Figure 4. Young's Modulus Characteristics of Polybutadiene and Butadiene-Isoprene (75/25)

Polymerization temperature 10° and −40° C.

polybutadienes made at 10° and −40° C., respectively. The 10° polymer is similar to their pattern at 50° C. (1) and shows two dense equatorial spots. The −40° C. polybutadiene not only shows the equatorial spots but other dense regions appear on the layer lines, indicating a substantially more oriented polymer. It seems reasonably clear then that increased linearity attends lower polymerization temperatures with polybutadiene.

Butadiene-Isoprene. If the loss of low temperature resistance of polybutadiene when made at lower polymerization temperatures was due to the formation of more linear polymeric chains, the introduction of a branched monomer should overcome the loss. This was accomplished by substituting 25 parts of isoprene for an equal amount of butadiene in the polymerization recipe.

The observations with regard to polymerization temperature, made from stress-strain data on the compounded stocks shown in Table V, are essentially the same as those made on polybutadiene or the butadiene-styrene copolymer. A general im-

provement in properties attended lower polymerization temperatures, but the Young's modulus curves shown in Figure 4 indicate that the behavior of the copolymer at low temperatures was greatly different. The introduction of 25 parts of isoprene eliminated the shift in slope of the 10° C. polymer, and the −40° C. polymer behaved in a normal manner similar to polybutadiene made at 50° C. This indicates that the pendant methyl group, when present in sufficient amounts, will prevent some crystallization, and that the advantages gained by low temperature polymerization are, at least in part, due to the more linear molecular chain produced.

Table V. Physical Test Data on Butadiene/Isoprene (75/25)

(Tread stock recipe)

	Polymerization Temperature			
	50° C.	10° C.	−25° C.	−40° C.
Conversion, %	76	62	60	66
Gel, %	3.98	14.6	1.72	22.5
Intrinsic viscosity, sec.	2.06	3.02	2.24	3.62
Williams plasticity, mm.	2.91	5.31	3.50	4.91
Cure, ° F.	280	270	270	270
Time of cure, min.	60	30	45	60
300% modulus, lb./sq. inch	875	1325	1825	..
Tensile strength, lb./sq. inch	1850	2125	2900	2125
Total elongation, %	450	420	400	..

Literature Cited

(1) Hanson, E. E., and Halverson, G., *J. Am. Chem. Soc.*, **70**, 779 (1948).
(2) Howland, L. H., Messer, W. E., Neklutin, V. C., and Chambers, V. S., *Rubber Age*, **64**, 459 (1949).
(3) Johnson, P. H., and Bebb, R. L., *J. Polymer Sci.*, **3**, 389 (1948).
(4) Johnson, P. H., Brown, R. R., and Bebb, R. L., "Effect of Sub-zero Polymerization on Polymer Properties," presented in the High Polymer Forum at the 113th Meeting, Am. Chem. Soc., Chicago, Ill., 1948.
(5) Starkweather, J. W., Bare, P. O., *et al.*, Ind. Eng. Chem., **31**, 210 (1947).
(6) Willis, J. M., and Wakefield, L. B., *et al., Ibid.*, **40**, 2210 (1948).

VISCOSITY-MOLECULAR WEIGHT RELATION FOR POLYBUTADIENE

EFFECT OF POLYMERIZATION TEMPERATURE

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THE relation between intrinsic viscosity and number average molecular weight, probably first used by Mark (15) and shown to hold for plastic materials by Houwink (11) and for polyisobutylenes by Flory (6), has now become generally accepted as

$$[\eta] = KM^a$$

A large number of other polymers have been evaluated by various investigators who have obtained an experimental value of about 0.62 to 0.67 for the exponent a in the case of rubberlike

polymers. Polybutadiene is one polymer for which data do not seem to exist on sufficiently narrow fractions to allow determination of the above relationship between intrinsic viscosity and molecular weight. Moreover, the influence exerted upon this relationship by the changes in the polymer structure which accompany variation in polymerization conditions has not been evaluated in the case of elastomers. Consequently, the intrinsic viscosity–molecular weight relationship for this polymer becomes of interest in two ways: for the routine evaluation of molecular weight from intrinsic viscosities of polybutadiene produced at

various polymerization temperatures; and from the standpoint of any indication that may be obtained of structural changes in the polymer as polymerization temperature is varied.

