TABLE I

Hydrochlorides of tetrahydropyran derivatives	M. p., °C. cor.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
4-Diethylaminoacetyl	152–155	$C_{11}H_{22}ClNO_2$	56.04	55.89	9.41	9.27
4-Piperidinoacetyl	177–179	$C_{12}H_{22}ClNO_2$	58.17	58.58	8.95	9.06
4-Morpholinoacetyl	214–219	$C_{11}H_{2}ClNO_3$	52.90	53.42	8.07	7.89
4-(1-Hydroxy-2-diethylamino ethyl)	140.5–142	$C_{11}H_{24}ClNO_2$	55.56	55.80	10.17	10.73
4-(1-Hydroxy-2-piperidino ethyl)	208–210	$C_{12}H_{24}ClNO_2$	57.70	57.37	9.69	9.99
4-(1-Hydroxy-2-morpholino ethyl)	213–216	$C_{11}H_{22}ClNO_3$	52.48	52.48	8.81	9.07
4-(1-Acetoxy-2-piperidino ethyl)	211–213	$C_{14}H_{26}ClNO_3$	57.62	57.26	8.98	9.30
4-(1-Acetoxy-2-morpholino ethyl)	223–225	$C_{13}H_{24}ClNO_4$	53.14	53.41	8.23	8.51

Preparation of Tetrahydropyran Alkamines.—A 15% alcoholic solution of the respective dialkylaminoacetyl tetrahydropyran hydrochloride was hydrogenated in the presence of platinum oxide under one atmosphere pressure. Absorption of hydrogen was complete after about six hours. The catalyst was filtered, the solvent removed under reduced pressure, and the crystalline hydrochloride recrystallized from alcohol and acetone. The salts appeared as colorless powders and were readily soluble in water.

Acetyl derivatives of the amino alcohols were prepared by warming the hydrochlorides with an excess of acetic anhydride in pyridine solution at 60° for eight hours. The solvents were distilled under reduced pressure, the residues treated with sodium carbonate solution, the oily esters extracted into ether and converted to the hydrochlorides.

4-Cyanotetrahydropyran.—Since 4-tetrahydropyran carbonamide is readily soluble in water,[8] it was advantageous to prepare it by bubbling dry ammonia into an ether solution of 4-tetrahydropyranoyl chloride. The mixture of the amide and ammonium chloride was used directly for the following dehydration.

A mixture of 27.4 g. of the crude amide thus obtained (containing 19.3 g. of the pure amide) and 32 g. of phosphorus pentoxide was heated in a Claisen flask at 180–200° under 20 mm. pressure; almost all of the crude nitrile distilled and the reaction was completed by raising the temperature of the bath to 280°. On redistillation the product boiled at 91–95° (17 mm.), or at 100–102° (25 mm.). The yield was 12.8 g.

In the alternative preparation of the nitrile by the method of Gibson and Johnson[8] the boiling point of ethyl 4-cyanotetrahydropyran-4-carboxylate was found to be 130–134° at 23 mm. This is in better agreement with the observation of these authors (b. p. (16 mm.) 125°) than with that of Henze and McKee[7] who recorded b. p. (16 mm.) 135°.

Summary

In order to test the significance of saturated monocyclic ether systems in analgesics, several tertiary tetrahydropyranyl amino alcohols were synthesized. One of them caused analgesia in the rat.

CHARLOTTESVILLE, VA. RECEIVED DECEMBER 14, 1942

[CONTRIBUTION FROM THE ESSO LABORATORIES, CHEMICAL DIVISION OF THE STANDARD OIL DEVELOPMENT COMPANY]

Molecular Weights and Intrinsic Viscosities of Polyisobutylenes[1]

BY PAUL J. FLORY

Introduction

The extensive investigations carried on by Staudinger and co-workers during the past thirteen years have done much to stimulate interest in one of the most important phases of high polymer chemistry, namely, the assignment of molecular weight values to these substances. Early in the course of these investigations, and on the basis of extremely meager experimental evidence, Staudinger[2,3] proposed his well-known relationship of proportionality between the molecular weight of a linear polymer and the ratio of the viscosity increment ($\eta_r - 1$) to concentration. With appropriate revisions introduced by Kraemer and Lansing,[4,5] this may be written

$$[\eta] = K_S\overline{M}_w \qquad (1)$$

where $\overline{M}_w$ is the weight average molecular weight, K_S is a constant and $[\eta]$ is the intrinsic viscosity,[4] or limiting ratio of viscosity increment to concentration, defined by

$$[\eta] = [(\eta_r - 1)/c]_{c=0} \cong [(\ln \eta_r)/c]_{c=0} \qquad (2)$$

η_r is the relative viscosity and c is the concentration in g. of solute per 100 cc. of solution. Staudinger and co-workers proceeded to determine the

---

[1] Presented before the Division of Rubber Chemistry at the Buffalo meeting of the American Chemical Society, September 11, 1942.

[2] H. Staudinger and W. Heuer, *Ber.*, **63**, 222 (1930); H. Staudinger and R. Nodzu, *ibid.*, **63**, 721 (1930).

[3] H. Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag von Julius Springer, Berlin, 1932.

[4] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

[5] E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

constant K from the intrinsic viscosities of low polymers in the molecular weight range of a few thousand or less where cryoscopic or ebullioscopic methods are applicable. By extrapolating (1) far beyond the range for which K was determined, they arrived at molecular weights of the order of a hundred thousand for cellulose derivatives, vinyl resins, polystyrenes and rubber. Since viscosities are easily measured, equation (1) appeared to offer a most attractive method for determining average molecular weights.

