Polymerization Experiments

Compounds I, VIII and IX gave no polymers alone or copolymers with butadiene, styrene, or methyl methacrylate, in the presence of benzoyl peroxide. Of the remaining compounds II, III, and V gave no polymers alone but copolymerized readily with the above olefins. Compounds IV and VI polymerized readily alone and also copolymerized with the above olefins. Several attempts were made to prepare 6-chloro-2-vinylquinoline (VII) by procedures analogous to those used for 2-vinylquinoline (VI). In every case rapid polymerization interfered with isolation of the monomer. The bulk polymers were prepared by heating the monomers at 70° in stoppered test-tubes with 0.5% benzoyl peroxide catalyst. Equal weights of monomers were used for the copolymers. The emulsion polymers with butadiene were prepared in sealed tubes at 40° (thermostat) using the formula: butadiene 7.5 g., vinyl monomer 2.5 g., water 18 g., soap 0.5 g., potassium persulfate 0.03 g., lauryl mercaptan (OEI) 0.06 g.

Summary

A series of vinylpyridines and vinylquinolines, some containing nuclear halogens, have been prepared and a preliminary study made of their polymerizing and copolymerizing characteristics.

LAFAYETTE, INDIANA RECEIVED DECEMBER 23, 1947

[CONTRIBUTION NO. 145 FROM THE GOODYEAR TIRE AND RUBBER CO., RESEARCH LABORATORY]

Viscosity–Molecular Weight and Viscosity–Temperature Relationships for Polystyrene and Polyisobutylene[1,2]

BY THOMAS G FOX, JR., AND PAUL J. FLORY

The simple empirical relationship[3]

$$\log \eta = A + C\overline{M}_w^{1/2} \qquad (1)$$

where η is the viscosity, $\overline{M}_w$ the weight average molecular weight and A and C are constants for a specified temperature, has been found to apply with remarkable accuracy to linear polyesters,[3,4] polyamides,[5] and to certain non-linear polymers as well.[5] Extension of this relationship to addition polymers of unsaturated compounds such as polyethylene[6] and polyisobutylene[7] and to polymeric dimethyl silicones[8] has been attempted recently with indications of success. However, either the molecular weights (weight average) were unreliably determined or the range was too limited for positive assurance that equation (1) may be applied to these polymers.

In the present investigation viscosities of two representative hydrocarbon polymers, polystyrene and polyisobutylene, of simple chain structure have been measured over wide ranges of molecular weight, molecular weight distribution and temperature. In addition to providing data with which to test the generality of equation (1), the present results demonstrate the nature of the dependence of the viscosity–temperature coefficient on molecular weight, molecular weight distribution and temperature. Apparent discrepancies which have appeared in the literature on viscosity–temperature coefficients for polystyrene have been accounted for. It is hoped that the results of this investigation will provide a basis for the better understanding of flow mechanisms in high polymers.

Experimental

Preparation and Fractionation.—Seven polymers of styrene varying in viscosity average molecular weight ($\overline{M}_v$) from 7000 to 350,000 were prepared by bulk polymerization at 60°. An average molecular weight in the desired range was obtained in each case by using appropriate concentrations of benzoyl peroxide and dodecyl mercaptan as shown in Table I. The reactions were stopped at conversions of approximately 25%. The polymers were separated by precipitation in an excess of vigorously stirred methanol, and were dried *in vacuo* at 60°.

Four polyisobutylenes with molecular weights as listed in Table I were fractionated.[9] Thus, the polymer known commercially as "Vistanex-LMH" with a viscosity average molecular weight of 69,000, was separated into a series of polymer fractions identified as PB1F1, PB1F2, and so on. The polymer PB5 consisted of a mixture of two large coarse fractions separated from PB2 and PB3.

All polymers were fractionated by single precipitation methods carried out at 30.0°. Solvent–precipitant combinations employed were methyl ethyl ketone–methyl alcohol for polystyrene and benzene–acetone for polyisobutylene. In each case the precipitant was added slowly with stirring to a solution containing 1.3 to 2.5 g. of polymer per 100 ml. of solvent (Table I) until a condition of permanent turbidity was reached. After adding an appropriate excess of the precipitant, the solution was warmed until it became clear, then subjected to gentle stirring while cooling slowly to 30.0°. The insoluble gel which settled out on standing overnight at this temperature was separated from the clear solution by decantation, washed with the non-solvent, and dried first on a steam

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[1] The work presented in this paper comprises a program of fundamental research on rubber and plastics being carried out under a contract between the Office of Naval Research and the Goodyear Tire and Rubber Company.

[2] Presented before the High Polymer Forum at the Atlantic City Meeting of the American Chemical Society, April 15, 1947.

[3] P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

[4] W. O. Baker, C. S. Fuller and J. H. Heiss, *ibid.*, **63**, 2142 (1941).

[5] J. R. Schaefgen and P. J. Flory, forthcoming publication.

[6] G. J. Dienes and H. F. Klemm, *J. Applied Phys.*, **17**, 458 (1946).

[7] R. L. Zapp and F. P. Baldwin, *Ind. Eng. Chem.*, **38**, 948 (1946).

[8] A. J. Barry, *J. Applied Phys.*, **17**, 1020 (1946).

[9] The polyisobutylene was supplied by the Standard Oil Co. of New Jersey. We are indebted to Mr. D. W. Young of the Esso Laboratories who made available to us PB7, a laboratory sample of low molecular weight.

TABLE I

THE POLYMERS USED FOR FRACTIONATION

Polystyrene

Polymer	Mole % peroxide	Mole % mercaptan	Extent of reaction	$\overline{M}_v$	Fractionation initial concn., g./100 ml.
14A	0.04	0	26%	349,000	2.0
11A	0.50	0	22	150,000	2.0
8A	1.0	0.010	28	60,000	2.0
6A	1.0	0.024	24	70,000	2.0
3D	1.0	0.055	28	45,000	2.0
4C	1.0	0.22	22	41,000	2.2
16A	4.0	6.5	20	7,060	2.0

Polyisobutylene

Polymer	Commercial designation	$\overline{M}_v$ (approximate)	Fractionation initial concn., g./100 ml.
PB1	Vistanex LMH	69,000	2.00
PB2	100,000 Grade	1,000,000	1.25
PB3	100,000 Grade	1,000,000	1.25
PB4	Vistanex LMS	45,000	2.50
PB5	....	1,000,000	1.33
PB7	....	3,100	2.5

bath and then *in vacuo* at 60°. By repeating this procedure a series of fractions was obtained from each polymer, the individual fractions usually representing 5 to 25% of the whole polymer (Table VIII). PB5F1 appears to be a notable exception, as it represents 46% of PB5. However, it represents only 23% of polyisobutylene B-100 since PB5 was obtained by combining fractions representing approximately half of that polymer.

Fractionation of the low molecular weight polystyrene 16A was carried out from acetone solution using as precipitant a mixture containing equal volumes of water and methanol. The acetone-soluble portion of 4C (about two-thirds of the whole) was fractionated in a similar manner.

Inasmuch as the *weight average* molecular weight on which the melt viscosity depends (*cf. seq.*) lies close to the *viscosity average* deduced from intrinsic viscosity measurements, it is evident that efficient fractionation should be unnecessary. Nevertheless, to confirm this expectation experimentally, polystyrene 3D was fractionated by the double precipitation method previously described.[10] The melt viscosity of one of these fractions did not differ significantly from that of a fraction of the same intrinsic viscosity which had been obtained by the single precipitation method. Hence all subsequent fractionations were carried out employing the single precipitation technique.