Experimental Procedure

Polybutadiene Preparation. Polymers were prepared in systems most practical for polymerization at each of the temperatures studied. Those polymerized at 50° C. were made in the GR-S system to different hydrocarbon conversions. The 5° and −20° C. polymers were made in standard redox type formulations (1, 17). All the polymers were essentially gel-free. Data on polymerization are recorded in Table I, which includes the isothermal volume decrease upon crystallization at −25° C. obtained by Lucas using the dilatometric method (14). This volume decrease in low temperature polybutadiene has been used as a measure of the degree of regularity of the polymer chain.

The relation between intrinsic viscosity and number average molecular weight has been determined for emulsion polybutadiene polymerized at three temperatures. The viscosity of polybutadiene made at 50° C. and to about 65% conversion is related to molecular weight as follows: $[\eta] = 72.5 \times 10^{-4} \times M^{0.45}$. Lowering the polymerization temperature to 5° C. changes the relation to $[\eta] = 26.4 \times 10^{-4} \times M^{0.55}$, while a further decrease in polymerization temperature to −20° C. results in a relationship of $[\eta] = 10.6 \times 10^{-4} \times M^{0.63}$. A similar increase in the exponent of the viscosity–molecular weight relationship is obtained for low conversion 5° and 50° C. polymer. These results are in agreement with the structural changes in the polymer which occur as polymerization temperature or conversion is lowered; all of which result in a more extended polymer chain based on an equivalent number of butadiene units in the molecule. The high intrinsic viscosity per unit molecular weight, as indicated by the larger exponent in the viscosity–molecular weight relation, is desirable characteristic in a polymer for general purpose usage, as it indicates a more linear, more ideal polymer chain.

the case of lower fractions. Viscosities calculated from the relation $[\eta] = (\ln \eta_r)/c$, where c is the concentration in grams per 100 ml. of solution, were plotted against the concentration and extrapolated to infinite dilution to obtain the intrinsic viscosity.

The number average molecular weights of the fractions were determined in toluene at 30.10° C. using osmometers of the static type. The construction of these osmometers and the procedure for measurement of osmotic pressure have been described (16). The osmotic rise was determined on four solutions of increasing concentration over the range of 0.1 to 0.7 gram per 100 ml. These values for osmotic rise, h, were divided by the concentration and plotted against the concentration to obtain the h/c vs. c curves, which were then extrapolated to infinite dilution to yield the number average molecular weights.

Results

Molecular Weights and Viscosities. The data obtained on the fractions of the polybutadienes made at 50° C. are recorded in Table II.

The intrinsic viscosities of the fractions of each of these polybutadienes are plotted on a log-log scale against their number average molecular weights in Figure 1. The straight line relating viscosity to molecular weight of the polybutadienes made to high conversion at 50° C. in the GR-S system is represented by the equation

$$[\eta] = 72.5 \times 10^{-4} \times M^{0.45}$$

Table I. Polybutadienes Used in Fractionation

Polymer	Polymerization Temperature, ° C.	System	Part DDM	Conversion, %	Volume Decrease, Ml./G. × 10³
A	50	GR-S	0.50	74	..
B	50	GR-S	0.50	63	0.1
C	50	GR-S	0.50	27.1	1.8
D	5	Redox	0.42	64.5	15.1
E	5	Redox	0.42	30.5	17.8
F	−20	Redox	0.50	65	23.3

Determination of Solution Properties. A study of the relationship of intrinsic viscosity to molecular weight requires that these properties be determined on polymer of narrow molecular weight distribution. Fractions of sufficient homogeneity were obtained by the usual fractional precipitation technique.

The fractionation was made upon 30 grams of whole polymer which had been purified by precipitation from 6 liters of c.p. toluene by the dropwise addition of 3 liters of c.p. methanol. After settling of the polymer, the supernatant liquid was poured off and the precipitated polymer was redissolved in 5 liters of c.p. toluene which contained 0.0075 gram per liter of phenyl-2-naphthylamine. Osmotic molecular weight of the whole polymer was obtained on a portion of this solution. Ten fractions of approximately equal size were also separated from this solution by dropwise addition of methanol and with constant stirring until incipient cloudiness at 25° C. was reached. The coacervate was allowed to settle overnight and the supernatant liquid was siphoned off. The precipitated polymer was dissolved in toluene containing phenyl-2-naphthylamine. This procedure was repeated on the highest molecular weight fractions to be certain of narrow molecular weight distributions. Solutions of the final fractions were evaporated to one half their original volume in vacuum at 70° C. in order to remove all methanol before the series of dilutions was made for osmotic pressure determinations.

