Rheological Properties of *cis*-Polybutadiene

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Synopsis

The steady-state viscosity of a number of *cis*-polybutadienes was determined as a function of shear rate and temperature by use of a capillary rheometer. Polymers investigated differed in molecular weight distribution and long chain branching. None of the polymers exhibited Newtonian behavior, even at the lowest shear rates attainable. Nevertheless, for polymers of similar molecular weight distribution and minimum branching, all the capillary viscometer data could be reduced to a single curve by a reduced variable treatment. The molecular weight shift function was found to be the same as for polymers exhibiting a Newtonian flow range, i.e., a 3.4th power law in weight-average molecular weight. Broadening the molecular weight distribution or increasing the degree of long-chain branching led to increasingly pronounced non-Newtonian behavior. Tensile creep experiments showed nonlinear viscoelastic behavior for all polymers studied, even at small strains. This behavior was most pronounced in the more highly branched polymers. At very low stresses some of these polymers exhibited extremely high viscosities, the strain being almost completely recoverable. Under larger stresses the viscosity of these rubbers dropped several decades and in the capillary extrusion experiments these polymers flowed readily. This is the same behavior observed previously in high molecular weight branched (multichain) narrow distribution polybutadienes. It is tentatively explained by a constraint of the branch points on the slippage of chain entanglements. The fact that all *cis*-polybutadienes exhibit this behavior, while linear polybutadienes made by organolithium initiation do not, suggests that all *cis*-polybutadienes may be branched to some extent.

I. INTRODUCTION

In two earlier reports[1,2] we described the rheological properties of linear and branched, narrow molecular weight distribution polybutadienes prepared by initiation with *n*-butyllithium. It was shown that these polymers behave in a characteristic manner quite unlike that of most polymers described in the literature, which do not exhibit similarly narrow distributions. Compared to *n*-butyllithium polybutadiene, *cis*-polybutadiene is not a narrow distribution elastomer, nor is freedom from long-chain branching assured in this rubber. Certain samples of this polymer exhibit branching introduced deliberately during or after polymerization, but unlike in the example of the *n*-butyllithium-initiated multichain polymers,[2] control over the branched structure is limited. For these reasons the rheological behavior of *cis*-polybutadienes is more complex and more difficult to interpret. The present report deals with a detailed study of the rheological behavior of various types of *cis*-polybutadienes made by the Phillips process utilizing iodine-containing catalysts.

II. EXPERIMENTAL

Polymers

It will prove convenient to group the polymers studied as follows: class
I: polymers of fairly narrow and similarly shaped molecular weight dis-
tribution containing a minimum of long chain branching, for which frac-
tionation and sedimentation velocity studies indicate a ratio of weight-
average to number-average molecular weight between 2 and 4; class II:
polymers of greatly broadened molecular weight distribution; class III:
polymers for which independent evidence of long chain branching exists
from their method of preparation, which evidence is confirmed by the
rheological behavior.

It is realized that the above classification is essentially arbitrary, since
no sharp lines of demarcation can be drawn, particularly between classes I
and III. This is because all *cis*-polybutadienes appear to be branched to
some extent and small amounts of crosslinking introduced in finishing the
polymer after polymerization may add to the initial branching to further
diminish the difference. Table I gives inherent viscosities determined in
toluene at 25°C. and viscosity-average molecular weights calculated from
correlations with light-scattering molecular weight data on fractions of
Class I polymer:

$$[\eta] = 6.68 \times 10^{-4}\bar{M}_w^{0.65} \tag{1}$$

$$\eta_{inh} = 6.93 \times 10^{-4}\bar{M}_w^{0.65} \tag{1a}$$

TABLE I
Inherent Viscosity and Molecular Weight Data[a]

Polymer	Class	η_{inh}	$\bar{M}_v/1000$
A	I	0.85	63
B		1.63	174
C		1.95	230
D		2.05	249
E		2.10	257
F		2.11	261
G		2.41	319
H		2.52	342
I		2.66	370
J		2.82	404
K	II	3.49	560
L	III	1.84	—
M		1.94	—
N		2.18	—
O		2.33	—
P		2.54	—
Q		2.43	—
R		2.53	—

[a] All polymers gel-free.

No attempt was made to calculate $\bar{M}_v$ for the class III polymers, since branching depresses the solution viscosity, which would lead to unrealistically low values of $\bar{M}_v$.

Viscosity Measurements

Two methods of determining rheological properties were used: capillary rheometry and tensile creep. The capillary extrusion rheometer was similar to the well known CIL (Canadian Industries, Ltd.) instrument. In determinations with the capillary rheometer, polymer is extruded through a die of known dimensions by nitrogen pressure. The shear stress is calculated from the pressure and the die dimensions and the shear rate from the amount of extrudate collected in unit time under steady-state conditions. In calculating the shear stress the applied pressure must be corrected for the pressure drop at the capillary entrance. The so-called Rabinowitsch[3] correction is applied in calculating the rate of shear. It yields the maximum shear rate at the wall. Details of these calculations have been reviewed recently by Philippoff and Gaskins.[4]

Most of the data were obtained with steel capillary dies of L/R ratio of about 10. Very low shear points were measured with glass capillaries of $L/R \cong 100$. The dies used to calculate the entrance correction had L/R ratios ranging from 0.3 to 1. The size of the entrance corrections was 9–12% for class I polymers, about 25% for class II, and 13–20% for class III.