More recent work, much of it by Staudinger and collaborators,[6,7] has shown that these values are too low; the constant K appears to decrease as the molecular weight increases. In each proved case of disagreement with his "rule" (the exceptions to which now far outnumber the instances of agreement) Staudinger insists that this is due to some peculiarity of the particular type of polymer molecule, *e. g.*, to an exceptional chain configuration or to branched chain structure.[7] K. H. Meyer,[8,9] who has persistently attacked the quantitative validity of Staudinger's equation, concludes that divergence from (1) cannot be regarded as an indication of branched, or non-linear, polymer structure since there is no assurance that a given linear polymer will obey equation (1).[9,10]

Viscosity measurements on solutions of polyoxyethylene glycols[11] in the molecular weight range of 1000 to 8200, and on polyesters[12] up to molecular weights of 30,000 (weight average) support a modified form of (1) in which a constant term has been added. Although available data pertaining to polymers of higher molecular weights indicate that Staudinger's equation is generally inapplicable, they are inadequate for conclusively establishing accurate relationships between molecular weight and intrinsic viscosity. For this purpose it is necessary to obtain intrinsic viscosities and absolute molecular weight values for a series of samples of a given polymer series having molecular weights distributed over a wide range. Inasmuch as the viscosity generally will depend on a different type of average molecular weight from that obtained by the absolute method employed (*cf. seq.*), the samples must be rendered as homogeneous as possible with respect to molecular weight (unless the type of distribution within each sample is known).

In the present investigation intrinsic viscosities of carefully fractionated polyisobutylenes have been compared with their absolute number average molecular weights determined by an osmotic pressure method. The higher polyisobutylenes (above *ca.* 400,000) possess molecular weights more than ten times the values obtained by extrapolating Staudinger's equation (1).[13] The existence of a simple empirical relationship between intrinsic viscosity and molecular weight has been established.

Experimental

Polymers.—Relevant data concerning the polymers from which the fractions were prepared are given in Table I. They were prepared by conventional low temperature polymerization techniques[14] using the catalysts indicated. In the preparation of polymer D, *n*-butylenes were intentionally mixed with the isobutylene in order to obtain a product of low average molecular weight. The *n*-butylenes act as poisons without entering the polymer to an appreciable degree.[14]

Table I

Polymer	Temperature of preparation, °C.	Catalyst	$[\eta]^a$
A	−27	$AlCl_3$	0.33
B	−85	BF_3	1.99
C	−78	$AlCl_3$	1.35
D	−47	BF_3	0.29

[a] Intrinsic viscosity measured in diisobutylene at 20°.

Fractionation.—A fractional precipitation procedure essentially similar to those previously applied to cellulose[15] and cellulose derivatives[16] and to various resins[17,18,19] was employed. Pure benzene (Barrett, "thiophene-free" grade) was used as the solvent, and c. p. acetone, dried and redistilled, was used as precipitant. From 15 to 25 g. of polyisobutylene was dissolved in from two to three liters of benzene. A quantity of acetone slightly in excess of that

---

(6) H. Staudinger and E. Husemann, *Ber.*, **68**, 1618 (1935); H. Staudinger and G. V. Schulz, *ibid.*, **68**, 2320 (1935); H. Staudinger and J. Schneiders, *Ann.*, **541**, 151 (1939).

(7) H. Staudinger and H. Warth, *J. prakt. Chem.*, **155**, 261 (1940); H. Staudinger and K. Fischer, *ibid.*, **157**, 19, 158 (1940–1941).

(8) K. H. Meyer and A. van der Wyk, *Helv. Chim. Acta*, **18**, 1067 (1935); *ibid.*, **19**, 218 (1936); *Z. Elektrochem.*, **40**, 446 (1934).

(9) K. H. Meyer, *Kolloid Z.*, **95**, 70 (1941).

(10) K. H. Meyer and M. Wertheim, *Helv. Chim. Acta*, **24**, 217 (1941).

(11) R. Fordyce and H. Hibbert, This Journal, **61**, 1912 (1939); E. L. Lovell and H. Hibbert, *ibid.*, **62**, 2140 (1940).

(12) E. O. Kraemer and F. J. Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932); P. J. Flory and P. B. Stickney, This Journal, **62**, 3032 (1940); W. O. Baker, C. S. Fuller and J. H. Heiss, *ibid.*, **63**, 3316 (1941).

(13) H. Staudinger and M. Brunner, *Helv. Chim. Acta*, **13**, 1375 (1930); see also ref. 3, p. 68.

(14) R. M. Thomas, W. J. Sparks, P. K. Frolich, M. Otto and M. Mueller-Cunradi, This Journal, **62**, 276 (1940).

(15) F. L. Strauss and R. M. Levy, *Paper Trade J.*, **114**, 211 (1942).

(16) See, for example, H. M. Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938).

(17) G. V. Schulz, *Z. physik. Chem.*, **B30**, 379 (1935); **B32**, 27 (1936).

(18) S. D. Douglas and W. N. Stoops, *Ind. Eng. Chem.*, **28**, 1152 (1936).