The viscosities were measured in toluene solutions at 25.9° C. with Ostwald viscometers for which the time of flow for pure solvent was approximately 154 seconds in order to minimize kinetic energy effects. Concentrations of the solutions varied from 0.02 to 0.08 gram per 100 ml. for the fractions of highest molecular weight and from about 0.08 to 0.32 gram per 100 ml. in

Table II. Intrinsic Viscosities and Molecular Weights of Fractions of Polybutadiene Polymerized at 50° C.

| Polymer	% of Whole Polymer	Intrinsic Viscosity	Molecular Weight × 10⁻³	μ Value
A. Whole, 74% conversion		7.00		
Fraction				
1	14.7	7.00	>3000	..
2	5.5	6.28	>3000	..
3	5.4	5.54	..	..
4	3.1	4.82	..	..
5	6.7	2.90	697	0.40
6	13.0	2.16	323	0.35
7	15.3	1.47	..	..
8	11.2	0.86	49	0.32
9	6.5	0.76	..	..
10	2.8	0.45	..	..
Unprecipitated	15.8	..	..	..
B. Whole, 63% conversion	..	3.08	119	0.34
Fraction				
1	10.6	6.62	..	..
2	5.5	6.20	..	..
3	7.5	4.67	2000	0.36
4	9.0	3.56	1035	0.35
5	12.7	2.42	400	0.32
6	15.0	1.57	150	0.32
7	19.1	1.05	70	0.35
8	10.3	0.82	36	0.33
9	5.8	0.59	..	..
10	2.9	0.43	..	..
Unprecipitated	1.6	..	..	..
C. Whole, 27.1% conversion	..	1.0	..	..
Fraction				
1 and 2	7.6	2.13	171	0.40
3	7.1	1.91	..	..
4	20.4	1.50	108	0.34
5	22.1	1.14	73	0.30
6	16.5	0.76	..	..
7	16.1	0.69	33	0.38
Unprecipitated	10.2	..	..	..
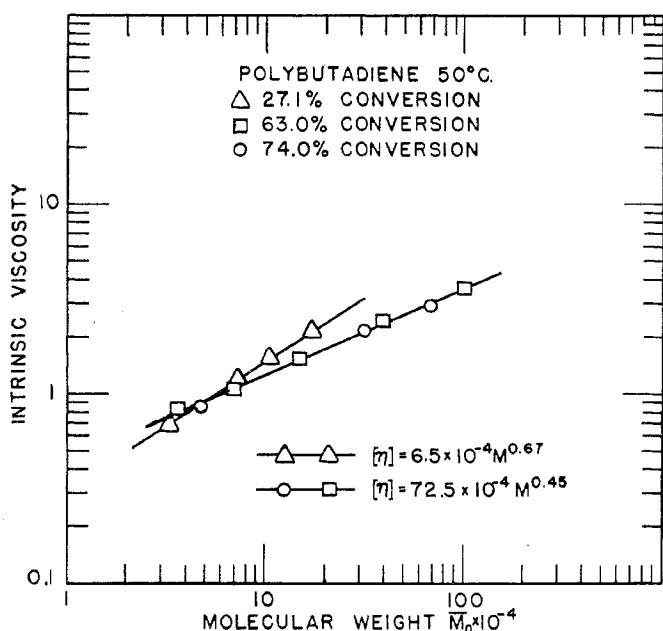
Figure 1. Viscosity–Molecular Weight Relation for Polybutadiene Polymerized at 50° C.

The same relation holds for two polymers which differ only in that the one, A, was carried to a conversion of 74%, somewhat higher than normal, for comparison with the low temperature polymers of around 64% conversion. Polybutadiene, B, was made to 63% conversion for a closer comparison with the polymers polymerized at the lower temperatures. The third 50° C. polymer, C, was made to 27.1% conversion to determine the effect of a large charge in conversion in the direction of obtaining a more linear polybutadiene. In this case a relationship of

$$[\eta] = 6.5 \times 10^{-4} \times M^{0.67}$$

was obtained. At low conversion the structure of emulsion polybutadiene made at 50° C. is such that its viscosity–molecular weight exponent is in the expected range.