Molecular Weight Determination.—Molecular weights of the polystyrene fractions have been calculated from their intrinsic viscosities, $[\eta]$, in freshly distilled benzene, using the relationship obtained by Ewart[11]

$$\log \overline{M}_v = (\log[\eta] + 4.013)/0.74 \tag{2}$$

where $\overline{M}_v$ is the viscosity average molecular weight.[10] Molecular weights of the polyisobutylenes have been obtained from their intrinsic viscosities in carbon tetrachloride, using the equation[12]

$$\log \overline{M}_v = (\log[\eta] + 3.345)/0.64 \tag{3}$$

The carbon tetrachloride was purified by successive washings with concentrated sulfuric acid, water, 10% sodium carbonate, and water, followed by drying over sodium sulfate and distilling. For the fractionated polymers it is permissible to replace $\overline{M}_v$ with $\overline{M}_w$.

The solution viscosities were measured at 30.08 ± 0.01° using a Ubbelohde no. 1 viscometer the calibration of which included the kinetic energy term.[13]

Relative viscosities, η_r, for solutions of the polystyrene fractions at different concentrations agreed with the relationship reported by Tingey[14]

$$(\ln \eta_r)/c = [\eta] - 0.125\,[\eta]^2 c \tag{4}$$

where c is expressed in g./100 ml. Consequently it was possible to determine the intrinsic viscosity from the efflux time for a single solution.

The value of $(\ln \eta_r)/c$ for polyisobutylene solutions with relative viscosities between 1.18 and 1.22 was arbitrarily taken to represent $[\eta]$. This value differs by approximately 2% from that obtained by extrapolation to infinite dilution. In some cases, particularly for high molecular weight samples, values of $(\ln \eta_r)/c$ for η_r in the above prescribed range were obtained by extrapolation from measurements in solutions of higher relative viscosities, the error thus introduced being less than 4%.

Molecular weights reported here are generally reproducible to ±3%. For certain of the polymers of higher molecular weight this uncertainty may be ±5%.

Capillary Viscometers.—Melt viscosities in the range of 1 to 10^6 poises were determined according to the procedure previously described.[3] The viscometers consisted of straight capillary tubes, 1.0 to 2.0 mm. in diameter, each marked at four points at appropriate distances from the lower tip. The time required to fill the viscometer capillary from one mark to the next under a predetermined pressure differential was measured. In this way three determinations could be carried out successively. Absolute viscosities in poises were calculated from

$$\eta = ktp \tag{5}$$

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

[11] R. H. Ewart, paper presented at the Atlantic City Meeting of the American Chemical Society, April 14, 1947. Recently A. I. Goldberg, W. P. Hohenstein and H. Mark, *J. Polymer Sci.*, **2**, 503 (1947), have proposed yet another intrinsic viscosity–molecular weight relationship for polystyrene. We prefer the Ewart expression for our purposes since it is derived from measurements made over a range similar to that covered in our experiments. Use of the Goldberg, Hohenstein and Mark equation, however, would not affect the general nature of the relationships reported in this paper.

[12] See reference 10. We are indebted to Dr. John Rehner, Jr., of the Esso Laboratories for providing information on the relationship between intrinsic viscosities of polyisobutylene in carbon tetrachloride compared to those in diisobutylene, the solvent originally used[10] in establishing the intrinsic viscosity–molecular weight relationship. According to Rehner, the ratio $[\eta]_{CCl_4}/[\eta]_{\text{diisobutylene}}$ is 1.255 ± 0.005 for all molecular weights.

[13] The calibration method outlined in ASTM Designation D445-39T was employed.

[14] H. C. Tingey, unpublished data referred to by R. H. Ewart, "Advances in Colloid Science," Vol. II, Interscience Publishers, New York, N. Y., 1946, p. 210.

where t is the measured time, p the pressure differential (2 to 30 cm. of mercury), and k is a calibration constant computed according to Poiseuille's law from the accurately measured dimensions of the tubes. As a check on the reliability of these calibrations, the constants k for several of the viscometers were independently determined from their tp products for an oil of accurately known viscosity, 493 poises at 30.0°, obtained from the National Bureau of Standards. The two methods agreed within ±1%.

Construction of the Coaxial Viscometer.—To measure viscosities in the range of 10^5 to 10^{11} poises there was constructed a coaxial falling-cylinder viscometer (shown schematically in Fig. 1) of the type described by Segel,[15] systematically studied by Traxler and Schweyer,[16] and used by various other workers.[17] It consists of a steel block 4″ × 3.5″ × 2″ containing a cylindrical cavity of diameter B and length L, the axis of the cavity coinciding with the long axis of the block. A steel rod of smaller diameter, A, is centered coaxially in the cavity, the ends of the rod projecting beyond the respective ends of the viscometer block. The annular space around the steel rod is filled with the sample. With the viscometer suspended with its long axis in a vertical position, the rate of fall, V, of the steel rod under the influence of a suspended weight, W, is observed. The viscosity is calculated from

$$\eta = KW/V \qquad (6)$$

where K is a constant determined from the dimensions of the instrument according to the equation

$$K = (g/2\pi L)\ln(B/A) \qquad (7)$$

where g is the gravitational constant. The instrument was designed with provisions for: (1) molding of the polymer in the annular space about the central rod, (2) obtaining adequate temperature control and (3) the application of a load to, and observation of the rate of fall of, the central cylinder. Important features of the construction are shown schematically in Figs. 2 and 3 (omitting the screws, guide pins, and other details which would make the drawings hopelessly complex).

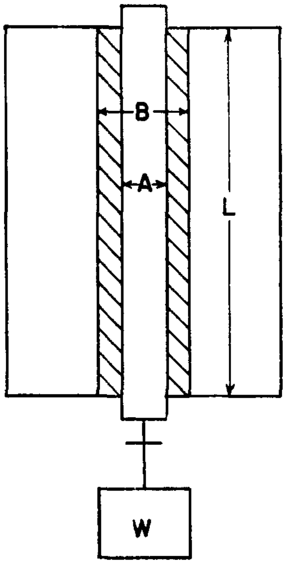

Fig. 1.—Schematic cross-sectional view of the coaxial falling-cylinder viscometer. The values of L, B and A are 10.16 cm., 1.122 cm. and 0.795 cm., respectively.

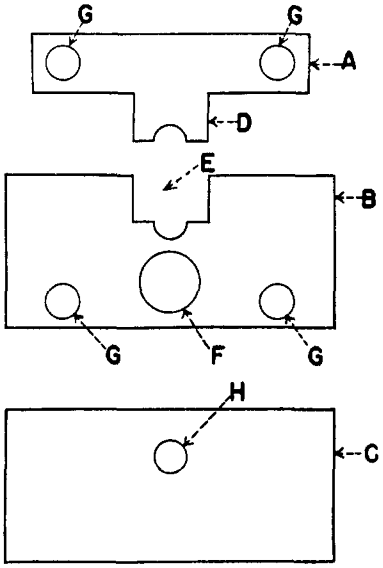

Fig. 2.—End view of the coaxial viscometer. Drawn approximately to scale.

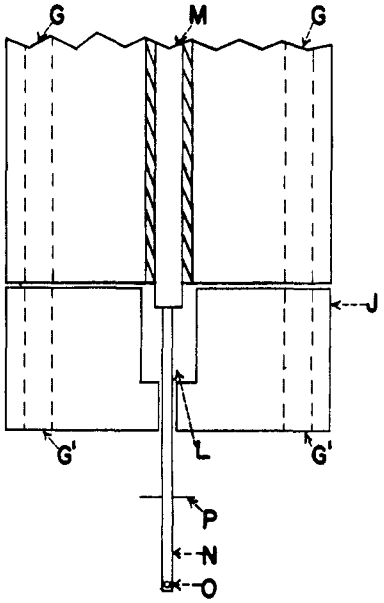

Fig. 3.—Cross-sectional view of the coaxial viscometer; not drawn to scale.

In order to permit molding of the sample within the instrument, the outer block was constructed in two parts, as illustrated by the end view of Fig. 2. As the two sections are brought together the projecting portion (D) of the top member (A) fits snugly into the trough (E) in the bottom section (B), thus providing the necessary compression of the polymer. Positioning of the steel rod in the

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[15] M. Segel, *Physik. Z*, **4**, 493 (1903).