(19) R. A. Blease and R. F. Tuckett, *Trans. Faraday Soc.*, **37**, 571 (1941).

required for incipient cloudiness at 25.0° was added. The solution was rendered homogeneous by warming, and allowed to cool slowly with gentle stirring for about two hours, after which it was immersed in a water thermostat maintained at 25.00 ± 0.05°, the stirring being continued for an additional thirty minutes. The stirrer was removed and the gelatinous precipitate was allowed to agglomerate and settle on the bottom of the flask for at least two hours, or until the supernatant solution became clear. The liquor was carefully decanted with due exercise of caution to prevent decantation of any of the precipitate. The precipitate was redissolved in a liter of warm benzene, and sufficient acetone was added to reproduce the same concentration (cc. of acetone per 100 cc. of benzene) used in the first precipitation. After re-precipitating and pouring off the liquor exactly as described above, the precipitate was steeped in methanol and dried at 70° in vacuum for two hours. The low molecular weight, highly plastic fractions were redissolved in benzene, recovered in a suitable container by evaporation on the steam-bath, then dried as above. Repetition of vacuum drying several days later brought the samples effectively to constant weight. This procedure proved preferable to a single prolonged drying period at 70°.

The combined liquors from the above precipitations were evaporated to small volume at about 60° in a stream of air in order to remove the acetone completely. Benzene was added to bring the solution to a volume of two liters, and acetone was added to a concentration slightly greater than that used in the preceding precipitation. The precipitation and re-precipitation of the second fraction were carried out as described above. Proceeding in this way there was obtained a series of fractions of regularly decreasing molecular weight, each fraction being the product of two precipitations. As the quantity of unprecipitated polymer decreased, the volume of the solution from which precipitation occurred was decreased accordingly. For the first precipitation of each fraction polymer concentrations were maintained in the vicinity of 1 g. per 100 cc. of solution, and for the re-precipitation from 0.1 to 0.2 g. per 100 cc. The desirability of using dilute solutions in order to obtain good fractionation has been pointed out by Schulz.[20] Consideration of the equilibria between the highly swollen precipitated phase and the "solvent" phase leads to similar conclusions.[21]

The sum of the products of the weight fraction times the intrinsic viscosity for each fraction was equal to the intrinsic viscosity of the original polymer within experimental error. Thus, degradation did not occur during the fractionations.

Intrinsic Viscosities.—Viscosities were measured in diisobutylene solution at 20.0° using carefully calibrated Ubbelohde suspended level viscometers. Empirical kinetic energy corrections were employed. Since the times of flow were of the order of 100 sec., these were invariably small. Suspended foreign matter was removed by filtration immediately preceding measurement.

Concentrations were suitably chosen to obtain relative viscosities in the range 1.15 to 1.4. Values of $(\ln \eta_r)/c$ calculated from relative viscosities in this range differed by less than 2% from the infinite dilution values.[22] Hence, they were accepted as intrinsic viscosities (see equation (2)) without extrapolation. Generally two values of $[\eta]$ agreeing within 2% were obtained.

Osmotic Pressure Determination.—The osmometers[23] which have been used are similar in design to one described by Meyer, Wolff and Boissonnas.[24] Each of them consists of two brass blocks, 4″ × 4″ × 1/2″, into the faces of which shallow cylindrical cells have been cut. The blocks are bolted firmly together with the membrane separating the cells. The membrane also acts as a gasket to prevent leakage between the blocks. In use the osmometer is placed with the faces of the block vertical. The cell containing pure solvent communicates with an upright Pyrex capillary of approximately 0.5 mm. bore; connection is provided by a metal-to-glass seal to a "Kovar" alloy[25] tube 1/8″ in diameter which in turn is soldered into a small hole leading to the top of the solvent cell through the upper edge of the brass block. The solution cell connects similarly to a larger upright tube in which another capillary tube of the same bore can be inserted. The difference in hydrostatic head between the two cells can be varied by raising or lowering this tube. An additional connection with each cell, by means of a small hole drilled downward from the upper edge of the block and meeting a horizontal hole drilled from the bottom edge of the cell, permits changing solution or solvent without dismantling the osmometer. A needle valve at the top of the hole effectively seals this connection during use.

The cells of the first osmometer to be constructed consist simply of shallow cylindrical holes 2 1/4″ in diameter by 3/16″ in depth. The membrane is supported on either side by brass disks 1/16″ thick and drilled with numerous 1/4″ holes. The disk for the solvent compartment was covered with a fine metal screen on the face next to the membrane. The disks fit into indentations around the rim of the cell. These indentations were carefully machined to assure light contact between the disks and the membrane without preventing the outer portions of the membrane from sealing the osmometer.

The cells of the second osmometer were cut into the blocks by machining within a 2 1/4″ circular area diagonal grooves 1/8″ wide by 1/8″ deep with semi-circular profile at their base.[26] Two sets of parallel grooves, each set perpendicular to the other, were cut across the area. The grooves were spaced 3/16″ apart, center to center, leaving island points 1/16″ square for supporting the membrane. In order to eliminate "dead end" channels, a circular groove was cut around the periphery of the cell area. The sets of points on the two blocks coincided accurately. One

---

[20] G. V. Schulz, *Z. physik. Chem.*, **B46**, 137 (1940); **B47**, 155 (1940).

[21] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); also additional work as yet unpublished.

[22] For polymers of higher molecular weight than are of interest here, the variation of $(\ln \eta_r)/c$ with c is greater.

[23] The assistance rendered by Mr. H. Hartvigsen in the design and construction of the osmometers is gratefully acknowledged.

[24] K. H. Meyer, E. Wolff, C. G. Boissonnas, *Helv. Chim. Acta*, **23**, 430 (1940).

[25] Obtained from Stupakoff Laboratories, Inc., Pittsburgh, Pa. A graded seal, "Kovar" to "Pyrex" was used. It was found necessary to cover the exposed Kovar tubing with a cement in order to prevent corrosion when immersed in the water-bath.