Two additional polybutadienes, made at 5° C. in a redox system, were fractionated in order to determine the effect of poly-

merization temperature on the viscosity–molecular weight relationship. The intrinsic viscosities and molecular weights of their fractions are presented in Table III. The relationship between these viscosities and molecular weights is plotted in Figure 2.

Lowering the polymerization temperature to 5° C. increased the exponent of the high conversion polymer significantly. The relationship for this polymer, D, made to 64.5% conversion, is

$$[\eta] = 26.4 \times 10^{-4} \times M^{0.55}$$

That for polymer E, which differs from polymer D only in that it was stopped at 30.5% conversion, is

$$[\eta] = 10.6 \times 10^{-4} \times M^{0.64}$$

Table IV. Intrinsic Viscosities and Molecular Weights of Fractions of Polybutadiene Polymerized at −20° C.

Polymer	% of Whole Polymer	Intrinsic Viscosity	Molecular Weight × 10⁻³	μ Value
F. Whole, 65% conversion	..	4.28	242	0.38
Fraction				
1	21.4	8.82	..	..
2	11.2	7.62	..	..
3	10.4	6.92	1200	0.40
4	6.6	5.10	..	..
5	9.8	4.79	638	0.36
6	12.8	3.32	323	0.34
7	7.9	2.27	211	0.31
8	8.2	1.65	103	0.34
9	4.8	1.13	64	0.25
10	3.2	0.67	29	0.32
Unprecipitated	3.2	..	..	..

Emulsion polybutadiene prepared at still a third temperature, −20° C., was fractionated with the results shown in Table IV and Figure 3. The relationship between viscosity and molecular weight of this polymer, made to 65% conversion, is

$$[\eta] = 10.6 \times 10^{-4} \times M^{0.63}$$

Polymerization at the lower temperature has enabled production of polybutadiene to 65% conversion which, at the same time, retains a structure characterized by the larger exponent found for the 50° C. polybutadiene only at low conversion.
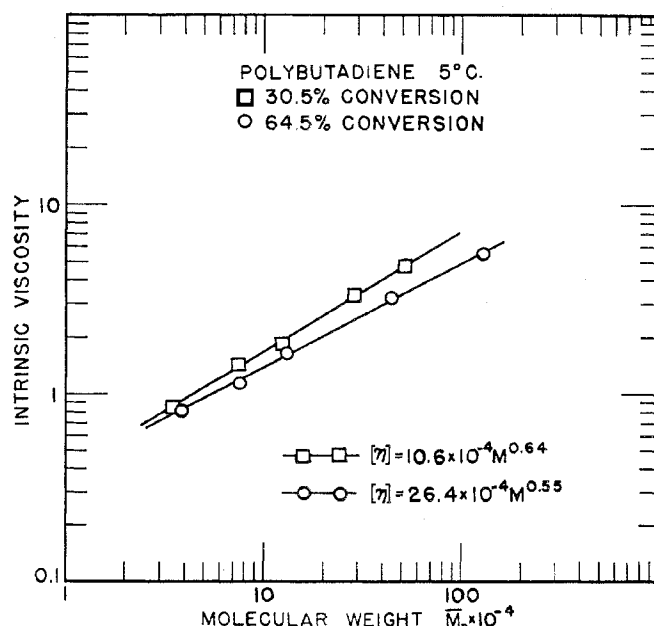
Table III. Intrinsic Viscosities and Molecular Weights of Fractions of Polybutadiene Polymerized at 5° C.

Polymer	% of Whole Polymer	Intrinsic Viscosity	Molecular Weight × 10⁻³	μ Value
D. Whole, 64.5% conversion	..	3.57	138	0.33
Fraction				
1	13.8	7.96	..	..
2	5.8	7.55	..	..
3	2.7	6.90	..	..
4	12.9	6.03	..	..
5	10.9	5.50	1300	0.36
6	15.0	3.20	450	0.32
7	9.1	2.62	..	..
8	10.3	1.67	132	0.31
9	7.4	1.25	76	0.30
10	7.3	0.82	39	0.28
Unprecipitated	4.8	..	..	..
E. Whole, 30.5% conversion	..	2.35	..	..
Fraction				
1	1.1	..	..	..
2	3.9⎫	4.75	527	0.33
3	3.0⎭	..	..	..
4	23.9	3.25	283	0.32
5	18.5	2.20	..	..
6	13.6	1.82	125	0.30
7	11.4	1.45	74	0.30
8	7.1	1.14	..	..
9	8.3	0.85	35	0.30
10	6.3	0.63	..	..
Unprecipitated	2.9	..	..	..

