nitrothiophene, 2-chlorothiophene, 2-bromothiophene, 2-iodothiophene, 2,5-dichlorothiophene and tetrabromothiophene.

2. The dipole moments for these compounds, calculated by use of the Debye equation, have been found to be 0.53, 4.23, 1.60, 1.37, 1.14, 1.12 and 0.73, respectively.

3. The dipole moment values show the general resemblance of the structures of these substituted thiophenes to those of the corresponding benzene derivatives. Deviations between observed moment values and those calculated on the basis of vector additivity have been attributed largely to dipole-polarizability interactions. The possibility of decreased participation of the sulfur electrons in the thiophene ring resonance for the chloro-derivatives is also considered.

RECEIVED AUGUST 16, 1948

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Viscosity–Molecular Weight Relations for Various Synthetic Rubbers[1]

BY ROBERT L. SCOTT,[2] WALTER C. CARTER AND MICHAEL MAGAT[3]

Introduction

Houwink[4] and Flory[5] have shown that the relation between the intrinsic viscosity of a high-polymer solution and the molecular weight of the polymer is of the form

$$[\eta] = KM^{a} \qquad (1)$$

where in the case of polyvinyl acetate compounds[4] and polymethacrylate[4] $a \sim 0.6$ and in the case of polyisobutylene[5] $a = 0.64$. More recently the authors[6] have shown that for natural rubber, the relation is

$$[\eta] = 5.02 \times 10^{-4} M^{0.667} \qquad (2)$$

In this paper, we are reporting viscosity–molecular weight relations for four more polymers: a butadiene–styrene copolymer (Buna S), sodium polymerized polybutadiene, a butadiene–acrylonitrile copolymer (Buna N), and neoprene. As will be shown, these measurements confirm the hypothesis that for these essentially linear polymers a is very close, if not equal to, two-thirds.

Experimental

Materials.—The rubber samples used in these experiments were kindly supplied by the Firestone Tire and Rubber Company of Akron, Ohio. The Buna S (GR-S) was of three kinds: one of low degree of conversion (100% soluble), one of medium degree of conversion (53.5% soluble) and one of high degree of conversion (32% soluble). The polybutadiene was polymerized with sodium according to methods similar to those used in the preparation of Russian SK.[7]

The toluene used was the commercial solvent dried with calcium chloride.

Fractionation.—Unlike natural rubber, the synthetic rubbers are not subject to rapid oxidative degradation in solution, so some of the precautions reported in the previous paper[6] are unnecessary. The rubbers were dissolved in toluene and fractionally precipitated[8] by methanol; in some cases fractions were refractionated into subfractions. Anti-oxidant ("Agerite," aldol - α - naphthylamine), although possibly unnecessary for these synthetics, was added to all solutions.

In certain polymers, a portion of the soluble fraction consists of "microgel," a material which is not easily removed by slow extraction with good solvents in the absence of agitation, but is more or less easily dissolved by energetic shaking, leaving only the insoluble cross-linked "macrogel." A second portion of the 100% soluble polymer was fractionated as follows: After extraction of the acetone-soluble fraction (9.0%) the rubber was dried under vacuum and then extracted with toluene in an atmosphere of carbon dioxide. Agitation of the mixture was avoided in order to minimize dispersion of the "microgel." At intervals of several days the supernatant liquid was carefully pipetted out and additional toluene added with as little disturbance to the swollen "microgel" at the bottom as possible. After much of the "sol" had been extracted in this way, fresh toluene was added and the mixture shaken. One or two shakes sufficed to bring the "microgel" into solution indicating that, for this sample at least, the bonds between the molecules of "microgel" are extremely weak. The resulting solution was completely stable, no material settling out after even a month's standing.[9] The "sol" and "microgel" portions were separately fractionated. A sample of the "macrogel" was degraded and solubilized by oxidation at high temperatures and subsequently fractionated.

Measurements.—The molecular weights of the fractions were calculated from osmotic pressures measured in a Flory-type osmometer, while solution viscosities were determined in an Ostwald viscosimeter. The details of these procedures were reported in the previous paper.[6]

For Buna N, the viscosity relation for various solvents was determined in the following manner: After measurements of the osmotic pressure and the viscosity in toluene, a sample of each fraction was dried in vacuum at room temperature and redissolved successively in acetone, chloroform and benzene[10] and its intrinsic viscosity in each of these solvents determined.

