×10^8	4×10^7	1.5×10^7	8.5×10^6
4	2.78×10^5	2.0×10^7	1.9×10^6	8.5×10^5	7.5×10^5

TABLE III
Viscosities of Low Molecular Weight Polyisoprenes at Various Temperatures

Polymer no.	$\bar{M}_v$	Viscosities, poise			
		27°C.	50°C.	75°C.	100°C.
5	8.87×10^4	—	—	1.55×10^4	8.85×10^3
6	4.56×10^4	1.20×10^4	1.85×10^3	6.55×10^2	3.75×10^2
7	2.30×10^4	2.5×10^2	8.0×10^1	4.1×10^1	2.5×10^1
8	5.81×10^3	7.9×10^1	2.2×10^1	8.8	3.8
Squalene	4.11×10^2	1.9×10^{-1}	8.5×10^{-2}	6.9×10^{-2}	2.8×10^{-2}

DISCUSSION

Variation of Viscosity with Molecular Weight

The equation

$$\eta = A \; \bar{M}_w{}^{3.4} \tag{9}$$

where η is the viscosity at zero shear rate, $\bar{M}_w$ is the weight-average molecular weight, and A is an experimentally determined constant, has been shown to apply for a number of polar and nonpolar polymers so long as $\bar{M}_w$ exceeds a critical value, generally $\sim 10^4$.[1a] A theoretical treatment[1a,11] is in good agreement.

By using the data of Tables II and III, equating $\bar{M}_v$ with $\bar{M}_w$ (since the polymers are almost monodisperse), and neglecting the values given for squalene ($\bar{M}_v = 4.11 \times 10^2$) and polymer 7 ($\bar{M}_v = 5.81 \times 10^3$), both of which are below the critical molecular weight, best straight lines were plotted through the remaining points by the method of least squares. The

TABLE IV
Values of Slopes of the Plots of log η vs. log $\bar{M}_w$

Temperature, °C.	Slope[a]
27	4.0 (±0.55)
50	3.98 (±0.21)
75	3.90 (±0.26)
100	3.93 (±0.28)

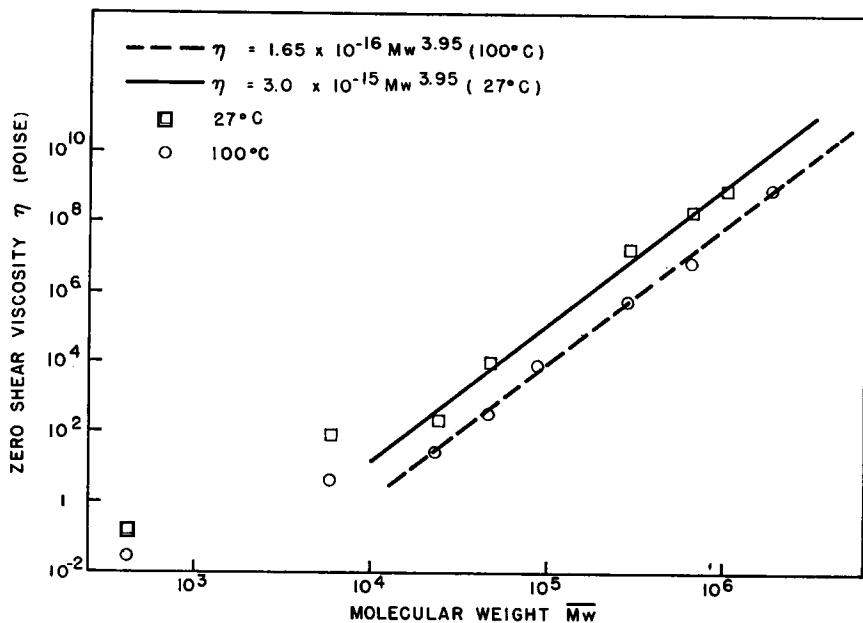[a] Values in parentheses are 95% confidence limits.

Fig. 2. Zero shear viscosities vs. molecular weight for polyisoprene at 27 and 100°C.

results at temperatures of 27 and 100°C. are shown in Figure 2 (the results at the other temperatures were similar) and values of the calculated slopes are given in Table IV.