The experimental technique used in the tensile creep was as follows. Thin strips (width 0.125 in., thickness 0.020–0.030 in., length 1.0–1.5 in.) of polymer were clamped in place in glass tubes positioned in a thermostated water bath. Two marks were placed on the strip, one at the top clamp and the other about 1.25 in. lower. Various weights could be attached below the second mark. At the beginning of the test the positions of the two marks were determined with a cathetometer while the strip was fully extended, but with the weight supported by a glass piston. The piston was then lowered rapidly and the displacement of the lower mark followed with the cathetometer. After the strip was extended the desired amount, the strip was cut at the bottom gage mark, removed from the tube and allowed to recover in horizontal position. The amount of recovery was determined by measuring the distance between the marks after 24 hr., or longer if subsequent measurements showed further recovery.

III. RESULTS AND DISCUSSION

Melt Viscosity Data

The shear stress versus shear rate data obtained by extrusion rheometry are given in full in Table II. The appearance of extrudate roughness is recorded by footnotes. The onset of extrudate roughness was not accompanied by a discontinuity in the flow curve or its first derivative, as would be

TABLE II
Capillary Extrusion Data

Polymer	Temperature, °K.	$f \times 10^{-6}$ dynes/cm.^{2}	$\dot{s}$, sec.$^{-1}$	Polymer	Temperature, °K.	$f \times 10^{-6}$, dynes/cm.^{2}	$\dot{s}$, sec.$^{-1}$
A	379	0.131	19.8	D	300	0.34	0.18
		0.22	41.3			0.65	0.49
		0.40	88.5			0.99	1.02
		0.57	129			1.36	1.71
		0.75	196			1.52	2.06
B	379	0.14	0.81			1.63	2.54
		0.36	2.83			1.97ᵃ	4.20
		0.49	4.66			2.27	6.49
		0.72	8.33	D	373	0.20	0.35
		0.88	11.1			0.34	0.78
		1.09	15.9			0.52	1.44
		1.25	20.2			0.66	2.22
		1.41	25.3			0.86	3.37
		1.63	33.8			0.99	4.46
		1.80ᵃ	41.4			1.23	6.66
		2.02	53.1			1.34	8.02
		2.16	62.6			1.51	10.2
		2.38	79.4			1.63	12.5
		2.53	98.6			1.89ᵃ	17.5
		2.72	117			2.03	21.9
C	300	0.66	0.58			2.20	27.1
		0.97	1.24			2.37	34.2
		1.20	1.95			2.55	43.3
		1.28	2.29			2.68	52.3
		1.67	4.40			2.86	66.2
		1.83	5.58			2.98	76.3
		1.98	8.02	E	300	0.64	0.32
		2.27ᵃ	10.4			0.96	0.68
		2.45	13.9			1.08	0.83
		2.61	16.9			1.28	1.32
		2.96	23.0			1.48ᵃ	1.76
C	373	0.19	0.52			1.59	2.22
		0.34	1.15			1.81	3.03
		0.53	2.22			1.91	3.69
		0.71	3.62			2.11	4.89
		0.87	5.12			2.25	5.90
		1.17	9.06			2.59	9.61
		1.37	12.4			2.73	11.0
		1.52	15.7			2.88	13.4
		1.76	22.4	E	379	0.35	0.79
		1.85	25.1			0.52	1.43
		2.11ᵃ	43.5			0.69	2.58
		2.18	40.4			0.85	3.69
		2.46	63.1			0.99	4.99
		2.50	64.8			1.18	6.81
		2.75	93.0			1.35	9.49
		2.90	114			1.53	12.5
		3.05	136			1.68ᵃ	15.7

TABLE II (*continued*)

Polymer	Temperature, °K.	$f \times 10^{-6}$ dynes/cm.²	$\dot{s}$, sec.⁻¹	Polymer	Temperature, °K.	$f \times 10^{-6}$, dynes/cm.²	$\dot{s}$, sec.⁻¹
		1.90	20.7			1.71	3.10
		2.03	24.5			1.87ᵃ	3.81
		2.21	31.0			1.97	4.97
		2.35	36.3			2.16	6.05
		2.53	45.9			2.27	8.16
		2.69	55.4	H	352	0.69	0.57
F	379	0.32	0.52			0.86	1.01
		0.52	1.10			1.02	1.42
		0.65	1.79			1.18	1.90
		0.83	2.53			1.34	2.16
		0.97	3.47			1.53	3.07
		1.19	5.01			1.71ᵃ	4.03
		1.31	6.47			1.84	4.96
		1.52ᵃ	8.34			1.97	6.18
		1.62	9.74			2.16	8.17
		1.84	12.7			2.26	9.87
		1.98	15.3	H	373	0.50	0.56
		2.20	19.5			0.65	0.87
		2.32	22.9			0.80	1.23
		2.54	28.9			1.14	2.52
		2.65	32.9			1.31	3.27
G	379	0.68	1.13			1.48	4.20
		0.81	1.54			1.64	5.19
		1.00	2.21			1.79	6.53
		1.18	3.19			1.96ᵃ	8.31
		1.32	3.96			2.13	10.8
		1.52	5.37			2.27	12.9
		1.68ᵃ	7.38			2.51	18.4
		1.89	9.03			2.63	21.2
		1.99	10.3			2.75	21.8
		2.23	14.0	H	442	0.33	0.56
		2.53	19.5			0.50	1.17
		2.83	29.1			0.69	1.81
H	300	1.65	1.15			0.84	2.48
		1.82	1.36			1.00	3.82
		1.94ᵃ	1.84			1.12	4.97
		2.15	2.58			1.36	7.18
		2.25	2.83			1.50	8.70
		2.45	3.85			1.66	11.9
		2.78	5.74			1.84	14.4
		2.88	6.59			1.96ᵃ	17.9
		3.10	7.80			2.13	21.5
		3.24	9.79			2.29	27.8
		3.37	12.2			2.44	33.9
H	339	1.04	1.00	I	379	0.35	0.27
		1.23	1.33			0.53	0.46
		1.35	2.14			0.69	0.76
		1.53	2.40			0.87	1.07