Figure 2. Viscosity–Molecular Weight Relation for Polybutadiene Polymerized at 5° C.

Discussion

The marked difference of the viscosity–molecular weight relationship for normal conversion polybutadiene made at 50° C. from those of other elastomers and even from that of polybutadiene made to low conversion at the same temperature or from polybutadiene made at −20° C. is rather unusual. The data of previous investigators have consistently indicated a value of approximately $^2/_3$ for the exponent in the viscosity–molecular weight relationship of other elastomers. Some of these results are presented in Table V.

Table V. Molecular Weight–Intrinsic Viscosity Relationships for Various Elastomers

Polymer	$[\eta] = K \times M^a$		Reference
GR-S	$[\eta] =$	$5.4 \times 10^{-4} \times M^{0.66}$	(8)
GR-S	$[\eta] =$	$5.5 \times 10^{-4} \times M^{0.67}$	(4)
Sodium polybutadiene	$[\eta] =$	$11.0 \times 10^{-4} \times M^{0.62}$	(4)
Butadiene-acrylonitrile	$[\eta] =$	$4.9 \times 10^{-4} \times M^{0.64}$	(4)
Neoprene GN	$[\eta] =$	$5.0 \times 10^{-4} \times M^{0.615}$	(4)
Natural rubber	$[\eta] =$	$5.0 \times 10^{-4} \times M^{0.667}$	(3)
Polyisobutylene	$[\eta] =$	$3.6 \times 10^{-4} \times M^{0.64}$	(6)

The only indication, other than that presented in this report, of a low value of the constant a for an elastomer in a good solvent is an "average" value deduced by Huggins (12) from data of Staudinger and Fischer (18) on several polybutadienes of different types. It was obtained on two or three broad fractions of both sodium and emulsion polybutadiene of varying degrees of modification. The value of 0.5 obtained in this manner for a in the relationship

$$[\eta] = 80 \times 10^{-4} \times M^{0.5}$$

is approximately the average of that of Carter, Scott, and Magat for sodium polybutadiene and the authors' value for 50° C. emulsion polybutadiene, the two types of polymer from which the average value was obtained. Investigation of the authenticity of a value of less than 0.50 for the exponent would in itself be of interest from a theoretical viewpoint. This value of 0.50 has been derived for linear and ideal polymer chains (5, 7). It is conceivable that polybutadiene polymerized at 50° C. is farther from an ideal structure than are the other polymers which have been investigated and for that reason has a low exponent of the viscosity–molecular weight relationship. Because a value of 0.45 might be considered to be within experimental error of the lower limit, an attempt was made to obtain a still lower exponent by investigation of a polymer made at a higher temperature. Cross linking to the point of excessive gel was encountered in the first polymer of this type. However, efforts to determine the effect of branching and cross linking on the exponent will be continued.

The fact that a decrease in polymerization temperature or conversion will bring the viscosity–molecular weight relationship of 50° C. polybutadiene in line with values reported for other elastomers is of exceptional interest when considered in light of the structural changes that are now known to result from variation in polymerization conditions. The over-all result of all the structural changes which are a function of polymerization temperature is that of greater polymer chain regularity. Lucas (14) has measured chain regularity in terms of isothermal volume change during crystallization and found a progressively greater crystallizability in polybutadiene as polymerization temperature was lowered (see also Table I).