[26] A somewhat analogous cell construction has been employed previously by R. E. Montonna and L. T. Jilk, *J. Phys. Chem.*, **45**, 1374 (1941).

set of supporting points was machined down 0.002″ below the level of the surface of the surrounding block in order to assure sufficient pressure on the portion of the membrane surrounding the cell to tightly seal the osmometer. With this arrangement over 95% of the membrane covering the cell area is in contact with solvent and solution, as against 50% for the other osmometer. Furthermore, there are no inaccessible crevices which would retain solution when the cell is emptied and hinder rapid attainment of equilibrium when filled. The cells of each osmometer hold about 8 cc. of liquid.

Two types of membranes were used. The first consisted of swollen cellophane,[27] No. 600, without water-proofing. After soaking the membrane in hot distilled water for a few minutes, it was placed in 7 *N* aqueous ammonium hydroxide for one hour at room temperature. It was then washed successively in distilled water, in alcohol, in a mixture of equal parts of alcohol and the solvent to be used, and finally in the pure solvent.

Much more permeable membranes were made by denitrating collodion films, according to the procedure described by Montonna and Jilk.[26] About 40 cc. of a mixture of 3 parts of Merck C. P. collodion (5%) and one part of ether was placed within an iron ring 5″ in diameter floating on a quiescent surface of clean mercury. The solvent was allowed to evaporate slowly until the membrane became sufficiently rigid to be removed from the ring. The last traces of solvent were removed by soaking in water. The outer edge of the membrane of irregular thickness was cut away. Denitration was carried out using ammonium hydrosulfide, exactly as described by Montonna and Jilk.[26] The denitrated membrane was washed thoroughly with water (instead of carbon disulfide[26]). Transfer to the organic solvent was carried out as described above for the cellophane membranes.

The more permeable denitrated collodion membranes could not be used for polymer fractions below about 50,000 average molecular weight because of passage of some of the polymer components through the membrane. When one of these membranes was used for a fraction below this limit, the observed pressure difference drifted downward and the liquid removed from the solvent compartment was found to contain a small amount of polymer. With higher fractions, the liquid removed from the solvent compartment was free of non-volatile material. The cellophane membranes, on the other hand, gave no evidence of solute permeation down to a molecular weight of about 5000 (see Table III). Consequently, cellophane membranes were used for low molecular weight fractions. Solutions of fractions above 50,000 average molecular weight yielded the same osmotic pressures with either type of membrane.

The osmometers were assembled as follows. The solvent cell, placed in a horizontal position, was filled with solvent. The membrane was set in place and the block containing the solution cell was set in place immediately without allowing the membrane to dry. The blocks were firmly bolted together. The solution cell was filled through the needle valve opening[24] leading to the bottom of the cell, then emptied by applying pressure to the upper opening, and refilled with fresh solution. Bubbles in either compartment were readily removed by oscillating the levels gently, after which the needle valves were inserted and tightened. Liquid levels were adjusted by adding (or removing) solution and solvent through the upper ends of the upright glass tubes connecting with the cells. At the end of an experiment the needle valve was removed from the solution compartment and the solution was blown out. The cell was filled twice with the next solution to be measured and emptied and re-filled a third time in order to ensure adequate rinsing. In this way the same membrane could be used over and over again. When it was desirable to do so, the solvent could be similarly replaced.

In order to eliminate fluctuations in the solvent level due to temperature variations, the cell was immersed in a water thermostat held at 25.00° in which temperature fluctuations amounted approximately to ±0.001°. Levels in the capillaries were read to 0.005 cm. with a cathetometer. The capillary inserted in the large tube connecting with the solution cell and the capillary attached to the solvent cell were cut from the same piece of tubing of calibrated uniform bore. The mean diameter varied by no more than ±0.5%. Since the capillary rise was of the order of 2 cm., the error due to difference in capillary rise in the two tubes was only about ±0.01 cm.

After placing the osmometer in the bath and adjusting the difference in levels to approximate the expected osmotic pressure, the position of the levels was measured with the cathetometer from time to time. After an hour or two, the levels were readjusted toward the approximate equilibrium value predicted empirically from the trend of the difference in levels. In some instances a second adjustment was made after another interval. Measurements were continued until the difference in level became constant within ±0.01 cm. change per hour. As the difference in densities of solvent and solution were negligible for the dilute solutions under investigation, the osmotic pressure in g. per sq. cm. was taken equal to the product of the solvent density and the difference in level in cm. This essentially static method proved to be more reliable and accurate than a more rapid dynamic method.

The course of the approach to equilibrium is shown in Fig. 1. After equilibrium has been attained displacement of the level in either direction is followed by gradual return to the *same* equilibrium pressure. There was no significant drift in the equilibrium pressure up to at least three days. The rate of approach to equilibrium was about 2 to 5% per minute for the denitrated collodion membranes; for the cellophane membranes the rate was about one-tenth of this, the values in each case varying somewhat from membrane to membrane. The apparent rate depends not only on the specific permeability of the membrane, but also on the rigidity with which the membrane is held in place. The advantage of greater specific permeability gained by the use of thinner membranes is outweighed by the decrease in rigidity. With the denitrated collodion membranes, equilibrium could usually be reached within about four or five hours; at least eight hours was required for the cellophane membranes.

Occasionally the solution compartment was filled with solvent and any equilibrium difference in level (apparently due to leakage) was observed. Generally this difference was less than ±0.02 cm., and for the more accurate work

---

(27) Supplied through the courtesy of E. I. du Pont de Nemours and Co.