(*continued*)

TABLE II (*continued*)

Poly-mer	Tempera-ture, °K.	$f \times 10^{-6}$, dynes/cm.²	$\dot{s}$, sec.⁻¹	Poly-mer	Tempera-ture, °K.	$f, \times 10^{-8}$, dynes/cm.²	$\dot{s}$, sec.⁻¹
		1.06	1.56			1.49	41.1
		1.24	2.07			1.71	58.1
		1.36	2.52			1.77	65.2
		1.59	3.36			2.01	90.7
		1.72ᵃ	3.95	M	373	0.47	0.94
		1.90	4.73			0.64	1.80
		2.07	5.97			0.79	2.56
		2.29	7.50			0.93	3.90
		2.39	8.47			1.05	4.89
		2.63	11.2			1.23	7.30
		2.74	13.4			1.55ᵃ	12.0
J	379	0.29	0.14			1.69	15.0
		0.51	0.30			1.85	18.6
		0.64	0.52			1.96	21.8
		0.82	0.73			2.15	28.2
		0.96	1.19			2.29	33.7
		1.18	1.59			2.45	41.0
		1.33	2.10			2.53	44.1
		1.50	2.43			2.80	56.7
		1.65ᵃ	3.12	N	373	0.87ᵃ	2.09
		1.82	3.94			1.02	3.07
		1.97	4.77			1.23	4.68
		2.19	5.93			1.36	5.76
		2.33	7.33			1.54	8.35
		2.54	9.00			1.71	10.3
		2.63	10.7			1.78	11.8
K	379	0.44ᵃ	0.76			2.01	16.3
		0.59	0.88			2.38	27.0
		0.73	1.47			2.67	43.2
		0.91	2.34	O	300	0.33	0.025
		1.05	3.54			0.68	0.088
		1.18	4.53			1.00ᵃ	0.25
		1.32	5.75			1.35	0.51
		1.49	7.79			1.65	0.94
		1.61	10.3			1.98	1.54
		1.77	12.4			2.32	2.60
		1.89	15.3	O	328	0.326	0.054
		2.06	19.1			0.64	0.23
		2.19	23.3			0.95ᵃ	0.59
		2.36	25.7			1.29	1.16
L	373	0.24ᵇ	0.41			1.61	2.10
		0.50	3.01			1.92	3.59
		0.61	3.79			2.24	5.67
		0.71	6.61			2.55	8.28
		0.83	9.31			2.80	11.4
		0.98	15.1	O	349	0.315	0.085
		1.20	25.5			0.63	0.34
		1.24	25.9			0.95	0.95
		1.46	41.7			1.27ᵃ	1.77

TABLE II (*continued*)

Polymer	Temperature, °K.	$f \times 10^{-6}$, dynes/cm.²	$\dot{s}$, sec.$^{-1}$	Polymer	Temperature, °K.	$f \times 10^{-6}$, dynes/cm.²	$\dot{s}$, sec.$^{-1}$
		1.57	3.29			1.18	2.95
		1.91	5.44			1.30	2.93
		2.21	8.82			1.46	3.78
		2.54	13.4			1.58	4.91
		2.70	16.3			1.74	5.82
O	373	0.103	0.0156			1.88	7.51
		0.136	0.027			2.03	8.78
		0.17	0.049			2.16	11.7
		0.325	0.119			2.35	14.0
		0.33	0.127			2.58	15.2
		0.66	0.58			2.65	19.6
		1.00	1.60	R	300	0.36	0.033
		1.32ᵃ	2.91			0.78	0.142
		1.65	4.97			1.01	0.25
		1.97	7.84			1.37	0.45
		2.33	12.9			1.70ᵃ	0.80
		2.62	18.5			2.12	1.42
P	373	0.32	0.27			2.45	2.29
		0.46	0.46			2.77	3.53
		0.63ᵃ	0.83	R	373	0.039	0.0062
		0.91	1.76			0.072	0.0165
		1.11	2.57			0.108	0.039
		1.20	3.15			0.147	0.055
		1.53	5.63			0.177	0.087
		1.72	7.31			0.36	0.224
		1.83	8.10			0.37	0.25
		2.17	13.7			0.68	0.66
		2.34	19.0			1.03	1.48
		2.47	20.2			1.41	2.77
		2.67	25.7			1.75ᵃ	4.34
Q	373	0.61ᵃ	0.88			2.10	7.21
		0.72	0.77			2.43	11.3
		0.90	1.31			2.80	17.3
		1.02	1.52				

ᵃ First appearance of extrudate roughness.
ᵇ Observation of roughness not made.

the case in true melt fracture. Data on rough extrudates were, therefore, used in correlations with temperature, shear rate, and molecular weight. The apparent freedom from complications arising from this phenomenon is further evidence for the general validity of the data.