Taking 3.9_5 as the mean slope, the values of A in eq. (9) may also be calculated from the mean (at any one temperature) of the values of log η and log $\bar{M}_w$. The equations given in Table V and plotted in Figure 2 were thus obtained. These results are in disagreement with eq. (9) in that they give a slope of 3.9_5 (± 0.2) rather than 3.4.

TABLE V
Variation of Zero Shear Viscosity of Polyisoprenes With Molecular Weight

Temperature, °C.	Equation
27	$\eta = 3.0 \times 10^{-15} \bar{M}_w{}^{3.9}{}_5$
50	$\eta = 5.5 \times 10^{-16} \bar{M}_w{}^{3.9}{}_5$
75	$\eta = 2.6 \times 10^{-16} \bar{M}_w{}^{3.9}{}_5$
100	$\eta = 1.6_5 \times 10^{-16} \bar{M}_w{}^{3.9}{}_5$

Before regarding this disagreement as proved, two possible sources of error should be considered.

(1) The value of the exponent in eq. (8) is wrong. This appears unlikely. The value given (0.728) is substantially higher than any value (0.650) which would allow the data in Table IV to fit eq. (9) within the 95% confidence limits.

(*2*) The zero shear viscosities estimated from Figure 1 and other similar figures and given in Tables II and III are inaccurate. This would appear more plausible. The zero shear viscosities measured at lower molecular weights are correct to within $\pm 10\%$, but errors of $\pm 50\%$ might not be impossible in estimating zero shear viscosities at higher molecular weights. However, if we assume the measured values at lower molecular weight to be correct and calculate values of the zero shear viscosities at high molecular weights using eq. (9), we obtain values of zero shear viscosities which are lower by up to an order of magnitude than measured apparent viscosities at observed shear rates.

We therefore conclude that polyisoprene constitutes an anomalous case as compared with numerous other polymers and that its zero shear viscosity may be expressed as

$$\eta = A \ \bar{M}_w{}^{3.95} \tag{10}$$

Variation of Bulk Viscosity with Shear Rate

An empirical relationship of the form

$$\eta_a/\eta = 1/[1 + K(\tau_1\dot{\gamma})^n] \tag{11}$$

where τ_1 is a relaxation time given by

$$\tau_1 = 12\eta\bar{M}_w/\rho\pi^2RT \tag{12}$$

where ρ is the density of the polymer, T is the absolute temperature, R is the gas constant, may be used to represent the shear behavior of many linear polymers, and the values $K = 0.6$ and $n = 0.75$ have been suggested as a universal relationship for all linear polymers.[22] In order to obtain values of K and n for the polymers studied here, the quantity $\log [(\eta/\eta_a) -1]$ was plotted against $\log \tau_1\dot{\gamma}$ for values of $\eta/\eta_a >1.05$. A best straight line may be drawn through these points by using the method of least squares,
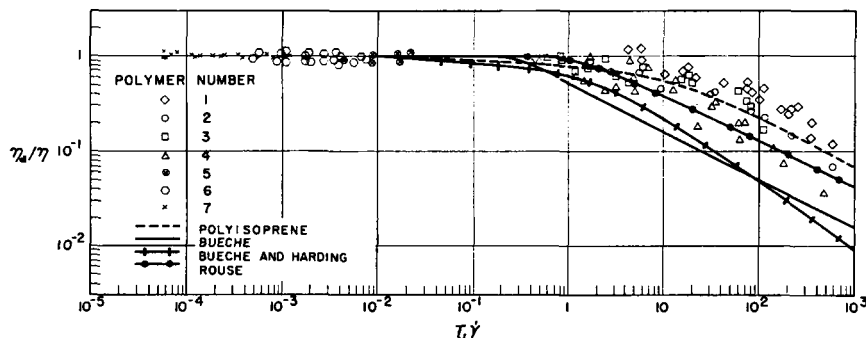

Fig. 3. Variation of bulk viscosity with shear rate for polyisoprene, determined experimentally and from theory according to eq. (13) and according to theories of Bueche,[17] Bueche and Harding,[22] and Rouse.[21]

and values of $K = 0.23$ and $n = 0.58$ were obtained. Thus the variation of bulk viscosity with shear rate is reasonably represented by the equation

$$\eta_a/\eta = 1/[1 + 0.23 \ (\tau_1\dot{\gamma})^{0.58}] \qquad (13)$$

Despite the considerable scatter (as shown in Fig. 3) these data differ appreciably from both the original Bueche theory[10] and from the previously suggested universal relationship.[22]