[16] R. N. Traxler and H. E. Schweyer, *Am. Soc. Testing Materials Proc.*, **36**, 523 (1936).

[17] A. Pochettino, *Nuovo cimento*, **8**, 77 (1914); C. J. Mack, *J. Phys. Chem.*, **36**, 2901 (1932); H. L. D. Pugh, *J. Sci. Instruments*, **21**, 177 (1944).

cavity during the molding operation is accomplished by two metal plates (C) which can be secured to the ends of the bottom section of the viscometer, each plate being provided with a hole (H) about 0.001″ larger in diameter than the rod.

Four symmetrically placed $^3/_8$″ holes (G) were bored through the length of the block for the insertion of either cartridge-type electrical heaters or copper tubes containing a cooling liquid. A larger hole (F) directly under the cylindrical cavity provides for the insertion of a Fenwal thermoswitch, which in conjunction with an electronic relay provides temperature control. To insure uniform temperature throughout the length of the polymeric cylinder, 1.5″ steel blocks (J in Fig. 3) can be attached at both ends of the viscometer. These blocks are provided with appropriate holes (G′, L) to permit insertion of the heaters and to allow for motion of the inner cylinder and its attachments.

Two thermocouple holes are provided, one being drilled in the core of the steel rod and the other in the side of the viscometer block, the latter reaching within 5 mm. of the annular cavity.

As shown in Fig. 3, a thin steel tube (N) attaches to the end of the steel rod (M) and projects out into the space below the instrument. Weights may be hung from a hole (O) which is drilled at the lower end of this tube. A needle (P) is fastened perpendicular to its length, providing a reference for observing the motion of the falling cylinder. Two rods projecting from the sides of the viscometer provide for its suspension between a pair of iron posts firmly bolted to a cast iron base.

Operation of the Coaxial Viscometer.—In preparation for the molding operation, the end plates (C) are first attached to the lower block (B) of the viscometer and the steel rod is inserted through the holes (H) in the end-plates. The upper and lower blocks are brought to temperature, usually 160°. An amount of polymer slightly in excess of that needed to fill the cavity is distributed evenly in the trough (E) and the upper block is set in place on the lower. The assembly is placed in a press equipped with heated platens and again brought to temperature. A load of 10,000 to 30,000 pounds is applied to close the viscometer assembly, the excess polymer being forced out through three vents drilled in the top of the viscometer. After about ten minutes the viscometer is cooled to room temperature under pressure, the pressure is removed and the two sections of the viscometer are securely fastened together with screws.

In order to make ready for viscosity measurements, the insulating end pieces (J) are substituted for the end plates (C), the heaters and the thermoswitch are inserted in the cavities (G, F) and the necessary electrical connections are made. The steel tube (N) is secured to the steel rod, the thermocouples are set in place, and the assembly is insulated with asbestos board and glass fabric. The instrument is mounted with its axis vertical and brought to the desired temperature. The desired weight is hung on the end of the steel tube and the position of the needle observed at various intervals.

In the experiments reported here, the temperature was controlled within ±2° between −9 and 200°, the readings of the two thermocouples agreeing within ±1°. A traveling microscope accurate to ±0.0005 cm. was used for most of the observations; one of lower accuracy, ±0.003 cm., was used in the initial experiments. Rates of fall varying from 1.5×10^{-7} to 3.5×10^{-3} cm./sec. were observed. Usually ten or more observations were made while the cylinder moved 0.15 to 0.30 cm., after which the viscometer was inverted and the load attached to the other end. Observations were repeated while the cylinder traveled in the opposite direction. The velocity of fall was observed to be independent of the direction of motion of the cylinder.

High Temperature Stability.—Both the melt viscosity and the intrinsic viscosity were observed to decrease on heating polystyrene to 217° in the presence of either air or nitrogen for periods of five minutes to two hours. However, in several instances an insoluble portion appeared and an increase in the intrinsic viscosity of the soluble portion was observed. It appears that degradation and cross-linking reactions occur simultaneously under these conditions. Addition of phenyl β-naphthylamine eliminated all evidence of gelation and reduced degradation to a negligible amount when polysytrene was heated at 217° in a nitrogen atmosphere for up to two hours. Accordingly, approximately 0.5% of this compound was incorporated into all high molecular weight polystyrenes by addition to a benzene solution of the polymer and subsequent evaporation.

No signs of gelation and only a slight decrease in the intrinsic viscosity were observed when polyisobutylene was heated to 217° in the presence of an inert atmosphere for periods of thirty to ninety minutes.

The $\overline{M}_w$ values reported here are derived from intrinsic viscosities measured after the melt viscosity had been determined. In most cases the molecular weights before and after melt viscosity determination agree within 5%.

Results

The Coaxial Viscometer.—The deformation taking place within the coaxial viscometer approaches simple shear; the difference between the outer and inner cylinder diameters being relatively small, the rate of shear is nearly uniform throughout the polymer. If the polymer undergoes Newtonian flow, (1) the motion of the falling cylinder will be linear with time, (2) the observed viscosity will be independent of the applied load and (3) the viscosity values will agree with those obtained by the capillary method.

Results shown in Table II and in Fig. 4 illustrate the constancy of the rate of displacement of the cylinder with polyisobutylenes at viscosities up to 10^{10} poises and loads up to 500 g.

TABLE II

THE DISTANCE (d) TRAVELED BY THE FALLING CYLINDER IN TIME (t)

Polyisobutylene

$\overline{M}_w = 660,000$

Load 558 g., T = 160° C.[a]			Load 158 g., T = 160° C.[a]		
t, sec.	d obs.	d calcd.[b]	t, sec.	d obs.	d calcd.[b]
0	0 cm.	0 cm.	0	0 cm.	0 cm.
87	0.088	0.088	263	0.078	0.074
128	.130	.129	510	.149	.144
191	.191	.193	667	.191	.188
294	.293	.294	809	.229	.228
348	.350	.351	1007	.285	.284
Load 58 g., T = 160° C.[a]			**Load 527 g., T = 8° C.[c]**		
t, sec.	d obs.	d calcd.[b]	t, sec. × 10^{-3}	d obs.	d calcd.[b]
0	0 cm.	0 cm.	0	0 cm.	0 cm.
146	0.016	0.016	97.2	0.0132	0.0150
320	.035	.035	153.9	.0223	.0237
674	.073	.073	183.6	.0280	.0283
809	.086	.087	270.0	.0414	.0416
1021	.110	.110	500.4	.0773	.0771

[a] $\eta = 3 \times 10^6$ poises at 160°. [b] d calcd. = Vt, where V is the "best value" for the velocity in cm./sec. [c] $\eta = 2 \times 10^{10}$ poises at 8°.

However, in many cases, particularly at the higher viscosities, there was observed an initial non-linear dependence of displacement on time which later became linear (*i. e.*, the straight lines in Fig. 4 do not go through the origin). It was assumed that the non-linear portion was due to a time-dependent elastic deformation which, however, reached completion in a relatively short time.[18] Since the elastic deformation was of no interest in this work, sufficient time was allowed in most of the experiments for the completion of the elastic deformation prior to observing the fall of the cylinder. Hence, the times recorded in Table II are referred not to the time of application of the load but rather to some arbitrary time thereafter.

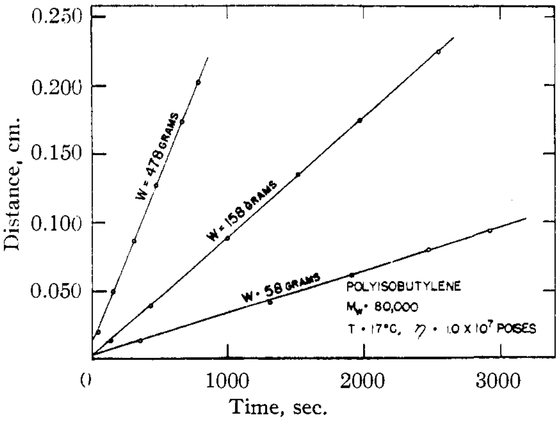

Fig. 4.—Motion of the falling cylinder *vs.* time. The initial observation (distance 0 at zero time) was made as soon as possible after attaching the weight.