Effect of Temperature on Melt Viscosity

The dependence of viscosity on temperature for *cis*-polybutadienes is found to be independent of shear stress or branching of the polymer. Figure 1 shows the success of temperature superposition for the rheological

curves of three typical (class I) polymers. The data have been reduced to 100°C. (373°K.). The reduction is performed by dividing the shear rate at each stress by a shift factor a_T, defined here as the ratio of the viscosity
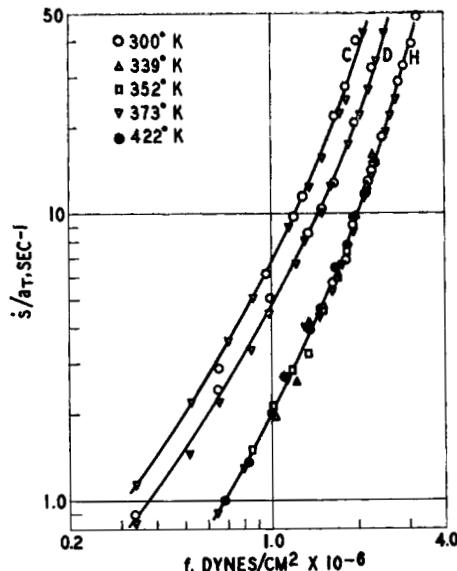
Fig. 1. Temperature superposition of rheological curves (reduced to 373°K.).
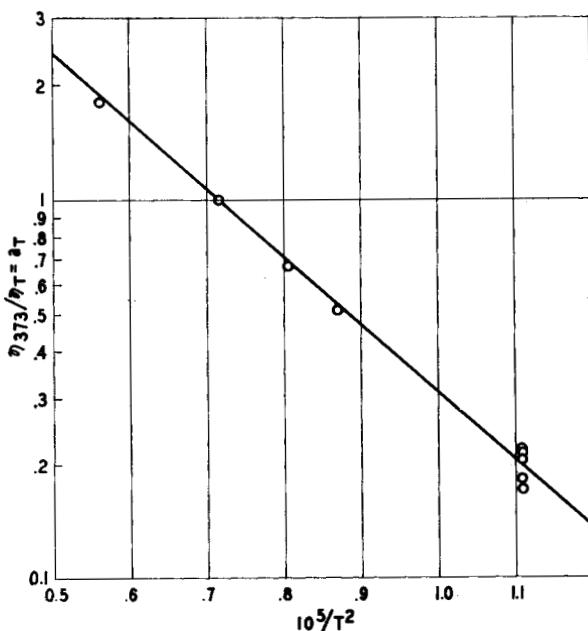
Fig. 2. Dependence of viscosity on temperature.

at the reference (373°K.) temperature to the viscosity at temperature T:

$$a_T = \eta_{373}/\eta_T \tag{2}$$

The shift factors necessary to produce superposition are shown in Figure 2 as a function of T^2. The line is represented by the equation

$$\log a_T = 1.29 - (1.8 \times 10^5/T^2) \tag{3}$$

which is of the general form proposed by Fox and Loshaek.[5] Superposition by the Williams, Landel, and Ferry equation[6] is not applicable to the data, because the temperatures in question are more than 100°C. above the glass transition (161°K. for *cis*-polybutadiene). A comparison of the temperature dependence for class III (more highly branched) polymers with that of class I is shown in Table III.

TABLE III

Polymer	Temperature, °K	a_T	a_T for Class I (from Fig. 2)
O	373	1.00	1.00
	349	0.690	0.650
	328	0.425	0.450
	300	0.180	0.195
R	300	0.180	0.195

Shear Rate–Molecular Weight Dependence of Viscosity

Unlike the *n*-butyllithium-initiated polybutadienes, which exhibit Newtonian flow up to relatively high shear rates, *cis*-polybutadienes do not exhibit a demonstrable Newtonian flow range. The existence of a true zero-shear viscosity related to weight-average molecular weight by the well known 3.4 power law is, therefore, in doubt. However, for polymers of similar molecular weight distribution and branching (class I) the following reduced variable treatment is, nevertheless, highly successful.

F. Bueche[7] has proposed that the ratio of the viscosity at any given shear rate to its zero-shear viscosity (η/η_0) is a function of the product $\dot{s}\eta_0$, where $\dot{s}$ is the shear rate. Since η_0 is in effect a molecular weight shift factor, being proportional to $\bar{M}_w{}^{3.4}$, it is suggested that η/a_M should be a universal function of $\dot{s}a_M$ for polymers of different molecular weights even if the molecular weight shift factor a_M can no longer be identified with a zero-shear viscosity. To generalize this relationship to include the effect of temperature we merely introduce the temperature shift factor a_T:

$$\eta a_T/a_M = f(a^{-1}_T a_M \dot{s})$$

This correlation holds for the class I polymers (A–J) with remarkable accuracy (Fig. 3). It furthermore turns out that a_M is related to molecular weight by the 3.4th power law, just as in the case of polymers exhibiting Newtonian flow. A plot of a_M versus molecular weight is shown in Figure
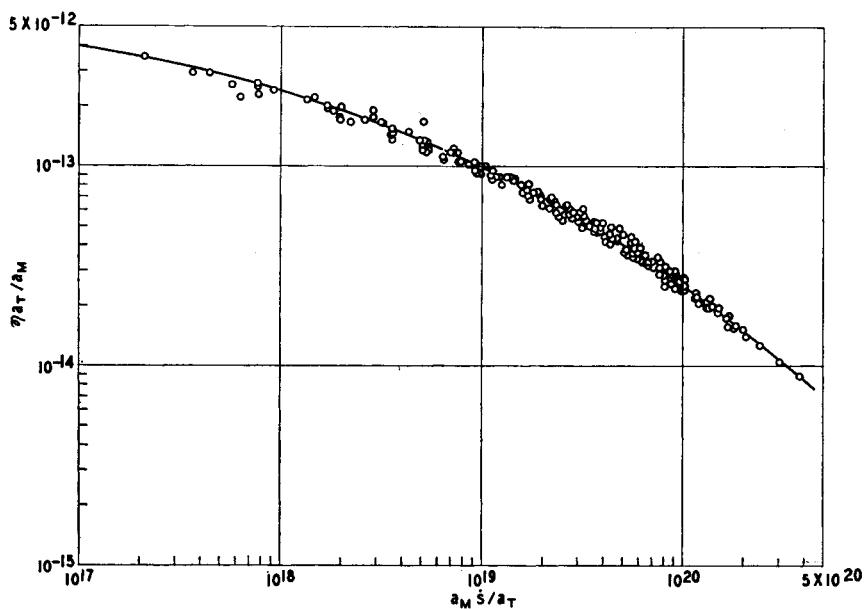
Fig. 3. Viscosity vs. rate of shear for class I polymers. Reduced variable treatment.
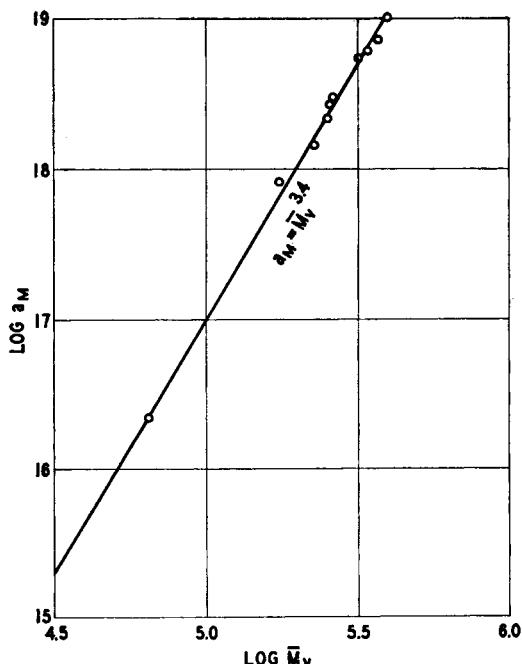
Fig. 4. Molecular weight dependence of viscosity for class I cis-polybutadienes.

4. The viscosity-average molecular weights were used in this correlation, rather than the usual weight-average. The distinction between $\bar{M}_w$ and $\bar{M}_v$ may, however, be ignored here, since for similar distributions the two averages will differ only by a constant factor. The correlation is, therefore, not affected.

Included in Figure 3 are data for different temperatures shifted to 100°C. At 100°C., a_T is equal to unity and the plot gives the viscosity–shear rate-molecular weight relation directly. The plot can, in principle, be used to obtain $\bar{M}_v$ from a single melt viscosity determination.

Broad distribution and more highly branched polymers do not follow the relationship of Figure 3, but display an even greater tendency toward non-Newtonian flow. Undoubtedly, even in the present correlation some of the scatter of the points is caused by minor differences in molecular weight distribution and branching rather than experimental error.

Broad Distribution Polymers

Polymer K was prepared by supplying an extremely high molecular weight fraction to a typical class I *cis*-polybutadiene. The composition of this polymer was

$$w_1 = 0.16, \; \eta_{\text{inh}_1} = 10.5, \; \bar{M}_{v_1} = 3{,}070{,}000$$

$$w_2 = 0.84, \; \eta_{\text{inh}_2} = 2.15, \; \bar{M}_{v_2} = 268{,}000$$
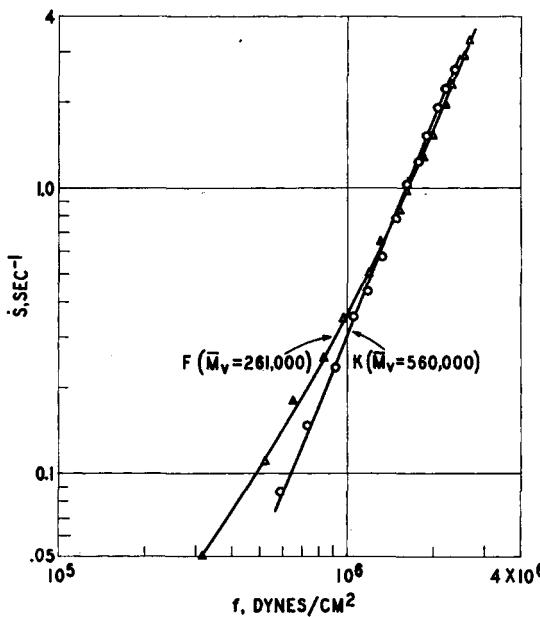
Fig. 5. Comparison of class I and class II polymers, temperature 379°K. (Note close correspondence of curves at the higher shear rates in spite of molecular weight difference.

where w_1 and w_2 are the weight fractions of the two main fractions making up the whole sample. Figure 5 compares the rheological curve of this bimodal distribution polymer with that of polymer F. The greatly increased shear response, or non-Newtonian flow, for the broad, bimodal distribution polymer is obvious. In spite of its very high mean molecular weight the bimodal polymer is less viscous at high shear rates than the lower molecular weight normal distribution rubber. At low shear rates the relative melt viscosities of the two polymers are reversed.