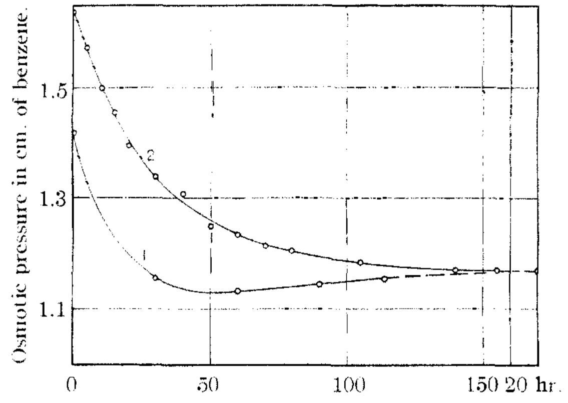


Fig. 1.—Establishment of osmotic equilibrium. After completing the observations shown on curve 1, the pressure was intentionally increased above the equilibrium value; the subsequent decrease in pressure is shown by curve 2 (Polymer C(4–9), 1.00 g./100 cc. in benzene; denitrated collodion membrane).

it was required to be so (*e. g.*, in experiments pertaining to osmotic pressure–concentration relationships).[28] In determinations on low molecular weight samples, where the resulting error was not significant, somewhat larger "residual" values were tolerated with the introduction of corresponding corrections on the observed osmotic pressures for the solutions. With solutions of high viscosity (higher concentration and molecular weight) the ultimate attainment of true equilibrium was slower,[28] although the permeability of the membrane naturally was the same. The difference is believed to arise from slow equilibration within the solution itself.[29]

Results

Osmotic Pressure–Concentration Relationships.—For correct evaluation of the number average molecular weight it is absolutely essential to extrapolate the osmotic pressure–concentration ratio π/c to zero concentration. This is especially important when dealing with high polymer solutions because of their rapid deviations from ideal solution laws at finite concentrations.[21,30,31,32]

For the purpose of establishing reliable procedures for extrapolation to zero concentration, osmotic pressures of several fractions differing in molecular weight were measured at 25.0° in cyclohexane and in benzene at various concentrations up to 2 g. per 100 cc. Attainment of the utmost accuracy was emphasized particularly in this portion of the investigation. The results are given in Table II. The polymer fractions are designated in the first column by a letter referring to the polymer from which the fraction was prepared (see Table I) followed by two numbers in parentheses which refer to the amounts of precipitant used in the isolation of the sample. Thus, C (4–9) refers to a fraction prepared from polymer C, which remained in the liquors from the standard precipitations (see above) using 4 cc. of acetone per 100 cc. of benzene, but which was precipitated by 9 cc. of acetone per 100 cc. of benzene. It has been found that the region of precipitation for a given concentration of acetone is accurately reproduced with different polymers, despite wide variations in their distributions and average

Table II

Osmotic Pressure *vs.* Concentration in Cyclohexane and Benzene at 25.0°

Polymer and Solvent		c in g./100 cc.	π in g./sq. cm.	π/c	$\pi/c - (\pi/c)_0$
B (0–3)	C_6H_{12}	2.04	10.82	5.31	5.01
B (0–3)	C_6H_{12}	2.00	10.58	5.29	4.99
B (0–3)	C_6H_{12}	1.50	5.73	3.82	3.52
B (0–3)	C_6H_{12}	1.02	2.57	2.52	2.22
B (0–3)	C_6H_{12}	1.00	2.42	2.42	2.12
B (0–3)	C_6H_{12}	0.76	1.32	1.74	1.44
B (0–3)	C_6H_{12}	.51	0.65	1.27	0.97
B (0–3)	C_6H_{12}	.34	.30	0.88	.58
		.00		(.30)[a]	
B (0–3)	C_6H_6	2.00	82	.41	.08
B (0–3)	C_6H_6	1.00	.37$_5$	.37$_5$	.04$_5$
B (0–3)	C_6H_6	1.00	.40$_5$	.40$_5$	.07$_5$
B (0–3)	C_6H_6	0.50	.15$_5$	.31	− .02
B (0–3)	C_6H_6	.50	.17$_5$	.35	.02
		.00		(.33)	
C (4–9)	C_6H_{12}	2.00	12.10	6.05	5.06
C (4–9)	C_6H_{12}	1.50	6.80	4.53	3.54
C (4–9)	C_6H_{12}	1.00	3.12	3.12	2.13
C (4–9)	C_6H_{12}	0.75	1.79	2.39	1.40
C (4–9)	C_6H_{12}	.50	0.93$_5$	1.87	0.88
C (4–9)	C_6H_{12}	.25	.36	1.44	.45
		.00		(0.99)	
C (4–9)	C_6H_6	2.00	2.14$_5$	1.07	.08
C (4–9)	C_6H_6	1.50	1.57$_5$	1.05	.06
C (4–9)	C_6H_6	1.00	1.02$_5$	1.02$_5$	.03$_5$
C (4–9)	C_6H_6	0.50	0.50$_5$	1.01	.02
		.00		(0.99)	
B (9–13)	C_6H_{12}	2.00	16.41	8.20	4.96
B (9–13)	C_6H_{12}	1.50	10.12	6.75	3.51
B (9–13)	C_6H_{12}	1.00	5.39	5.39	2.15
B (9–13)	C_6H_{12}	0.50	2.07$_5$	4.15	0.91
		.00		(3.24)	
A (14–25)	C_6H_{12}[b]	1.00	10.77	10.77	2.10
A (14–25)	C_6H_{12}[b]	0.75	7.64	10.19	1.52
A (14–25)	C_6H_{12}[b]	.50	4.89	9.78	1.11
A (14–25)	C_6H_{12}[b]	.25	2.25	9.00	0.33
		00		(8.67)	

[a] The π/c values in parentheses have been obtained by extrapolation. [b] A cellophane membrane was used in the experiments on A (14–25). Denitrated collodion membranes were used in all other experiments.