Observed viscosity values for polyisobutylenes are independent of the applied load at least up to 500 g., provided the viscosity be less than 10^9 poises. Typical data illustrating this point are given in Table III. The apparent viscosity decreases with increasing load for higher values.

TABLE III

THE APPARENT VISCOSITY AS A FUNCTION OF APPLIED LOAD

Polyisobutylene, $\overline{M}_w = 660,000$

T = 160°			T = 8°	
Direction of motion	Load, g.	η, poises	Load, g.	η, poises
Out	558	2.97 × 10^6	3970	0.84 × 10^{10}
In	558	2.95	2140	1.50
Out	213	3.00	1020	1.55
In	158	3.02	527	1.84
Out	58	2.88	Extrapolated to zero load	1.97 × 10^{10} poises
In	58	2.85		
Average (2.95 ± 0.05) × 10^6 poises				

The viscosity at zero load, where the limiting flow characteristics may be assumed to correspond to ideal Newtonian behavior, was obtained in such cases by linear extrapolation (Fig. 5).

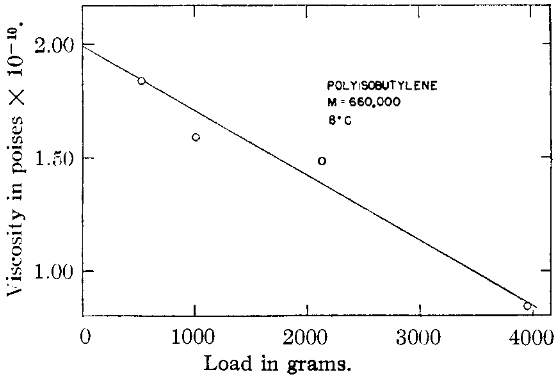

Fig. 5.—The apparent viscosity *vs.* load, employing the coaxial falling-cylinder viscometer.

Measurement of the viscosity of polyisobutylene of molecular weight 80,000 by this method yielded 88,000 poises at 87° which, from the temperature coefficient of flow (*cf. seq.*), corresponds to 79,000 poises at 89°. A similar determination at the latter temperature using a capillary viscometer yielded 80,700 poises. Thus, the two methods are consistent.

Attempts to measure accurately the viscosity of high molecular weight polystyrene in the coaxial viscometer were unsuccessful. Frequently the apparent viscosity was observed to vary with time and/or with the applied load. The results

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[18] A. P. Alexandrov and J. S. Lazurkin, *Acta Physicochim. U. R. S. S.*, **12**, 647 (1940).

TABLE IV

VISCOSITY–TEMPERATURE RELATIONS FOR POLYSTYRENE[a]

Polymer	M	$T°$	η_T, poises	Polymer	M	$T°$	η_T, poises
11AF3	134,000	217	11,400	16AF5	4900	217	1.03
		190.5	68,000			190.5	2.1
		160	1,350,000			160	8.7
						138	43.8
6AF3	80,000	217.2	1,703			110	950
		210.2	2,525			99.5	3750
		201.2	4,315			88.5	28,300
		190.7	9,200			81.7	182,000
		177.8	27,400				
				16AF6	3700	138	3.44
8AF4	32,200	217	131			110	25.6
		190.5	709			88	229
		160	12,900			74.0	2360
		138	375,000			64.5	8400
		130	2,320,000			53.0	197,000
4CF2	25,700	217	70.3				
		201.1	168				
		177.8	1060				
		156.5	11,500				

[a] The same sample of each polymer fraction was used for measurements at the several temperatures.

which appeared most reliable were lower than the corresponding values obtained with capillary viscometers by a factor of at least three. These discrepancies are believed to have been caused by air bubbles trapped in the polystyrene. All efforts to mold high molecular weight polystyrenes in the viscometer so that they were reasonably free of bubbles failed. On the other hand, polyisobutylene could be molded almost bubble-free with no great difficulty.

Viscosity–Temperature Relationships.—The viscosities of fifteen polystyrene fractions ranging in molecular weight from 3700 to 134,000 were measured with capillary viscometers at various temperatures. The maximum temperature range covered was 217 to 53°. Representative data are given in Table IV, and the data for thirteen of the fractions are plotted as log (η_T/η_{217}) *vs.* $1/T$ (°A.$^{-1}$) in Fig. 6. The viscosity ratio is employed in order to facilitate comparison of results for polymers differing in molecular weight. The relationship between log (η_T/η_{217}) and $1/T$ is non-linear. The data for eight fractions with molecular weights from 25,700 to 134,000 may be represented by a single curve (curve 1 of Fig. 6) when plotted in this manner. For fractions of lower molecular weight, a series of curves are obtained, their slopes being lower the lower the molecular weight. This dependence of the viscosity–temperature coefficient on the molecular weight is further illustrated in Fig. 7 where log (η_T/η_{217}) for temperatures of 160, 176 and 190° are plotted *vs.* the molecular weight. (The molecular weights employed here and in Tables IV, V and VI are based on intrinsic viscosity measurements and, hence, to the extent that the particular type of average requires specification when dealing with fractionated samples, they represent viscosity averages. For reasons which will appear later, however, the particular average is not specified.) The temperature-coefficient for polystyrene at a given temperature increases with increasing molecular weight up to approximately

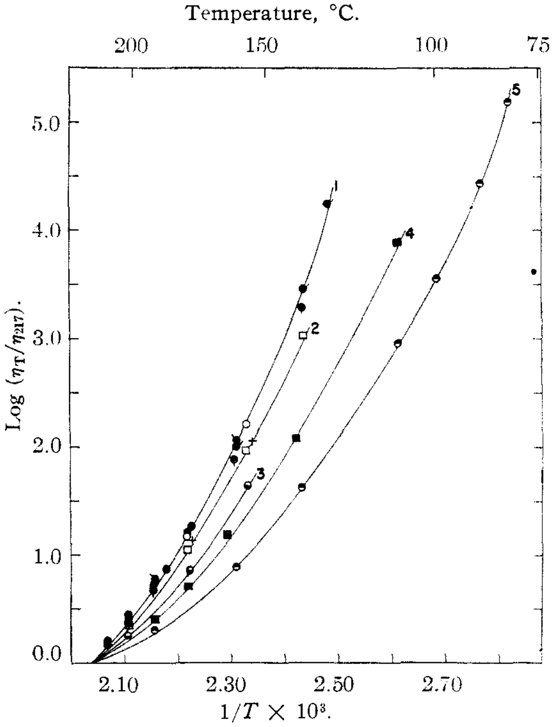

Fig. 6.—Log (η_T/η_{217}) *vs.* $1/T$ (°A.$^{-1}$) for polystyrene fractions of various molecular weights: curve 1, ● 134,000, ● 80,000, 69,500, 49,700, 44,000, ● 32,200, ○ 26,600, ● 25,500; curve 2, + 13,500, □ 11,000; curve 3, ◒ 7400; curve 4, ■ 5100; curve 5, ◓ 4900.

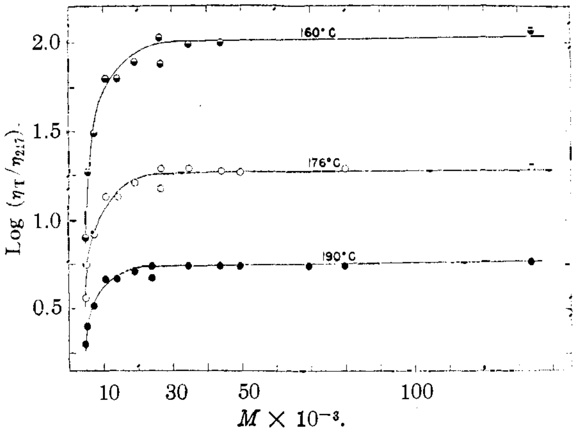

Fig. 7.—Log (η_T/η_{217}) *vs.* M for polystyrene fractions.