The data may also be compared with the relationship of Rouse.[21] This relationship was originally derived for materials under oscillating stress but by using the approximation of equivalence of shear rate and angular vibrational frequency[28] we may apply it to steady flow conditions.[29] Like Bueche's relationship it predicts $n = 0.5$, and, as may be seen from Figure 3, it does not adequately represent our data.*

Variation of Bulk Viscosity with Temperature

Theories of polymer flow[10] indicate that the viscosity of any polymeric material should be proportional to the exponential of the reciprocal absolute temperature, and since the zero shear viscosity of a polyisoprene sample is directly proportional to A [as defined in eq. (10) and tabulated in Table V], then we may expect

$$\log A \propto 1/T \qquad (14)$$

Figure 4 shows that this simple relationship does not hold. However, we may express the temperature relationship as

$$\log A = a + (b/T) + (c/T^2) + (d/T^3) \qquad (15)$$

where

$$a = -101.14$$

$$b = 8.999 \times 10^4$$

$$c = -3.19222 \times 10^7$$

$$d = 3.816 \times 10^9$$

Combined Equation

From eqs. (10) and (13)

$$\eta_a = A\bar{M}_w{}^{3.95}/[1 + 1.22 \ (A\dot{\gamma}/T)0.58 \ \bar{M}_w{}^{2.87} \times 10^{-5}] \qquad (16)$$

* In Figure 3, we have actually plotted η/η_a versus $2\tau_{1R}\dot{\gamma}$. This is because the Rouse theory uses a relaxation time τ_{1R} which is half the relaxation time used in the Bueche theory and defined by eq. (12). Thus, the plotted experimental points [having values of $\tau_1\dot{\gamma}$ calculated from eq. (12)] should all be shifted to the left by a factor of 2 when compared with the Rouse theory. Instead of this, for the sake of convenience, we have shifted the theoretical curve to the right by the same amount.
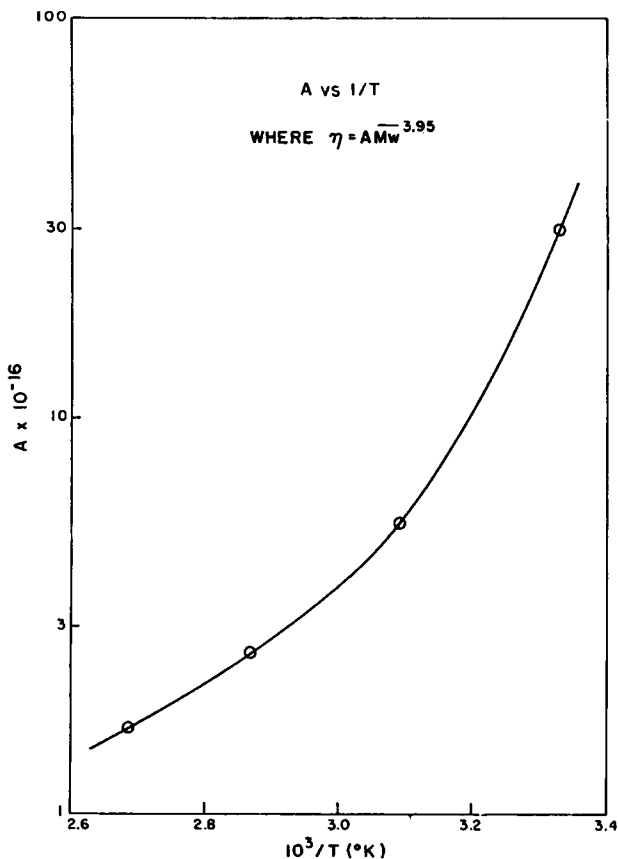
Fig. 4. Variation of zero shear viscosities with temperature.

This is a useful method for estimating the apparent viscosity of any monodisperse linear polyisoprene of about 90% cis-1,4 structure to about ± 20%. At high shear rates it will reduce to the expression

$$\eta_a = 0.2 \ A^{0.42}(T/\dot{\gamma})^{0.58}\bar{M}_w{}^{1.13} \times 10^4 \tag{17}$$

and at low shear rates it will, of course, reduce to eq. (10).