---

(28) G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942), encountered similar "residual" osmotic pressures.

(29) S. R. Carter and B. R. Record, *J. Chem. Soc.*, 660, 664 (1939), were able to hasten equilibration with the aid of a stirring device operating within the osmometer.

(30) H. Mark, "High Polymers," Vol. II, Interscience Publishers, Inc., New York, 1940, pp. 228–245.

(31) K. H. Meyer, *Z. physik. Chem.*, **B44**, 383 (1939); *Helv. Chim. Acta*, **23**, 1063 (1940); K. H. Meyer and A. J. A. van der Wyk, *ibid.*, **23**, 488 (1940).

(32) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Annals New York Acad. Sciences*, **43**, 1 (1942); This Journal, **64**, 1712 (1942).

molecular weights.[33,34] Thus, the figures in parentheses are indicative of the molecular weight region covered by the fraction. In order to obtain fractions of sufficient size for this work, it was expedient to separate comparatively broad cuts, which consequently are not as homogeneous as the fractions used in the investigation of the intrinsic viscosity-molecular weight relationship.

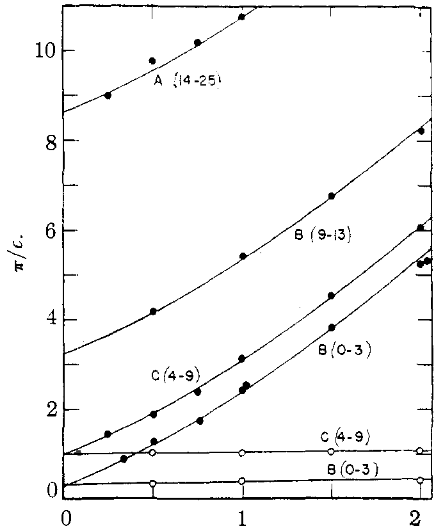


Fig. 2.—Osmotic pressure-concentration ratio *vs.* concentration for cyclohexane (●) and benzene (O) solutions.

The ratios of π/c given in the fourth column of Table II are plotted against c in Fig. 2. A linear relationship between π/c and c has been deduced on theoretical grounds by Huggins[32] and the author[21] and, in general, experimental investigations[10,24,30] on various polymer solutions seem to support this deduction. The points for the cyclohexane solutions definitely describe curves with upward concavity. A similar curvature in the plot of π/c *vs.* c for rubber solutions in benzene has been observed by Gee and Treloar.[28] They contend furthermore that the slope at a given concentration varies with the molecular weight of the sample. Over the range investigated here no definite dependence of slope on molecular weight has been observed for the polyisobutylene solutions. To demonstrate this the curves in Fig. 2 for the cyclohexane solutions have been drawn purposely with identical shapes, so that they are all superimposable by suitably shifting the ordinate axes. This is further shown by the $(\pi/c) - (\pi/c)_0$ values given in the last column of Table II and plotted against c in Fig. 3. This quantity, which may be looked upon as the deviation from the classical ideal solution law, varies with concentration in a manner which shows no significant dependence on molecular weight.

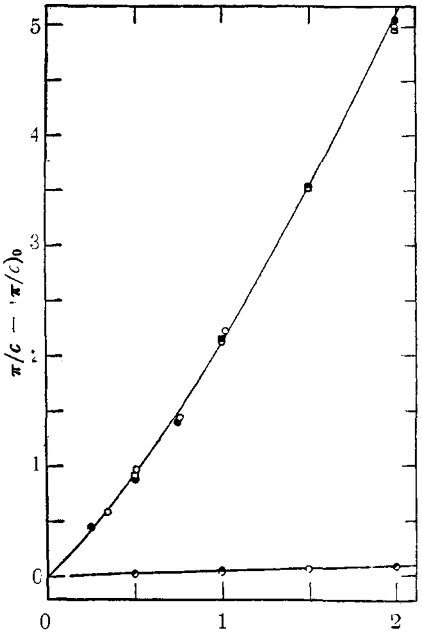


Fig. 3.—Deviation from van't Hoff's law *vs.* concentration for cyclohexane (upper curve) and benzene (lower straight line) solutions: ● = B(0–3); O = C(4–9); □ = B (9–13).

The π/c values for benzene solutions of polyisobutylene exhibit much smaller variations with concentration (see Fig. 2 and the last column of Table II), as would be expected[21] from the fact that polyisobutylene of high molecular weight is on the verge of precipitation when dissolved in benzene at 25°.[35] Straight lines with small positive slope have been drawn through these points. Values of $(\pi/c) - (\pi/c)_0$ for benzene solutions are also plotted in Fig. 3.

The significant feature of the results shown in Fig. 2, so far as the present investigation is concerned, is the gratifying coincidence of the extrapolations of the curves for the same polymer in cyclohexane and in benzene, in spite of the marked difference in the dependence of π/c on concentration. This fact confirms the reliability of the ex-

---

(33) Intrinsic viscosities at the mean points of separation of the fractions (which doubtless widely overlap one another) can be computed readily from the complete fractionation data. The reciprocals of these intrinsic viscosities are found to increase linearly with the volume of precipitant, in analogy with the similar relationship of G. V. Schulz and B. Jirgensons, *Z. physik. Chem.*, **B46**, 105 (1940).