Long-Chain Branching

Studies of model branched narrow distribution polybutadienes have shown that long-chain branching has a pronounced effect on the rheological curve.[2] Whereas the zero-shear viscosity may be raised or lowered as a result of branching, depending on the molecular weight, the effect on shear response is always to increase it, i.e., to render the flow increasingly non-Newtonian. For polymers of high ($\bar{M}_w \geqslant 300,000$) molecular weight we would expect the zero-shear viscosity to be raised relative to the linear polymer, but above a sufficiently high shear rate lower viscosities than for linear polymer would be expected.

The cis-polybutadienes of class III were, without exception, prepared by methods insuring or at least favoring the introduction of long chain branches into the molecule. Shear response curves for some of these polymers are shown in Figures 6 and 7 with comparable curves for class I polymer
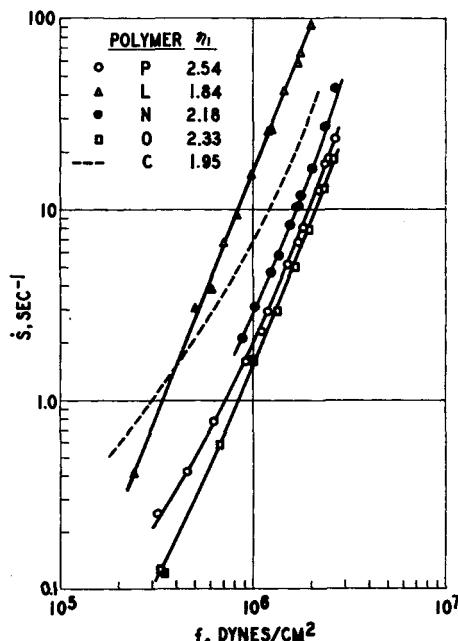
Fig. 6. Comparison of class I and class III polymers; temperature 373°K.
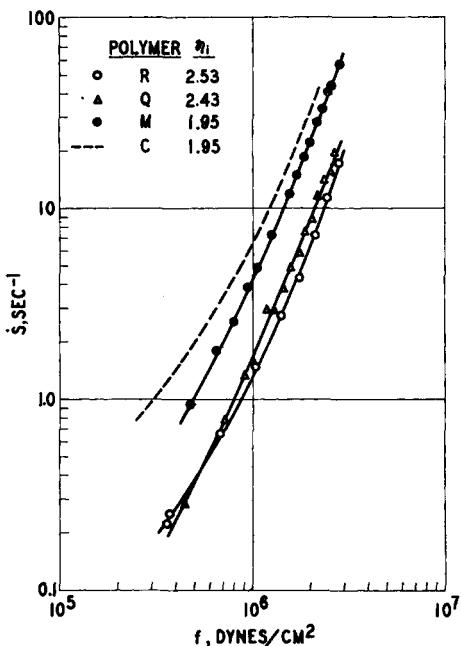
Fig. 7. Comparison of class I and class III polymers; temperature 373°K.

shown by dashed lines.   The increasingly non-Newtonian character of the more highly branched polymers is apparent.   For the reason that the polymers represent somewhat different molecular weight distributions and degrees of branching, a more detailed analysis of the data is not possible.

Tensile Creep

The tensile creep experiments were performed originally in an attempt to attain lower shear stresses than in the capillary viscometer and, thereby, arrive at Newtonian viscosities.   This, however, proved impossible. The creep curves obtained displayed nonlinear viscoelastic behavior down to the lowest stresses experimentally attainable, with viscosities rising to extremely high values as the applied stress was decreased.   This behavior is illustrated in Figures 8 and 9.   These show the apparent compliance J as a function of time at various applied stresses:

$$J \equiv \Delta l A_0 / l_0 F$$

where Δl is the elongation, F the load, l_0 the original length, and A_0 the cross section of the sample.   For runs in which the fractional extension $\Delta l / l_0$ did not exceed 10%, viscosities were calculated by the permanent set method:

$$\eta = F l_0 t / 3 A_0 \Delta l$$

where Δl is now the amount of permanent, nonrecoverable deformation after a creep experiment of duration t.   Since the shear rate is not well defined in tensile creep experiments, we have plotted the creep viscosities of some of the polymers, along with the capillary extrusion data against shear
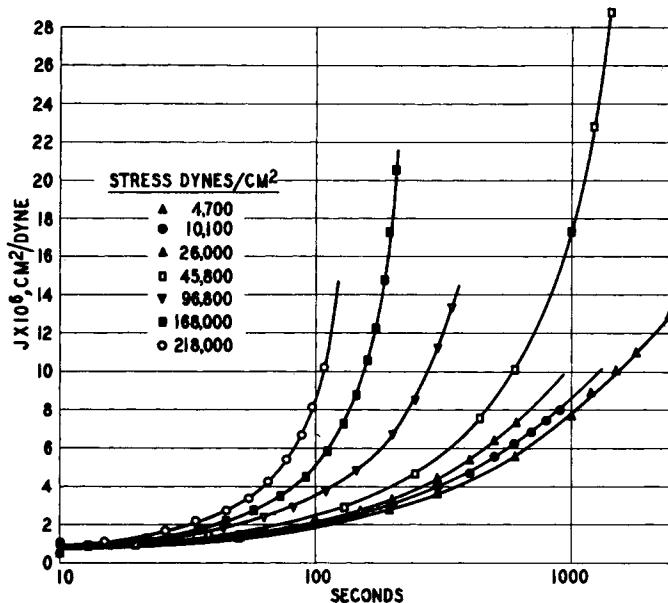