25,000 beyond which it is approximately constant.

Corresponding results for polyisobutylene over the molecular weight range from 11,200 to 660,000 are presented in Table V.

TABLE V

VISCOSITY–TEMPERATURE RELATIONS FOR POLYISOBUTYLENE[a]

Polymer	T, °C.	η_T, poises	Method of measurement
PB2F2	217	7.6×10^5	Capillary
M = 660,000	160	2.95×10^6	Coaxial
	141	5.28×10^6	Coaxial
	119	1.20×10^7	Coaxial
	100	2.57×10^7	Coaxial
	78	7.80×10^7	Coaxial
	28	2.04×10^9	Coaxial
	8	1.97×10^{10}	Coaxial
PB4F1	217	1100	Capillary
M = 80,000	190	2090	Capillary
	160	4800	Capillary
	138	10,100	Capillary
	89	80,700	Capillary
	87	8.8×10^4	Coaxial
	78.5	1.38×10^5	Coaxial
	38	1.83×10^6	Coaxial
	17	1.0×10^7	Coaxial
	3.5	4.1×10^7	Coaxial
	−9	2.58×10^7	Coaxial
PB1F3	216.5	1150	Capillary
M = 81,500	201.0	1640	Capillary
	179.0	2810	Capillary
	156.0	5600	Capillary
PB1F4	217	340	Capillary
M = 56,500	201.4	485	Capillary
	181.5	880	Capillary
	157.0	1750	Capillary
	110.0	9830	Capillary
PB1F5	217.0	119	Capillary
M = 38,200	200.8	168	Capillary
	178.6	305	Capillary
	155.6	634	Capillary
PB1F7	216.5	22.9	Capillary
M = 22,400	181.0	56.1	Capillary
	137.7	206	Capillary
	110.0	643	Capillary
	80.5	2760	Capillary
PB1F8	217.2	6.45	Capillary
M = 11,200	181.9	14.2	Capillary
	138.1	57.6	Capillary
	110.0	184	Capillary
	79.0	884	Capillary
	55.5	3530	Capillary

[a] The same sample of each polymer fraction was used for measurements at the several temperatures.

TABLE VI

THE APPARENT ENERGY OF ACTIVATION FOR VISCOUS FLOW

Polyisobutylene

Mol. wt. range	E_T, kcal./mole 217°	200°	150°	100°	50°	0°
11,200 to >1,000,000	10.3	10.6	12.0	13.2	13.7	19.3

Polystyrene

Polymer	M	E_T, kcal./mole 217°	200°	175°	150°	138°	125°	100°	88°	82°
Several	>25,000	24	30	38	52	66	>100	..	..	..
4CF3	19,000	22	27	35	42	..	...	..	..	..
4CF5	7,400	18	23	27	35	..	...	..	..	..
4CF6	5,100	8	21	26	32	..	...	..	..	..
16AF5	4,900	7	12	20	28	32	35	44	60	85
16AF6	3,700	..	..	..	..	..	22	27	32	37

Both types of viscometers were employed for measurements on each of the two highest molecular weight fractions. The capillary method alone was employed for the other polyisobutylenes. The data for the various fractions are represented by a single curve in Fig. 8. The viscosity-temperature coefficient appears to be independent of molecular weight over the range investigated. The corresponding curve for high molecular

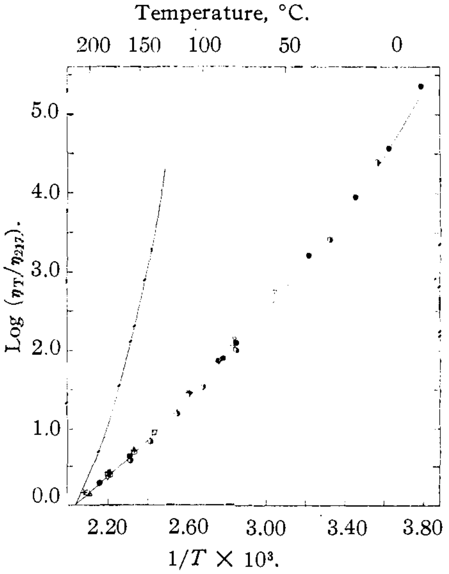

Fig. 8.—Log (η_T/η_{217}) *vs.* $1/T$ (°A.$^{-1}$) for polyisobutylene fractions of various molecular weights: ◑ 660,000, ● 80,000, ○ 81,500, + 56,500, △ 38,200, □ 22,400, ▽ 11,200. The curve to the left, representing high molecular weight polystyrene, is a duplicate of curve 1 of Fig. 6.

weight polystyrene (curve 1 of Fig. 6) has been included for comparison.

The present results are in good agreement with those of Ferry and Parks[19] on the viscosity of an unfractionated polyisobutylene of cryoscopic molecular weight 4900, as obtained from falling sphere and rotating cylinder measurements. As shown in Fig. 9, their data fall on or near the curve for polyisobutylene (from Fig. 8) provided the viscosity of their polymer at 217° (which they did not determine) is assumed to be 7.94 poises.

Both polymers exhibit a non-linear relationship between log η_T and $1/T$. The "apparent" energy of activation, E_T, for viscous flow at temperature T, defined as $2.3R[\mathrm{d}(\log \eta)/\mathrm{d}(1/T)]$, increases with decreasing temperature for both polystyrene and polyisobutylene. As shown in Table VI (see also Fig. 8), E_T for high molecular weight polystyrene in this temperature range is greater than the corresponding value for polyisobutylene and it increases more rapidly with decreasing temperature. The dependence of the viscosity–temperature coefficient for polystyrene on molecular weight below 25,000 is reflected in the diminished values of E_T in this range.

Viscosity and Molecular Weight.—The viscosities of the lower polyisobutylenes were measured at 217° by capillary viscometers; the coaxial method was used in most cases on the higher polymers. These latter measurements were carried out at several lower temperatures and the corresponding values at 217° were obtained by extrapolation using the viscosity–temperature dependence presented above. The validity of these extrapolations is confirmed by close agreement between values extrapolated from measurements at different temperatures, as shown in Table VII. Viscosities for polystyrene at 217° were obtained by the capillary method.

TABLE VII

EXTRAPOLATION OF COAXIAL VISCOMETER DATA TO 217°

Polymer	T, °C.	log η_T	Extrapolated log η_{217}	Average log η_{217}
PB5F1	160	8.05	7.40	7.40
PB5F2	160	7.69	7.04	7.02 ± 0.03
	115	8.34	6.99	
PB5F3	160	6.74	6.09	6.08 ± 0.01
	112	7.47	6.07	
PB2F4	88	6.38	4.50	4.51 ± 0.01
	38	7.73	4.51	

All of the above data as obtained at 217° or extrapolated to that temperature are summarized in Table VIII and in Figs. 10 and 11 where log η_{217} is plotted against $\overline{M}_w^{1/2}$. Curves drawn through the sets of points for the two polymers are of the same general character. While certain limited portions of the data may be approximated by straight lines, no linear relationship is valid over a wide molecular weight range. For polystyrenes below 25,000 the viscosity–molecular weight relationship is of little significance since for these polymers the viscosity–temperature behavior is dependent on the molecular weight. However, for convenience these data have been included and a dotted line has been drawn through the points.