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[1] This research was carried out during 1943 on a grant from the Reconstruction Finance Corporation, Office of Rubber Reserve, for fundamental research on the physical properties of synthetic rubbers.

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[4] R. Houwink, *J. prakt. Chem.*, **157**, 15 (1940–1941).

[5] P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

[6] W. C. Carter, R. L. Scott and M. Magat, *ibid.*, **68**, 1480 (1946).

[7] For details of the preparation of SK see A. Talalay and M. Magat, "Synthetic Rubber from Alcohol," Interscience Publishers, New York, N. Y., 1945.

[8] In the fractionations of GR-S, the inhibitor, anti-oxidant and the lowest molecular weights were extracted with acetone before the remainder of the soluble material was extracted with toluene.

[9] No significance should be attached to the relative amounts of "sol," (23%) and "microgel" in view of the crude method of separation; the "microgel" portion undoubtedly contains some "sol."

[10] No significant oxidative degradation was observed in Buna N fractions, unlike natural rubber where the breakdown is rapid, or Buna S where the breakdown is slow but appreciable.

Results

The viscosity–molecular weight measurements on the five series of fractions of GR-S (Buna S, 75% butadiene, 25% styrene) are shown in Fig. 1.

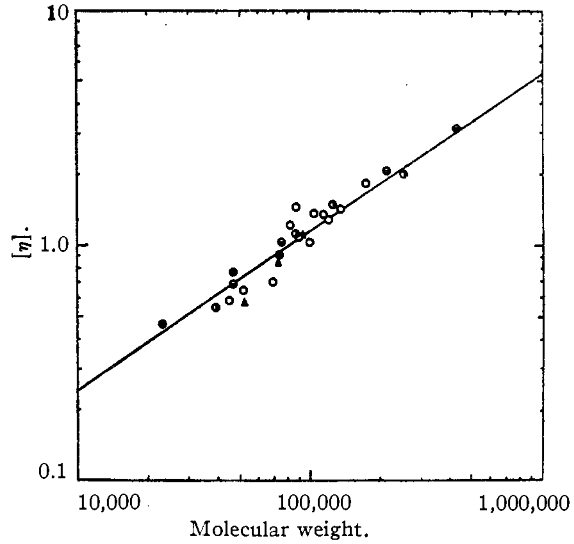

Fig. 1.—Viscosity of GR-S (Buna S) in toluene: ○, GR-S medium conversion-sol; ●, GR-S medium conversion-degraded macrogel; ◑, GR-S, low conversion-"sol"; ⊖, GR-S low conversion, "microgel"; △, GR-S high conversion.

The same log–log straight line relation seems to hold approximately for all types of GR-S independent of the degree of conversion or the nature of the material: "sol," "microgel," or degraded "macrogel." Analytically the intrinsic viscosity of GR-S in toluene at 25° may be expressed as

$$[\eta] \text{ (toluene)} = 5.25 \times 10^{-4} M^{2/3} \qquad (3)$$

This relation is accurate to at least 10% for molecular weights between 25,000 and 500,000 and probably is valid for much higher molecular weights. Lower molecular weights could not be measured with our osmometer because of the permeability of the membrane.

The relations found for the other three polymers are shown in Table I and Figs. 2 and 3

TABLE I

Polymer	Solvent	$K \times 10^4$	a
Buna N	Toluene	4.9	0.64
	Acetone	5.0	.64
	Chloroform	5.4	.68
	Benzene	1.3	.55
Neoprene	Toluene	5.0	.615
Sodium polymerized polybutadiene	Toluene	11.0	.62

The reader may judge the accuracy of the determination of the exponent a from the experimental data in Figs. 1–3. For GR-S a is probably 0.67 ± 0.05. For the other polymers the accuracy is considerably better.

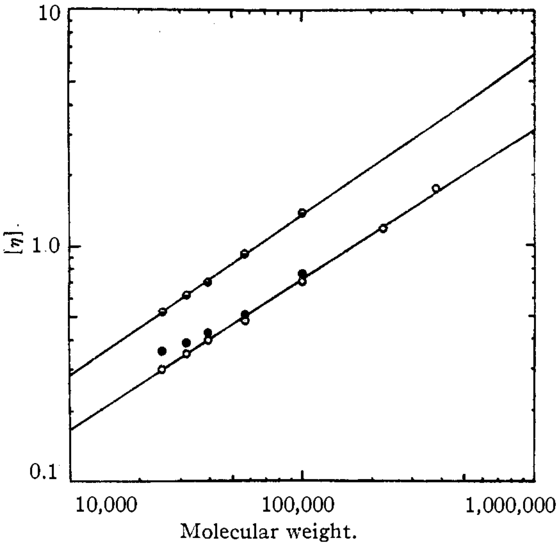

Fig. 2.—Viscosity of Buna N solutions: ○, toluene; ●, benzene; ⊖, chloroform.