Hanson and Halverson (9) have developed a technique for obtaining x-ray diffraction patterns of polymers stretched at low temperature and have also shown an increased degree of crystallinity in polybutadiene as its polymerization temperature was lowered. Beu and co-workers (2) have shown, by x-ray diffraction patterns, that the ability of polybutadiene to crystallize becomes greater as polymerization temperature is decreased. Under their test conditions, a very sharp diffraction pattern was obtained
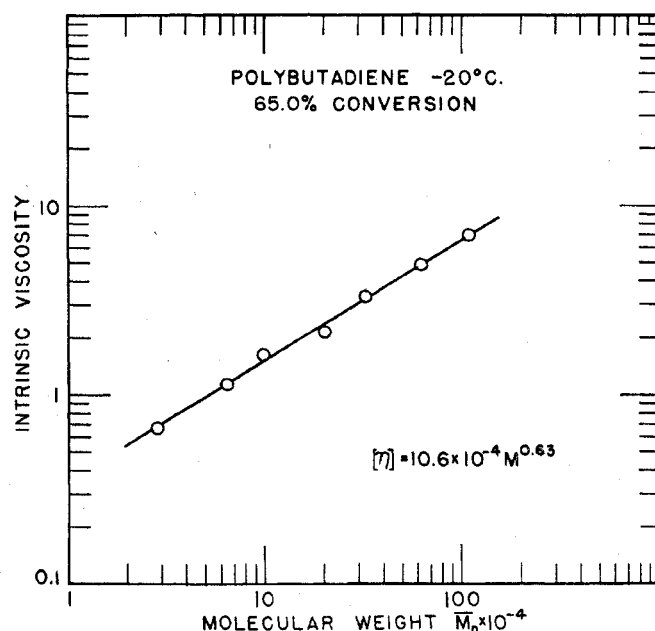

Figure 3. Viscosity–Molecular Weight Relation for Polybutadiene Polymerized at −20° C.

on polymer made at −20° C.; the pattern was still fairly sharp at 5° C. but had entirely disappeared above 30° C., temperatures which correspond to those for which the viscosity–molecular weight relationships were obtained. Thus, the dilatometric and x-ray diffraction methods both agree that a more regular polymer chain is produced as polymerization temperature is lowered.

The differences in the fine structure of the polymer chain which make possible a greater crystallizability have been investigated by Hart and Meyer (10) using infrared absorption techniques. Their results, included in Table VI and confirmed by those of perbenzoic acid oxidation (13), reveal little difference in the number of external double bonds in polymers made at different temperatures. Although the percentage of external double bonds decreases but 3.6% as polymerization temperature is lowered, exponent a increases significantly at normal conversion. It is evident, therefore, that the number of external double bonds has little influence on the viscosity–molecular weight relationship in this case.

Table VI. Microstructure and Viscosity–Molecular Weight Exponent of Polybutadiene

Polymerization Temperature, ° C.	Conversion, %	$[\eta]$-Mol. Wt. Exponent	External[a] Double Bonds	Configuration[a] % trans	% cis
50	63	0.45	23.2	62	14.8
50	27	0.67			
5	64.5	0.55	21.1	71.6	7.3
5	30.5	0.64			
−20	65	0.63	19.6	79.6	..

[a] Data of Hart and Meyer (10).

The other microstructural feature listed in Table VI, cis-trans configuration, has been considered to influence the regularity of the polymer chain to a great extent on the basis of x-ray diffraction data. Just how far this carries over to the extension of a polymer chain in solution cannot be said definitely on the basis of present data. Although the increase in the exponent of the viscosity–molecular weight relationship of the 63 to 65% conversion polybutadienes could be correlated with a decrease in cis-trans heterogeneity as polymerization temperature is lowered, it is felt that the cis-trans ratio might be independent of conversion as is the external double bond content of polybutadiene (13). In this

case, one could not explain the greater extension of the polymer chain at low conversion which is indicated by the exponent of 0.67 for the 50° C. polymer at 27% conversion.

There is, however, still another structural feature which is not listed in Table VI, that of branching and cross linking, which is the predominant change in the polymer chain as a function of conversion. This branching becomes more pronounced as conversion progresses. Such branched and cross-linked chains would be less extended for a given molecular weight than are unbranched chains and would be characterized by a smaller value for exponent a in the viscosity–molecular weight relationship. Therefore, the decrease in the value of the exponent as conversion is raised may be indicative of a greater degree of branching. Thus, the same exponent (about 0.67) of the viscosity–molecular weight relationship is obtained either by lowering the conversion at a given temperature, in which case less branching is the main variable, or by lowering polymerization temperature at a constant high conversion, in which case less branching, more trans molecules, and more 1,4 addition all contribute to a more extended molecule. It is, therefore, felt that branching and cross linking are the chief factors being measured by this method although evaluation of the cis-trans ratio in low conversion, 50° C. polybutadiene remains to be done in order to prove this point.

A high exponent a in the viscosity–molecular weight relation of polybutadiene produced under a given series of polymerization conditions would, then, be desirable for a crystallizable, general purpose elastomer because it indicates a more linear, more ideal polymer chain.