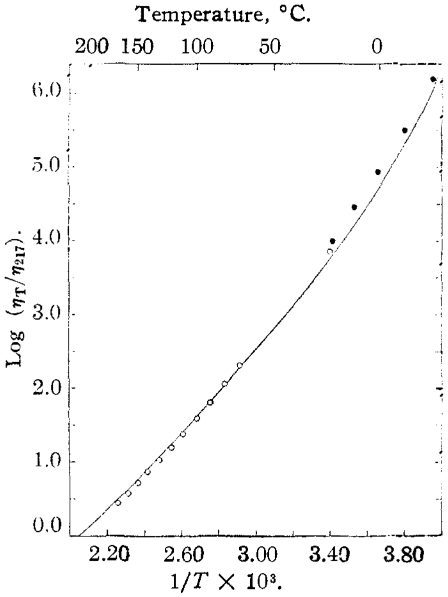

Fig. 9.—Log (η_T/η_{217}) vs. $1/T$ (°A.$^{-1}$) for polyisobutylene. The solid line is a reproduction of the curve for polyisobutylene in Fig. 8. The points represent data obtained by Ferry and Parks (ref. 19) on an unfractionated polyisobutylene of cryoscopic molecular weight 4900. The open circles represent falling sphere data; the dark circles represent data obtained with a rotating cylinder viscometer. The value of η_{217}, which they did not measure, was arbitraily taken as 7.94 poises.

The similarity in behavior of these two polymers is further illustrated if these data are plotted as log η_{217} vs. log $\overline{M}_w$. In such plots, the two sets of points may be represented fairly satisfactorily by two straight lines, with identical slopes. However, the approximate linearity of these log–log plots probably is of limited significance, the correct function being of a more complicated nature.

The Viscosities of Mixtures.—Any choice of a particular molecular weight average in Figs. 7, 10, and 11 is necessarily arbitrary so far as the foregoing data are concerned, inasmuch as the various molecular weight averages, $\overline{M}_n$, $\overline{M}_v$, and $\overline{M}_w$ for fractionated samples are similar. In order to establish the particular averages (if any) on which the viscosity and the viscosity–temperature coefficients depend explicitly, seven mixtures of polystyrene fractions and two of polyisobutylene were prepared as detailed in Table IX by evaporating benzene solutions of two fractions of widely separated molecular weights. The melt viscosities of the mixtures were observed at 217° and several lower temperatures (Table IX). In Table X val-

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[19] J. D. Ferry and G. S. Parks, *Physics*, **6**, 356 (1935).

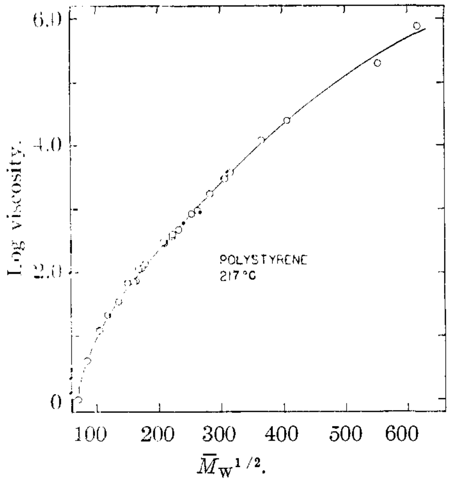

Fig. 10.—Log η_{217} vs. $\bar{M}_W^{1/2}$ for polystyrene fractions: measurements were made with capillary viscometers. The viscosity–temperature curves for polystyrenes below 25,000 are not parallel; hence the dotted line through the points for these polymers is for convenience only.

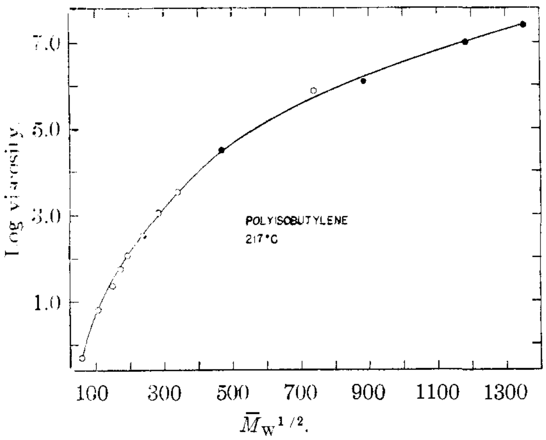

Fig. 11.—Log η_{217} vs. $\bar{M}_W^{1/2}$ for polyisobutylene fractions: observations with the coaxial viscometer (extrapolated), ●; with capillary viscometers, ○.

ues of $\bar{M}_n$, $\bar{M}_v$ and $\bar{M}_w$ for these mixtures are given (Columns 6, 2, and 4, respectively) as calculated by the usual equations

$$\bar{M}_n = \sum_i w_i \Big/ \sum_i (w_i/M_i), \quad (8)$$

$$\bar{M}_v = \Big[\sum_i w_i M_i^a \Big/ \sum_i w_i\Big]^{1/a} \quad (9)$$

$$\bar{M}_w = \sum_i w_i M_i \Big/ \sum_i w_i \quad (10)$$

where w_i is the weight fraction of the species of molecular weight M_i, and a is the exponent in the equation relating the intrinsic viscosity to molecular weight. The experimental values of $\bar{M}_v$ (Column 3), obtained from intrinsic viscosities, agree rather well with the calculated values, although for the higher molecular weight mixtures discrepancies as great as 6% occur.

TABLE VIII

VISCOSITY–MOLECULAR WEIGHT RELATIONSHIPS

Polymer fraction	% of unfractionated polymer	$\bar{M}_w$	η_{217},[a] poises	Method of measurement
		Polyisobutylene		
PB5F1	46.0	1,830,000	2.5×10^7	Coaxial extrapolated to 217°
PB5F2	23.6	1,400,000	1.0×10^7	Coaxial extrapolated to 217°
PB5F3	24.7	783,000	1.2×10^6	Coaxial extrapolated to 217°
PB2F2	25.0	548,000	7.6×10^5	Capillary at 217°
PB2F4	15.4	221,000	3.2×10^4	Coaxial extrapolated to 217°
PB1F2	14.4	115,000	3390	Capillary at 217°
PB1F3	11.1	81,500	1150	Capillary at 217°
PB4F1	20.0	80,000	1100	Capillary at 217°
PB1F4	12.0	56,500	330	Capillary at 217°
PB1F5	10.0	38,200	118	Capillary at 217°
PB1F6	9.0	29,900	55.8	Capillary at 217°
PB1F7	6.4	22,400	22.8	Capillary at 217°
PB1F8	7.8	11,200	6.5	Capillary at 217°
PB7F4	4.0	3,500	0.50	[b]
		Polystyrene		
14AF2	26.0	381,000	7.5×10^5	Capillary at 217°
14AF3	19.4	307,000	2.0×10^5	Capillary at 217°
14AF4	11.2	229,000	8.5×10^4	Capillary at 217°
11AF2	22.2	186,000	3.6×10^4	Capillary at 217°
14AF5	6.0	167,000	2.5×10^4	Capillary at 217°
11AF3	11.5	134,000	1.2×10^4	Capillary at 217°
8AF1	31.3	100,000	3710	Capillary at 217°
3DF3	5.8	94,000	2970	Capillary at 217°
6AF3	40.8	80,000	1703	Capillary at 217°
3DF3′	19.5	69,500	930	Capillary at 217°
3DF6	9.5	63,800	803	Capillary at 217°
3DF7	7.0	54,400	459	Capillary at 217°
6AF4	29.5	49,700	368	Capillary at 217°
3DF4′	21.7	49,700	398	Capillary at 217°
7AF3	20.0	44,000	287	Capillary at 217°
3DF8	9.2	43,300	299	Capillary at 217°
8AF4	15.0	32,200	131	Capillary at 217°
3DF5′	18.3	30,100	118	Capillary at 217°
3DF10	6.0	28,500	112	Capillary at 217°
6AF5	13.7	26,600	70.5	Capillary at 217°
16AF2	8.5	25,500	71.2	Capillary at 217°
4CF2	15.8	25,700	70.3	Capillary at 217°
3DF11	4.0	22,800	67	Capillary at 217°
4CF3	20.6	18,900	34	Capillary at 217°
3DF6′	12.1	14,200	21.5	Capillary at 217°
4CF4	21.3	11,000	12.0	Capillary at 217°
4CF5	11.5	7,200	4.1	Capillary at 217°
16AF5	14.0	4,900	1.0	Capillary at 217°

[a] Some of the viscosity values represent averages obtained from measurements at 217° on two or more samples of the same polymer fraction. These are generally reproducible to ±5% or better, although the uncertainty in the extrapolation of the coaxial data to 217° (Table VII) may be as high as ±15%. [b] A special pipet type viscometer consisting of a fine capillary and a small bulb was employed in measurements on this lowest fraction.