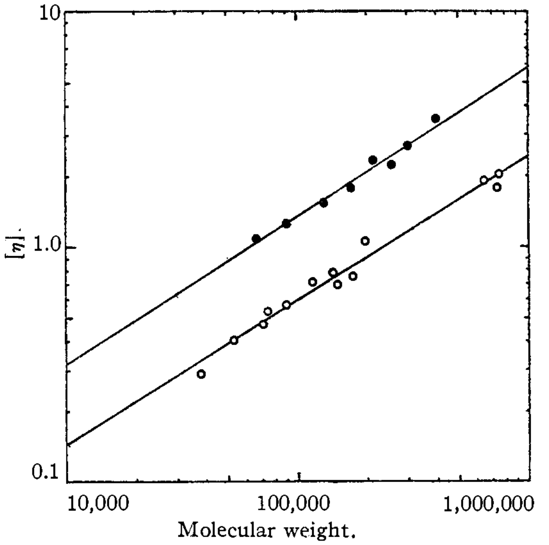

Fig. 3.—Viscosity of sodium polymerized polybutadiene (●) and neoprene (○) in toluene.

The data for Buna N in different solvents are further shown in Table II.

TABLE II

INTRINSIC VISCOSITY OF BUNA N SOLUTIONS

Fraction	1	2	3	4	5	6	7
Mol. wt. × 1000	25.0	31.8	39.5	57.0	101	224	380
Toluene	0.30	0.35	0.40	0.48	0.71	1.16	1.76
Acetone	.317	.38	.405	.475	0.715		
Chloroform	.52	.62	.70	.93	1.38		
Benzene	.36	.39	.43	.51	0.76		

No systematic work was done on polyisobutylene since this polymer has been studied exhaustively by Flory.[5] However, at the beginning of our work Dr. Flory kindly sent us three fractions of known molecular weight to check the accuracy of our osmometer. As seen in Table III the agreement between the data of the two laboratories is quite satisfactory.

TABLE III

POLYISOBUTYLENE FRACTIONS

No.	Osmotic molecular weight Flory	Osmotic molecular weight Scott and Magat	Intrinsic viscosity In toluene (Scott and Magat)	Intrinsic viscosity In diisobutylene (Flory)
1	206,000	223,000	0.635	0.90
2	515,000	495,000	1.25	1.64
3	1,200,000	1,340,000	2.06	2.82

We have used these data to determine in a very rough way the dependence of the viscosity in toluene on the molecular weight. Figure 4 shows this relation (in broken line since based on but three points it is only very approximate) and the well-established relation for the viscosity in diisobutylene.[5] These relations expressed analytically are

$$[\eta] \text{ (toluene)} = 2.6 \times 10^{-4} M^{0.64} \tag{4}$$

$$[\eta] \text{ (diisobutylene)} = 3.60 \times 10^{-4} M^{0.64} \tag{5}$$

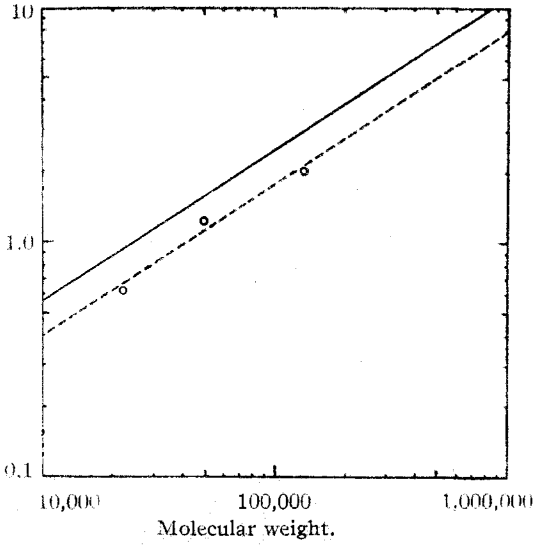

Fig. 4.—Viscosity of polyisobutylene: —, in diisobutylene (Flory); --O--, in toluene (this paper).