(34) G. V. Schulz, *Z. Elektrochem.*, **45**, 652 (1939).

(35) H. C. Evans and D. W. Young, *Ind. Eng. Chem.*, **34**, 461 (1942).

TABLE III

MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES[a] OF POLYISOBUTYLENE FRACTIONS

Polymer	[η]	Membrane[b] and solvent		c, g./100 cc.	π, g./sq. cm.	π/c	(π/c)₀	$\overline{M}_n$
A (7–8)	0.866	Col.	C_6H_{12}	0.50	1.08	2.16	1.25	202,000
				1.00	3.44	3.44	1.34	189,000
A (8–9)	.698	Col.	C_6H_{12}	0.50	1.38_5	2.77	1.86	136,000
				1.00	3.89	3.89	1.79	141,000
A (10–12)	.495	Col.	C_6H_{12}	0.50	2.05	4.10	3.19	79,300
				1.00	5.32	5.32	3.22	78,600
A (12–14)	.370	Col.	C_6H_{12}	0.50	2.94	5.88	4.97	50,900
				1.00	7.06	7.06	4.96	51,000
A (14–17)	.303	Col.	C_6H_{12}	0.51	3.73	7.31	6.38	39,700
A (17–20)	.260	Col.	C_6H_{12}	.47	4.61	9.80	8.94	28,300
A (24–30)	.203	Col.	C_6H_{12}	.375	5.04	13.43	12.77	19,800
A (30–40)	.165	Col.	C_6H_{12}	.375	7.04	18.77	18.11	13,970
				.75	14.80	19.75	18.28	13,830
A (40–55)	.137	Col.	C_6H_{12}	.50	11.97	23.94	23.03	10,980
				.25	5.78	23.12	22.70	11,130
A (55–85)	.118	Cel.	C_6H_{12}	.25	7.85	31.40	30.98	8,170
A (85–125)	.089	Cel.	C_6H_{12}	.25	11.36	45.44	45.02	5,620
				.375	17.0	45.4	44.8	5,660
B (2.5–3)	3.04	Col.	C_6H_6	1.00	0.23_5	0.23_5	0.19_5	1,300,000
				1.00	.23	.23	.19	1,330,000
C (3–3.5)	2.29	Col.	C_6H_6	1.00	.30	.30	.26	970,000
				0.50	.14	.28	.26	970,000
C (3.5–4)	1.87	Col.	C_6H_6	1.00	$.44_5$	$.44_5$	$.40_5$	625,000
				0.50	$.21_8$	$.43_5$	$.41_5$	608,000
C (4.5–5.5)	1.35	Col.	C_6H_{12}	0.50	$.76_5$	1.53	.62	408,000
				1.00	2.77	2.77	.67	378,000
C (5.5–6.5)	1.12	Col.	C_6H_{12}	0.50	0.87	1.74	.83	304,000
				1.00	2.92	2.92	.82	308,000
C (6.5–8)	0.83	Col.	C_6H_{12}	0.50	1.11	2.22	1.31	193,000
				1.00	3.29	3.29	1.19	213,000
		Cel.	C_6H_{12}	1.00	3.33	3.33	1.23	206,000
C (10–12)	.551	Col.	C_6H_{12}	0.50	1.74	3.48	2.57	98,400
				0.50	1.73	3.46	2.55	99,200
				1.00	4.66	4.66	2.56	98,800
D (10–11)	.522	Col.	C_6H_{12}	0.50	1.90	3.80	2.89	87,500
				1.00	4.99	4.99	2.89	87,500
D (11–12)	.460	Col.	C_6H_{12}	0.50	2.18	4.36	3.45	73,300
				1.00	5.64	5.64	3.54	71,500
D (25–29)	.209	Cel.	C_6H_{12}	0.50	5.98	11.96	11.05	22,900
D (35–43)	.152	Cel.	C_6H_{12}	.25	4.72	18.88	18.46	13,700
				.50	9.91	19.82	18.91	13,370
D (55–67)	.113	Cel.	C_6H_{12}	.25	7.40	29.60	29.18	8,660
				.50	15.25	30.50	29.60	8,540

[a] Intrinsic viscosities measured in diisobutylene at 20.0°.

[b] The abbreviations "Col." and "Cel." refer to denitrated collodion and cellophane membranes, respectively.

trapolation procedure for the purpose of determining $(\pi/c)_0$, and hence the number average molecular weight. Most of the molecular weight determinations have been carried out in cyclohexane; for the samples of highest molecular weight benzene has been used. Extrapolations to infinite dilution have been based on the curve and straight line in Fig. 3 representing $\pi/c - (\pi/c)_0$ *vs.* c for cyclohexane and benzene solutions, respectively.

Molecular Weight–Intrinsic Viscosity Relationship.—The van't Hoff equation

$$\overline{M}_n = RT/(\pi/c)_0$$

relating number average molecular weight to π/c *at zero concentration* possesses an indisputably rigorous thermodynamic basis. With the osmotic pressure in g. per sq. cm., c in g. per 100 cc. and $T = 298$°K. this becomes

$$\overline{M}_n = 2.53 \times 10^5/(\pi/c)_0 \qquad (3)$$

Intrinsic viscosities in diisobutylene and osmotic pressure results leading to values of $\overline{M}_n$ computed from this equation are presented in Table III for several series of polyisobutylene fractions, each representing a relatively narrow range of molecular weight. A log-log plot of mean values of $\overline{M}_n$ *vs.* $[\eta]$ is shown in Fig. 4 to be strictly linear within experimental error. A broken line of slope equal to unity, representing the Staudinger relationship by means of which previous molecular weight values for polyisobutylene have been calculated, is also included.