Fig. 8. Tensile creep as a function of stress at 300°K.; polymer H.
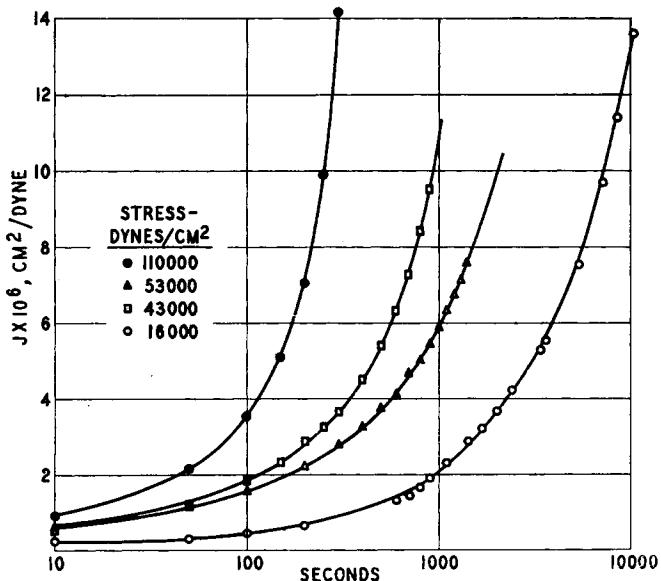
Fig. 9. Tensile creep as a function of stress at 300°K., polymer M.

stress (Fig. 10). The creep viscosities were placed at the value of the maximum shear stress, i.e., half the tensile stress. This figure again demonstrates the lack of a Newtonian flow range.

The results can be explained qualitatively by the existence of an easily disrupted structure. Although relatively unknown in amorphous, unfilled polymers, it is not a new effect having been described by Plazek and co-
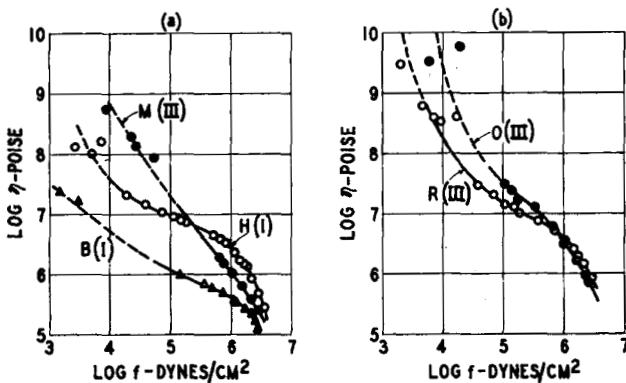
Fig. 10. Viscosity from creep and capillary extrusion data as a function of shear stress at 300°K. (Note the extremely high viscosities of polymers M, O, and R at the lowest stresses, a result of increased branching).
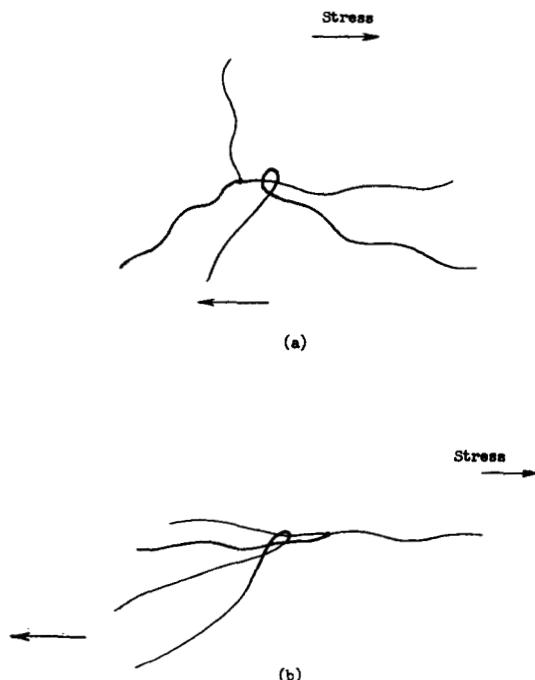
Fig. 11. Schematic representation of branching-entanglement interaction (hypothetical).

workers[8] for several systems, including a high molecular weight polymethyl-siloxane.[9]   Its origin in amorphous polymers is not known.

It seems clear that the behavior described here is related to the presence of long-chain branches in the polymer molecules.   This belief is based on the following evidence reported by us earlier.[2]   The n-butyllithium-initi-ated polybutadienes up to 600,000 molecular weight do not exhibit this be-havior as long as degradation is carefully avoided.   On the other hand polybutadienes of controlled, branched structure (trichain stars) do show the effect at sufficiently high molecular weight, i.e., above 200,000.   In the present study the class III polymers show the effect most dramatically.   This is clearly shown by a comparison of Figures 8 and 9 and the viscosity curves of Figure 10a for polymers H and M.   The latter, while lower in solution viscosity, is more highly branched.   It exhibits higher creep vis-cosities and a more pronounced dependence on stress.