Discussion

At about the same time as our research was carried out, Ewart and co-workers at the United States Rubber Company Laboratories measured solutions of fractionated GR-S in a glass osmometer using cellophane membranes.[11] While most, if not all, of their measurements were made upon benzene solutions, they fit our relation for toluene solutions remarkably well. Figure 5 shows the results of two different series of data by Ewart and French[12] and Tingey, Ewart and Hulse[13]; the line is our relation for toluene taken from Fig. 1. It should be emphasized that the U. S. Rubber measurements were made in an entirely different osmometer using a different kind of membrane, so that the possibility of systematic error is almost certainly excluded.

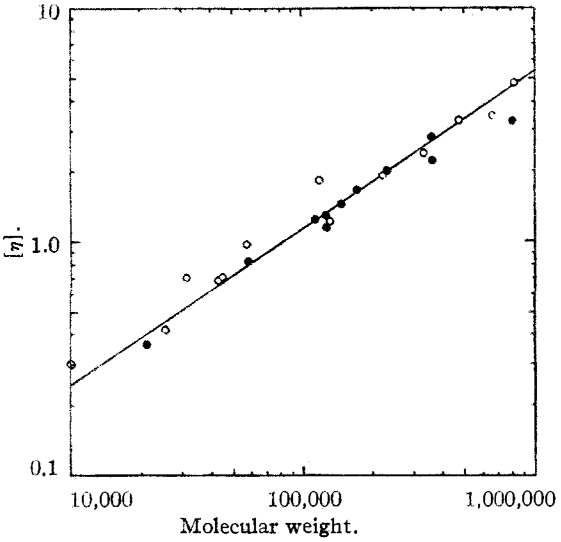

Fig. 5.—Viscosity of Buna S (GR-S) in benzene (U. S. Rubber Company measurements): ○, Ewart and French; ●, Tingey, Ewart and Hulse.

In the previous paper on natural rubber,[6] the authors have discussed in some detail the various theories which attempt to explain the viscosity of high polymer solutions. Since those comments seem to be equally valid for these data, they need not be repeated here, but one additional point is worth consideration. The intrinsic viscosity should be a function of the chain length rather than the actual molecular weight.[14] Since the chain length is proportional to the molecular weight, the viscosity should be proportional to some inverse power of w, the weight per chain atom. That this seems to be true can be seen from Table IV.

TABLE IV

Polymers	w	$K \times 10^4$
Polybutadiene	13.5–27[15]	6.34
GR-S	18–20	5.25
Hevea	18	5.02
Buna NM	15–26[15]	3.35
Neoprene GN	22	2.73
Polyisobutylene	28	2.01

(w = molar weight per chain carbon atom)

The value of the empirical constant K is given for a variety of rubbers (in toluene solutions); to secure uniformity, they are all recalculated for $a = 2/3$. We see that as w increases, there is a systematic decrease in K, corresponding to lower solution viscosities for equal molecular

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[11] D. M. French and R. H. Ewart, *Anal. Chem.*, **19**, 165 (1947).

[12] R. H. Ewart and D. M. French, private communication. Most but not all of these data were reported in reference 9.

[13] H. C. Tingey, R. H. Ewart and G. E. Hulse, private communication.

[14] Hence the expression of concentration in "base moles" in some treatments of the so-called Staudinger "law."

[15] Depending on the extent of 1,2 and 1,4 additions. Russian SK is said to be 75% 1,2 additions.

weights. This shift of the intrinsic viscosity–molecular weight curves is summarized graphically in Fig. 6. The theoretical expressions of Huggins[16] and of Hulburt, Harmon, Tobolsky and Eyring[17] represent the viscosity as proportional to inverse powers of the weight per chain atom so in this respect at least they are approximately valid.

It is interesting to note that of the various theories only that of Haller[18] predicts accurately the dependence of the viscosity on the two-thirds power of the molecular weight.[19]

Acknowledgments.—The authors wish to thank Dr. Paul J. Flory and the Esso Laboratories for furnishing the three fractions of polyisobutylene; the Firestone Tire and Rubber Company, in particular Dr. J. H. Dillon, for furnishing the rubber samples; Professor Arthur V. Tobolsky for several helpful discussions; and Professor Hugh S. Taylor for his generous interest and valuable advice.