CONCLUSION

The following conclusions may be drawn from this work.

(1) Monodisperse linear polyisoprenes of about 90% cis-1,4 structure approach Newtonian behavior at low shear rates.

(2) The zero shear viscosities of these polyisoprenes are determined by their molecular weights according to the relationship

$$\eta = A\bar{M}_w{}^{3.9\mathstrut}$$

where

$$\log A = -101.14 + \frac{8.999 \times 10^4}{T} - \frac{3.19222 \times 10^7}{T^2} + \frac{3.816 \times 10^9}{T^3}$$

(3) At finite shear rates the apparent viscosities of polyisoprene obey the relationship

$$\eta_a = \frac{A \bar{M}_w^{3.9i}}{1 + 1.22 \, (A\dot{\gamma}/T)^{0.58} \bar{M}_w^{2.87} \times 10^{-5}}$$

APPENDIX

A mathematical treatment due to Bueche[17] gives a relationship, applying to all polymers, between the zero shear viscosities and the apparent viscosities at a finite shear rate $\dot{\gamma}$.

$$\eta_a/\eta = 1 - \frac{6}{\pi^2} \sum_{n=1}^{N} \frac{\dot{\gamma}^2 \, \tau_1^2}{n^2 \, (n^4 + \dot{\gamma}^2 \, \tau_1^2)} \left(2 - \frac{\dot{\gamma}^2 \, \tau_1^2}{n^4 + \dot{\gamma}^2 \, \tau_1^2} \right) \quad (18)$$

where

$$\tau_1 = 12 \, \bar{M}_w \eta / \rho \, \pi^2 R T$$

Values of η_a/η have been calculated for $0.05 < \tau_1\dot{\gamma} < 10^4$ and are given in Table VI.

TABLE VI

$\tau_1\dot{\gamma}$	η_a/η
0.05	0.995
0.1	0.988
0.4	0.841
0.7	0.656
1.0	0.525
2	0.354
4	0.253
10	0.160
50	0.0717
10^2	0.0507
3×10^2	0.0293
10^3	0.0160
3×10^3	0.00925
10^4	0.00507

The summation indicated in eq. (18) was made on an IBM 650 computer and continued until the sum term in eq. (18) was unchanged in its eighth significant figure. In the case of the final value (at $\dot{\gamma}\tau_1 = 10^4$) this required about four hundred terms.

The results are plotted in Figure 5. By using a simple two-parameter equation the relationship can be expressed as

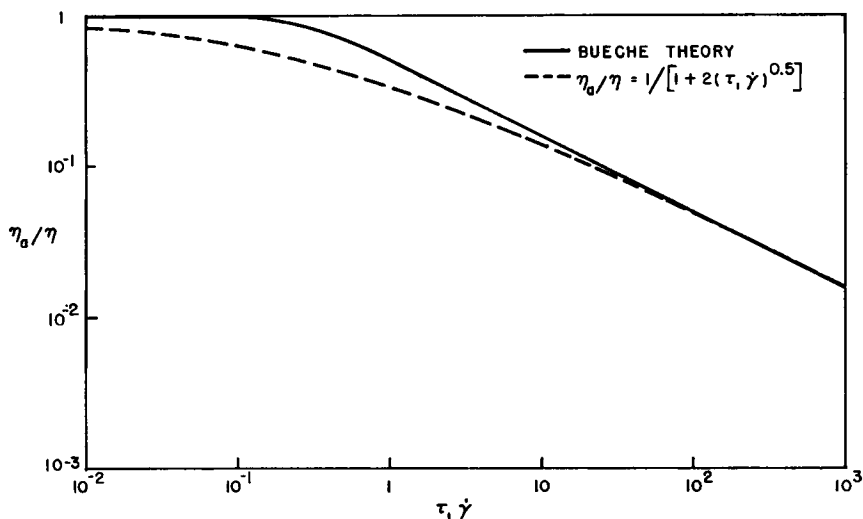$$\eta_a/\eta = 1/[1 + 2(\tau_1\dot{\gamma})^{0.5}] \quad (19)$$

Fig. 5. Theoretical values of the bulk viscosities of polymers.

although a fairly significant deviation is observed at intermediate values of $\tau_1\gamma$.