TABLE IX

THE VISCOSITIES OF MIXTURES

Designation	Mol. wts. and proportions of components[a]		η_T in poises 217°	190°	160°	138°	$\log\left(\frac{\eta_{190}}{\eta_{217}}\right)$	$\log\left(\frac{\eta_{160}}{\eta_{217}}\right)$
			Polystyrene					
A	389,000(0.5)	78,000(0.5)	80,500	....	....	..	...	...
B	389,000(0.5)	35,000(0.5)	50,000	....	....	..	...	...
C	100,000(0.5)	31,000(0.5)	796	4560	88,000	..	0.758	2.044
D	78,000(0.5)	31,000(0.5)	532	2820	55,000	..	0.724	2.014
E	138,000(0.25)	8,240(0.75)	67.4	307	2720	..	0.658	1.606
F	44,000(0.5)	5,180(0.5)	22.4	80	681	6710	0.553	1.483
G	26,000(0.5)	5,180(0.5)	9.2	33.4	273	2590	0.560	1.472
			Polyisobutylene					
H	233,000(0.5)	38,200(0.5)	4960	9240	216,000	..	0.270	0.639
I	81,500(0.5)	30,000(0.5)	321	....	.....	..	...	...

[a] Figures in parentheses represent proportions by weight.

TABLE X

MOLECULAR WEIGHTS OF THE MIXTURES

Designation	$\overline{M}_v$ calcd.	$\overline{M}_v$ obs.	$\overline{M}_w$ calcd.	$\overline{M}_{217}$	$\overline{M}_n$ calcd.	$\overline{M}_T$
			Polystyrene			
A	217,000	212,000	233,000	219,000	130,000	......
B	190,000	179,000	213,000	195,000	64,000	......
C	63,800	60,600	65,500	62,500	47,500	$\geq$25,000
D	51,600	53,600	54,500	55,200	44,200	$>$25,000
E	32,500	33,000	40,700	24,700	10,800	10,000
F	22,300	20,900	24,500	14,900	9,250	7,500
G	14,700	13,800	15,600	9,400	8,600	7,500
			Polyisobutylene			
H	121,000	121,000	135,000	134,000	66,000	Normal
I	53,700	52,700	55,800	55,700	44,000	......

The quantity designated as "$\overline{M}_{217}$" (Column 5) represents the molecular weight of a homogeneous fraction exhibiting the same viscosity at 217° as the mixture; the $\overline{M}_{217}$ values have been deduced from the measured viscosities of the mixtures at 217° (Table IX) and the previously established curves relating viscosity to molecular weight for the fractions (Fig. 10 or 11). Values of $\overline{M}_{217}$ for both of the polyisobutylene mixtures and for the polystyrene mixtures for which $\overline{M}_n$ is greater than 25,000 are in good agreement with the corresponding *weight average* molecular weights. For each of the polystyrene mixtures for which $\overline{M}_n$ is less than 25,000 (E, F, G), $\overline{M}_{217}$ lies between the number average and viscosity average molecular weights.

The quantity designated as "$\overline{M}_T$" (Column 7) represents the molecular weight of the polystyrene fraction having the same viscosity–temperature relationship as that of the mixture, as deduced from the observed values of (η_T/η_{217}) for the mixture (Table IX) and the curves of Fig. 7. For the two polystyrene mixtures with $\overline{M}_n$ greater than 25,000 (C, D) the viscosity–temperature coefficients are identical with those previously observed to be characteristic of polystyrene fractions having molecular weights in excess of 25,000. For each of the mixtures of lower molecular weight (E, F, G), $\overline{M}_T$ is approximately equal to the *number average* molecular weight of the mixture.

The ratio η_T/η_{217} for polyisobutylene mixture H at $T = 160°$ and 190° (Table IX) was observed to be in agreement with the corresponding value for the polyisobutylene fractions. As with the fractions, no dependence on molecular weight is evident.

Generalizing the above results obtained on simple mixtures of fractions, we conclude that the melt viscosities of polystyrenes for which the *number average* molecular weight is greater than 25,000 and of all polyisobutylenes (above a molecular weight of 11,200 at least) are explicit functions of the *weight average* molecular weight, regardless of the degree of molecular weight heterogeneity. Further, the viscosity–temperature coefficients for these polymers are independent of molecular weight distribution as well as of molecular weight. For polystyrenes of $\overline{M}_n$ less than 25,000, the viscosity–temperature coefficient varies with, and is determined by, the *number average* molecular weight, being otherwise independent of the molecular weight distribution. The melt viscosities of polystyrenes in this molecular weight (number average) range are not uniquely determined by any specific average molecular weight.

Discussion

Failure of equation (1) to accurately represent the dependence of melt viscosities of polystyrene and polyisobutylene on molecular weight is surprising in the face of the number of instances, covering a variety of polymers, in which the square root relationship has been reported to hold. Perusal of these various sets of results reveals, however, either that the molecular weight range covered generally was too limited for a conclusive decision or that the molecular weights were determined by methods which fail to yield an accurate measure of the weight average or something consistently proportional to it. These aspects of previous investigations on the applicability of equation (1) are summarized in Table XI. Only in the case of the glycol–dibasic acid polyesters has the relationship been demonstrated to apply precisely over a manifold range; it probably applies similarly to the polyamides. The results for polyesters and polyamides are limited to moderate molecular weights, however; it is conceivable that the square root relationship may fail for higher molecular weight polymers of these series.

TABLE XI

Polymer	Mol. wt. range	Mol. wt. determination	Reference
Glycol–dibasic acid polyesters	500–20,000 (40-fold)	End-group titration	3
Polyundecanoates	5,000–22,200 (4-fold)	End-group titration	4
Polyamides	2,880–37,100 (13-fold)	Stoichiometric proportion of reactants	5
Polydimethylsiloxane	2,500–160,000 (64-fold)	Osmotic pressure[a]; end group titration; light scattering	8
Polyisobutylene	134,000–545,000 (4-fold)	Intrinsic viscosity	7
Polyethylene	12,000–36,000 (3-fold)	Staudinger viscosity[b]	6
Paraffin wax–polyethylene mixtures	400–17,000 (42-fold)	Staudinger viscosity[b]	6

[a] Since these three methods were applied to different polymers none of which were fractionated, the results should not be strictly comparable on a weight average basis. [b] Molecular weights by this method are undoubtedly of limited significance.

The difference in the nature of the viscosity–molecular weight relationship for polystyrene and polyisobutylene on the one hand and that for polyesters and polyamides on the other cannot be dismissed as a mere consequence of the displacement of the respective molecular weight ranges covered. Enlarged plots of log η *vs.* $\overline{M}_w^{1/2}$ using the data for polystyrene and polyisobutylene fractions within the molecular weight range covered for the polyesters and polyamides (or, preferably, over the same range of chain lengths) show definite deviations from linearity which considerably exceed the experimental error; the polyester and polyamide plots, on the other hand, are precisely linear.[3] The conclusion cannot be avoided that the square root relationship applies to certain polymers such as the polyesters (at least up to moderate molecular weights), but that it cannot be applied to other polymers such as those investigated here, except, perhaps, as a short range rough approximation.[20] It may be significant that these polyesters and polyamides possess regularly occurring polar groups conducive to crystallization whereas polyisobutylene and polystyrene are nonpolar in character.