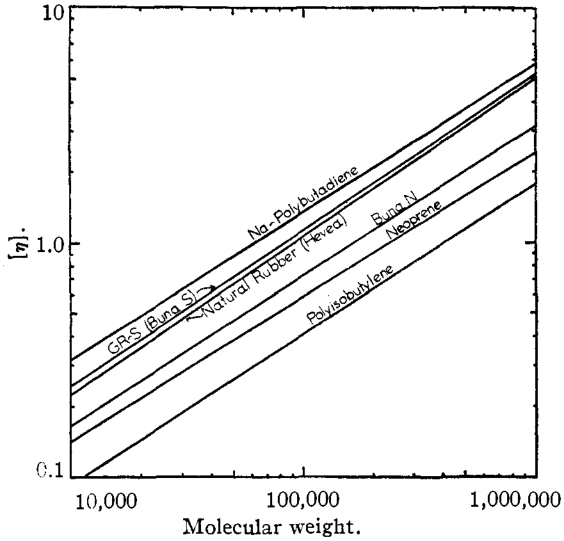

Fig. 6.—Viscosity–molecular weight relations for toluene solutions of various polymers.

Summary

Measurements on six different high polymers have shown that the intrinsic viscosity of the solutions depends on approximately the two-thirds power of the molecular weight. Dependence of the viscosity on the weight per chain atom of the polymer is indicated.

LOS ANGELES 24, CALIFORNIA RECEIVED APRIL 20, 1948

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[16] M. L. Huggins, *J. Phys. Chem.*, **42**, 910 (1938); **43**, 439 (1939); *J. Appl. Phys.*, **10**, 700 (1939).

[17] H. M. Hulburt, R. A. Harmon, A. V. Tobolsky and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943).

[18] W. Haller, *Kolloid Z.*, **56**, 257 (1931).

[19] Since this paper was first submitted to the Editor of The Journal, two new theories of viscosity have appeared, one by P. Debye and A. M. Bueche (*J. Chem. Phys.*, **16**, 573, 1948) and one by J. G. Kirkwood and J. Riseman (*ibid.*, **16**, 565, 1948). On preliminary inspection, it seems that our data are entirely consistent with these new theories, but rather than further delay publication of these results, we postpone a detailed discussion to a subsequent paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Kinetics of Semicarbazone Formation with Para Substituted Acetophenones[1]

BY ROBERT P. CROSS AND PAUL FUGASSI

The kinetics of the reactions of *d*-carvone with semicarbazide and other carbonyl reagents have been investigated previously by Stempel and Schaffel[2] and Mariella[3] using a polarimetric method. It is the purpose of this investigation to examine the kinetics of semicarbazone formation with para substituted acetophenones by a competitive method in which *d*-carvone and acetophenone react simultaneously with semicarbazide, present in sufficiently low concentration that the carbonyl reagent distributes itself between the two ketones. The extent of reaction of the *d*-carvone is determined polarimetrically.

Experimental Technique

Preparation of Compounds.—*d*-Carvone was obtained from Magnus, Mabee and Reynard. It was purified by preparing the solid hydrosulfide.[4,5] After several recrystallizations of the hydrogen sulfide compound, *d*-carvone was recovered by treating the compound with concentrated sodium hydroxide solution and steam distilling the mixture. Following extraction of the carvone with ether, the extract was vacuum distilled several times and a fraction collected boiling at 78° at 3 mm. The physical constants of our sample agreed with those found by Stempel and Schaffel.[2] Semicarbazide hydrochloride (an Eastman Kodak Co. product) was recrystallized from hydrochloric acid solution. Acetophenone was purified by the method of Flexser, Hammett and Dingwall.[6] The sample of acetophenone used boiled at 193° at 743 mm. *p*-methoxyacetophenone and *p*-chloroacetophenone were prepared by the method of Adams and Noller.[7] The

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[1] Abstracted from the thesis submitted by Robert P. Cross on August 12, 1947, to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science. Presented before the Division of Physical and Inorganic Chemistry at the 113th meeting of the American Chemical Society at Chicago, April, 1948.

[2] Stempel and Schaffel, THIS JOURNAL, **66**, 1158 (1944).

[3] Mariella, Thesis, Carnegie Institute of Technology, October 4, 1945.

[4] Wallach, *Ann.*, **305**, 224 (1889).

[5] Hooper, Macbeth and Price, *J. Chem. Soc.*, 1147 (1934).

[6] Flexser, Hammett and Dingwall, THIS JOURNAL, **57**, 2103 (1935).

[7] Adams and Noller, "Organic Synthesis," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 109–111.