It will be observed that our values of η_a/η differ from those obtained by Bueche for $\tau_1\dot\gamma = 4$, and $\tau_1\dot\gamma = 50$ [which is the largest value of $\tau_1\gamma$ for which Bueche has taken the summation shown in eq. (18)]. When Bueche's values of η_a/η are plotted on double logarithmic paper they give a sigmoidal curve and suggest the possibility of a "second Newtonian viscosity" occurring at $\eta_a/\eta \sim 0.03$. In fact in our first computations we obtained such a second Newtonian viscosity extending from $\tau_1\dot\gamma \approx 500$ out to $\tau_1\dot\gamma = 10,000$. Increasing the accuracy of the computation continuously decreased the value of this second Newtonian viscosity. It is thus a mathematical artifact depending on the degree of accuracy of the summation, and for an exact summation it does not exist at all.

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Résumé

On a étudié l'influence du poids moléculaire, de la vitesse de cisaillement et de la température sur le comportement visqueux de plusieurs polyisoprènes linéaires, monodispersés contenant environ 90% de structure *cis* 1,4. Les viscosités situées entre 10^{10} et 10^5 poises ont été mesurées au moyen d'un viscosimetre a double cône et a plateau tandis que les viscosités situées entre 10^4 et 10^{-2} poises ont été mesurées au moyen d'un viscosimètre à cylindre tournant. Pour de tels polyisoprènes la variation de viscosité Newtonienne (à cisaillement nul) η avec le poids moléculaire moyen en poids dans le domaine de poids moléculaires situé entre 2×10^4 et 10^6 peut être représenter par $\eta = A \bar{M}_w{}^{3.95}$ où A est un paramètre dépendant de la température et donné par

$$\log A = -101.14 + \frac{8.999 \times 10^4}{T} - \frac{3.19222 \times 10^7}{T^2} + \frac{3.816 \times 10^9}{T^3}$$

On a également déterminé la variation de viscosité apparente η_a avec la vitesse de cisaillement $\dot{\gamma}$ et on peut formuler une équation combinée comme

$$\eta_a = A \bar{M}_w{}^{3.95} / [1 + 1.22 (A\dot{\gamma}/T)^{.58} \bar{M}_w{}^{2.87} \times 10^{-5}]$$

On compare cette équation avec d'autres expressions concernant la variation de viscosité avec le poids moléculaire, la température et la vitesse de cisaillement.

Zusammenfassung

Der Einfluss des Molekulargewichts, der Schergeschwindigkeit und der Temperatur auf das Viskositätsverhalten verschiedener linearer monodisperser Polyisoprene mit etwa 90% *cis*-1,4-Struktur wurde untersucht. Viskositäten von 10^{10} bis 10^5 Poise wurden in einem Doppelkegel-Plattenviskosimeter gemessen, während solche von 10^4 bis 10^{-2}

Poise mit einem Rotationszylinderviskosimeter gemessen wurden. Für solche Polyisoprene kann die Abhängigkeit der Newtonschen (Schub Null) Viskosität η, vom Gewichtsmittelmolekulargewicht im Molekulargewichtsbereich von 2×10^4 bis 10^6 durch $\eta = A\bar{M}_w{}^{3.95}$ wiedergegeben werden, wo A ist ein temperatur-abhängiger Parameter, gegeben durch

$$\log A = 101.14 + \frac{8.999 \times 10^4}{T} - \frac{3.19222 \times 10^7}{T^2} + \frac{3.816 \times 10^9}{T^3}$$

Weiters wird die Abhängigkeit der scheinbaren Viskosität η_a von der Schergeschwindigkeit $\dot{\gamma}$ bestimmt und damit eine kombinierte Gleichung formuliert

$$\eta_a = A\bar{M}_w{}^{3.95}/1 + 1.22\,(A\dot{\gamma}/T)^{0.58}\,\bar{M}_w{}^{2.87} \times 10^{-5}$$

Diese Gleichung wird mit anderen Ausdrücken für die Abhängigkeit der Viskosität von Molekulargewicht, Temperautur und Schergeschwindigkeit verglichen.