It is noteworthy that the melt viscosity appears to be determined explicitly by the weight average molecular weight (except for low molecular weight polystyrenes) in all cases where the effect of molecular weight heterogeneity has been tested.

Recently attempts have been made to interpret the effects of polymer molecular weight and of plasticizer content on softening points[21] and brittle temperatures[22] through the use of relationships based on equation (1). In the light of our results, which refute the general applicability of equation (1), these treatments are of questionable value.

Both polystyrene and polyisobutylene, in common with linear polyesters[3] and many other complex liquids,[23] exhibit non-linear relationships between ln η and $1/T$. If the usual relationship

$$\eta = De^{E/RT} \qquad (11)$$

where E is the activation energy for viscous flow, is to be applied here, either D or E (or both) must be temperature dependent. Hence, to regard the value of $R[\mathrm{d}(\ln \eta)/\mathrm{d}(1/T)]$ as the energy of activation probably is incorrect. The value of E_T considered here is merely a measure of the slope of the log η *vs.* $1/T$ curve at the specified temperature, although for convenience it has been designated as an apparent energy of activation.

There exists in the literature much disagreement concerning the temperature coefficient of viscosity of polystyrene. Spencer and Williams arrived at an estimate for E_T of 8 to 12 kcal. from viscosity measurements between room temperature and 100° on concentrated solutions of polystyrene in several aromatic solvents.[24,25] The linear extrapolation involved in obtaining E_T from the properties of solutions in which the maximum concentration was 50% by weight of polystyrene is of doubtful validity. The viscosity–temperature coefficient as deduced by the same authors[24] from Nason's results[26] on the rates of extrusion at high stresses is of uncertain significance. Observations of Foote[27] on the flow of polystyrene in capillary molds under high pressures indicated a dependence of E_T on temperature, his estimates varying from 40 to 80 kcal. between 200 and 100°. Many of these experiments involved high stresses and the accuracy was admittedly low. Wiley's measurements[28] on the elongation of a strip of polystyrene under a constant load permit a calculation of E_T of 18 kcal. and 79 kcal. at 190 and 150°, respectively, a variation in excess of that reported here. Perhaps, as has been suggested elsewhere,[21] the viscous and elastic effects have not been separated in this case.

Thus, while the confusion concerning the viscosity–temperature coefficient of polystyrene may be due in part to the variation of E_T with tempera-

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(20) Investigations now in progress on the viscosities of very low molecular weight polyisobutylene and of polyesters of exceptionally high molecular weight are expected to clarify the difference in the behavior of polymers of these two series.

(21) R. F. Tuckett, *Trans. Faraday Soc.*, **39**, 158 (1943).

(22) R. F. Boyer and R. S. Spencer, "Advances in Colloid Science," Vol. II, Interscience Publishers, New York, N. Y., 1946, p. 28; R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **2**, 157 (1947).

(23) R. H. Ewell, *J. Applied Phys.*, **9**, 252 (1938).

(24) R. S. Spencer and J. L. Williams, *J. Colloid Sci.*, **2**, 117 (1947).

(25) J. D. Ferry, THIS JOURNAL, **64**, 1330 (1942).

(26) H. K. Nason, *J. Applied Phys.*, **16**, 338 (1945).

(27) N. M. Foote, *Ind. Eng. Chem.*, **36**, 244 (1944).

(28) F. E. Wiley, *Ind. Eng. Chem.*, **33**, 1377 (1941).

ture and with molecular weight (for $\overline{M}_n$ less than 25,000), it is chiefly attributable to the low accuracy and unreliability (for this purpose) of much of the data on which previous estimates were based.[29]

Tuckett[21] has suggested that any apparent increase of E_T with decreasing temperature above a value of 20 kcal. is due to the simultaneous occurrence of a slow time–dependent elastic deformation, the activation energy of which he assumes to be greater than that for viscous flow. Elastic effects and other non-Newtonian disturbances were eliminated in the present work by operating at low rates of shear and at relatively large deformations. Results obtained with the capillary viscometers invariably were found to be independent of the pressure employed; the highest viscosities, determined with the coaxial viscometer, were derived from measurements made after elastic deformation appeared to have reached equilibrium. The successful elimination of any complicating elastic effects in our experiments is confirmed by the independence of the viscosity–temperature coefficient of molecular weight (except for polystyrenes for which $\overline{M}_n$ is less than 25,000). This behavior is contrary to that predicted by Tuckett on the basis of the aforementioned assumptions. Tuckett's assumption that E_T for viscous deformation is approximately independent of temperature and that it may not exceed 20 kcal. is not substantiated.

Since the viscosity–temperature coefficient has been observed to depend on the *number average* molecular weight, a commercial polystyrene with a high intrinsic viscosity will not necessarily possess the limiting viscosity–temperature coefficient for high molecular weight polystyrene. The presence of even a small amount of low molecular weight material (*e. g.*, unreacted monomer or an impurity) may cause the number average molecular weight to be less than 25,000, although the weight average molecular weight may be high. This suggests also that the efficiency of low molecular weight compounds as plasticizers for polystyrene is perhaps due to their ability to lower $\overline{M}_n$ (and thus E_T).

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. Robert E. Marshall in carrying out the fractionations and measuring solution viscosities.

Summary

1. The viscosities of polystyrene and polyisobutylene fractions over molecular weight ranges of 4900 to 381,000 and 3,500 to 1,830,000, respectively, have been determined at 217°. The viscosities of polystyrene fractions covering the molecular weight range of 3,700 to 134,000 were measured at several temperatures, the maximum range being 53 to 217°. Similar data were obtained for polyisobutylene fractions in the molecular weight range of 11,200 to 660,000 over a maximum temperature range of -9 to 217°.

2. The viscosity–molecular weight relationships have been expressed in graphical form. Log η_{217} is not a linear function of $\overline{M}_w^{1/2}$ for either of these polymers over the wide range in the molecular weight investigated.

3. Both polymers exhibit non-linear relationships between log η and $1/T$. The viscosity–temperature coefficient is independent of molecular weight except for polystyrene fractions of molecular weight less than 25,000, for which the coefficient at a specified temperature decreases with decreasing molecular weight.

4. From the viscosities of mixtures of fractions of widely separated molecular weights at 217° and at several lower temperatures, the following generalizations have been made: (a) The melt viscosities of these polymers at a specified temperature are determined by the weight average molecular weights, regardless of heterogeneity, except for polystyrenes of number average molecular weight less than 25,000. For the latter the melt viscosity is not uniquely determined by $\overline{M}_n$, $\overline{M}_v$, or $\overline{M}_w$, but appears to be some function of the particular molecular weight distribution. (b) The viscosity–temperature coefficient of these polymers is independent of both molecular weight distribution and molecular weight except for polystyrenes with $\overline{M}_n$ less than 25,000. For the latter the viscosity–temperature coefficient is determined by the number average molecular weight, being otherwise independent of molecular weight distribution.

5. The results of previous investigations on the viscosity–molecular weight and viscosity–temperature relationships of polymeric materials have been discussed.

6. A coaxial falling-cylinder viscometer was designed for determining the viscosity of high molecular weight polyisobutylene. Details have been given concerning its construction and use.

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(29) Since this manuscript was written, Spencer and Dillon, *J. Colloid Sci.*, **3**, 163 (1948), have reported viscosity–temperature data for high molecular weight polystyrene which are in substantial agreement with the present results. They have also investigated the dependence of viscosity on shearing stress. According to their results, our viscosity values for polystyrenes above 100,000 should in no case be in error by more than about 10% due to failure to extrapolate to zero shearing stress.