We may visualize the effect of long-chain branching as an impediment to the slippage of entanglements which decreases with increasing stress.   At higher stresses the conformance of our data on class I cis-polybutadiene with the $\bar{M}_w{}^{3.4}$ power law indicates that substantially normal entanglement coupling prevails.   At low stresses, however, structures such as shown in Figure 11a could be expected to increase resistance to flow, requiring ex-penditure of additional work to overcome this resistance by an untangling effect (Figure 11b).   In the more highly branched systems, class III cis-polybutadiene or the trichain polybutadienes, some of the effect persists to higher shear rates and contributes to making the flow increasingly non-Newtonian over the entire flow range.

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Résumé

On a déterminé la viscosité à l'état stationnaire d'une certain nombre de cis-poly-butadiènes en fonction de la vitesse de cisaillement et de la température, en utilisant un rhéomètre à capillaire.   Les polymères étudiés différaient par la distribution des poids moléculaires et la ramification des longues chaînes.   Aucun des polymères ne montrait un comportement Newtonien, même aux plus basses vitesses de cisaillement

possibles. Néanmoins, pour des polymères avec une distribution de poids moléculaires analogue et un minimum de ramification, toutes les données des viscosimètres à capillaire pourraient être ramenées à une simple courbe en réduisant les variables. On a trouvé que la fonction de glissement du poids moléculaire était la même que pour des polymères possédant un domaine d'écoulement Newtonien, c.à.d. une puissance de 3.4 pour le poids moléculaire moyen en poids. Si on étend la distribution des poids moléculaires ou si on augmente le degré de ramification des longues chaines, on aboutit à un comportement de plus en plus éloigné de celui prévu par Newton. Des expériences d'écoulement par traction montrent un comportement viscoélastique non-linéaire pour tous les polymères étudiés, même pour des petites tensions. Ce comportement est le plus prononcé dans le cas les polymères les plus ramifiés. Sous de très faibles tensions, quelques-uns de ces polymères sont caractérisés par des viscosités extrêmement élevées, la tension étant presque complètement recouvrable. Sous de plus grandes tensions, la viscosité de ces caoutchoucs tombent de plusieurs décades et dans les expériences d'extrusion capillaire, ces polymères s'écoulent facilement. Nous sommes en présence ici d'un comportement analogue à celui observé auparavant dans le cas des polybutadiènes à haut poids moléculaire ramifiés (plusieurs chaînes) et à distribution étroite, ce qu'on a essayé d'expliquer par une contrainte des sites de ramification sur les glissements des enchevêtrements de la chaîne. Le fait que les *cis*-polybutadiènes présentent ce comportement alors que les polybutadiènes linéaires obtenus par initiation par les organolithiens ne le suivent pas, suggéré que tous les *cis*-polybutadiènes doivent être ramifiés jusqu'à un certain point.

Zusammenfassung

Die Viskosität einer Reihe von *cis*-Polybutadienen im stationären Zustand wurde als Funktion der Schergeschwindigkeit und der Temperatur mit einem Kapillarrheometer bestimmt. Die untersuchten Polymeren unterscheiden sich durch ihre Molekulargewichtsverteilung und ihre Langkettenverzweigung. Nicht einmal bei den niedrigsten erreichbaren Schergeschwindigkeiten zeigten die Polymeren Newton'sches Verhalten. Nichtsdestoweniger konnten für Polymere mit ähnlicher Molekulargewichtsverteilung und minimaler Verzweigung alle Kapillarviskosimetriedaten auf eine einzige Kurve mit reduzierten Variablen zurückgeführt werden. Die Molekulargewichtsverschiebungsfunktion war dieselbe wie bei einem Newton-Fliessbereich, d.h. ein 3,4-Potenzgesetz für das Gewichtsmittel des Molekulargewichts. Eine Verbreiterung der Molekulargewichtsverteilung oder ein Anwachsen des Langkettenverzweigungsgrades führte zu einem zunehmenden Abweichen vom Newton'schen Verhalten. Kriechversuche zeigten sogar bei geringer Dehnung ein nicht-lineares viskoelastisches Verhalten aller untersuchten Polymeren. Dieses Verhalten war bei den höher verzweigten Polymeren am ausgeprägtesten. Bei sehr geringer Spannung zeigten einige Polymere extrem hohe Viskosität; die Verformung bildet sich fast vollständig wieder zurück. Unter grösserer Spannung nimmt die Viskosität dieser Kautschuke um einige Dekaden ab, und bei den Kapillarextrusionsversuchen trat ein leichtes Fliessen der Polymeren auf. Genau dasselbe Verhalten wurde früher bei hochmolekular verzweigten (Vielketten-) Polybutadienen enger Verteilung beobachtet. Das wird versuchsweise durch eine Behinderung des Gleitens der Kettenverschlingungen durch die Verzweigungspunkte erklärt. Die Tatsache, dass alle *cis*-Polybutadiene dieses Verhalten zeigen, hingegen nicht die linearen durch Organolithiumstart erzeugten Polybutadiene, spricht dafür, dass alle *cis*-Polybutadiene bis zu einem gewissen Grad verzeigt sind.