Acknowledgment

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Literature Cited

(1) Bebb, R. L., et al., private communication, Firestone Tire & Rubber Co. to Office of Rubber Reserve.
(2) Beu, K. E., Reynolds, W. B., Fryling, C. F., and McMurry, H. L., J. Polymer Sci., 3, 465 (1949).
(3) Carter, W. C., Scott, R. L., and Magat, H., J. Am. Chem. Soc., 68, 1470 (1946).
(4) Ibid., 71, 220 (1949).
(5) Debye, P., and Bueche, A. M., J. Chem. Phys., 16, 573 (1948).
(6) Flory, P. J., J. Am. Chem. Soc., 65, 372 (1943).
(7) Flory, P. J., J. Chem. Phys., 17, 303 (1949).
(8) French, D. M., and Ewart, R. H., Anal. Chem., 19, 165 (1947).
(9) Hanson, E. E., and Halverson, G., private communication, Firestone Tire & Rubber Co. to Office of Rubber Reserve; J. Am. Chem. Soc., 70, 779 (1948).
(10) Hart, E. J., and Meyer, A. W., private communication, United States Rubber Co. to Office of Rubber Reserve.
(11) Houwink, R., J. prakt. Chem., 157,15 (1940).
(12) Huggins, M. L., IND. ENG. CHEM., 35, 980 (1943).
(13) Kolthoff, I. M., Lee, T. S., and Mairs, M. A., J. Polymer Sci., 1, 220 (1947).
(14) Lucas, V. E., Johnson, P. H., Wakefield, L. B., and Johnson, B. L., private communication, Firestone Tire & Rubber Co. to Office of Rubber Reserve.
(15) Mark, H., "Der feste Körper," p. 103, Leipzig, S. Herzel, 1938.
(16) Sands, G. D., and Johnson, B. L., Anal. Chem., 19, 261 (1947).
(17) Schulze, W. A., Trojan, J. E., Fryling, C. F., and Reynolds, W. B., private communication, Phillips Petroleum Co. to Office of Rubber Reserve.
(18) Staudinger, H., and Fischer, Kl., J. prakt. Chem., 157, 158 (1941); Rubber Chem. and Technol., 15, 523 (1942).

GR-S LATEX POLYMERIZED AT LOW TEMPERATURES

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The field of low temperature–polymerized latex is in a state of rapid development. Work is in progress on concentration methods, butadiene-styrene ratio, and the possibility of polymerizing directly to 60% solids by employing higher conversions.

THE impossibility of obtaining adequate gum tensile strength without sacrifice of low temperature flexibility has vexed the rubber industry since the earliest work with GR-S latices. Although tensile strengths of 2500 pounds or more can be obtained with 50/50 butadiene-styrene latex, vulcanized films of this material begin to stiffen at 32° F. (0° C.) and at 14° F. (−10° C.) are usually too stiff to be usable. On the other hand, vulcanized films of 70/30 butadiene-styrene latex are still flexible at −20° F. (−28.9° C.) but gum tensile strength of this material generally does not exceed 400 pounds. Borders and Juve have discussed this situation as applying to tread stock compounds (1). Liska (6) gives data showing the effect of low temperatures on stiffening of natural rubber and of butadiene-styrene copolymers of various monomer ratios.

Another troublesome feature of GR-S latices has been their poor wet strength. This deficiency manifests itself when a mold-cured product such as foam sponge is stripped from the mold in preparation for drying. The wet stock is so tender under such circumstances that extreme care must be exercised to prevent tearing.

As a result of this situation usage of GR-S latices has settled into well-defined channels. In cases where the latex film is supported by some other material or where low temperature stiffness is not important, it may be used alone. This comprehends such uses as tire-cord solutioning, paper saturation, pressure-sensitive adhesives, and can sealing. In other cases, where the foregoing properties are important, it has been found that a certain amount of GR-S can be blended into natural latex with only minor sacrifice in physical properties but with considerable improvement over straight natural latex in aging and with appreciable reduction in material cost. Finally, in certain uses where stringent requirements on both cold stiffening and tensile strength must be met, or where wet film strength is highly important, straight natural latex must be used.

Exceptional Properties of Cold Latex

In 1947 it became evident that, with fields for GR-S latex already well exploited, a substantial increase in usage could be real-