The equation of the straight line drawn through the points in Fig 4 is

$$\log M = 5.378 + 1.56 \log [\eta] \qquad (4)$$

or

$$[\eta] = KM^a \qquad (5)$$

where $K = 3.60 \times 10^{-4}$ and $a = 0.64$. Equation (5) is the equivalent of one recently proposed by Houwink[36] for polymeric methyl acrylate, methyl methacrylate, polyvinyl acetate and polyvinyl alcohol on the basis of results of Staudinger and Warth.[7] These results covered a comparatively brief molecular weight range and the effectiveness of the coarse fractionation employed by Staudinger and Warth in suppressing the difference between the "viscosity average" and the number average molecular weights is doubtful. Nevertheless, Houwink[36] found $a = 0.6$, in close agreement with our value for polyisobutylene.

Discussion

Previous comparisons[13,37,38] of polyisobutylene solution viscosities with their molecular weights have been confined to the molecular weight range below about 10,000. The single measurement[13] upon which Staudinger[3] apparently based his "constant" for polyisobutylene was carried out on a polymer having a cryoscopic molecular weight of 1490 and an intrinsic viscosity in tetralin of 0.044. The molecular weight calculated by extrapolating equation (4) down to this intrinsic viscosity (ignoring the difference in solvents) is 1800. The discrepancy is no larger than should be expected to arise from the probable degree of heterogeneity of the sample used by Staudinger and Brunner.[13]

Kemp and Peters[38] have compared intrinsic viscosities of polyisobutylenes with "molecular weights" calculated from cryoscopic measurements ($\Delta T/c$) at arbitrarily chosen *finite* concentrations. They reject extrapolated $(\Delta T/c)_0$ values for this purpose on the grounds that they give "inordinately high molecular weights." There is no basis whatever for using anything that can be derived from their results other than $(\Delta T/c)_0$ values, necessarily determined by extrapolation, for the calculation of the number average molecular weight.

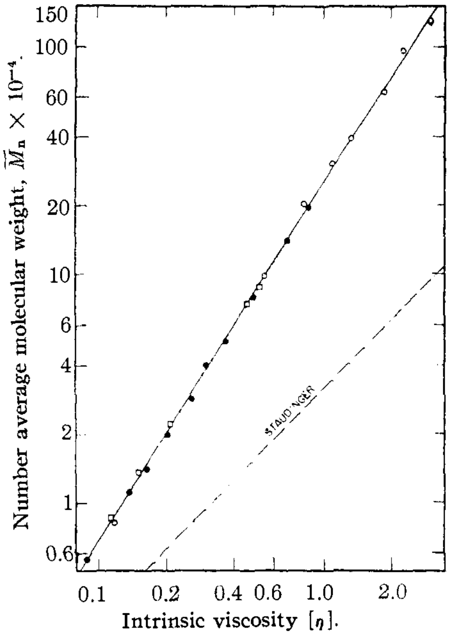


Fig. 4.—Log $\overline{M}_n$ *vs.* log $[\eta]$ for polyisobutylene fractions from Polymer A (●), Polymer C (○), Polymer D (□), and from Polymer B (◇). Molecular weights calculated from Staudinger's relationship are shown by the broken line.

Even after extrapolating the results of Kemp and Peters to zero concentration, they are of doubtful value for establishing viscosity–molecular weight relationships because of the ineffective fractionation procedure which was employed in the preparation of their samples. Synthetic polyisobutylenes invariably contain species covering a broad molecular weight range. Kemp and Peters obtained only a few fractions (one of them constituted 88% of the initial polymer) from each synthetic product, and these did not differ greatly in average molecular weight. The conclusion is unavoidable that these fractions consisted of very broad cuts. The viscosity averages of some of their samples may have been several times their number average molecular weights.

There is no actual disagreement between earlier cryoscopic measurements and the osmotic pres-

---

(36) R. Houwink, *J. prakt. Chem.*, **157**, 15 (1940).

(37) R. M. Thomas, J. C. Zimmer, L. B. Turner, R. Rosen and P. K. Frolich, *Ind. Eng. Chem.*, **32**, 299 (1940).

(38) A. R. Kemp and H. Peters, *ibid.*, **34**, 1192 (1942).

sure results reported here. The wide discrepancies between previous molecular weight values for polyisobutylenes and those established here result from several factors: (a) failure to extrapolate cryoscopic measurements to zero concentration, (b) inadequate fractionation, and, most important of all, (c) the use of the intrinsically incorrect Staudinger equation for extrapolating far beyond the range of the cryoscopic measurements.

The much greater sensitivity of the osmotic pressure method permits its application up to molecular weights of about 1,000,000. Results obtained for higher fractions are insufficiently accurate for significant comparison with equation (4). However, the good agreement obtained over the preceding two-hundred-fold molecular weight range would seem to justify estimation of higher molecular weights by extrapolating the line in Fig. 4. Under suitable conditions it is possible to synthesize polymers of isobutylene[14,37] having intrinsic viscosities as high as 10. The corresponding molecular weight calculated from (4) is about 10,000,000. So far as the author is aware there is no record in the literature of another synthetic (linear) polymer known to have a molecular weight approaching this figure. Polyisobutylenes of even higher intrinsic viscosity can be obtained by fractionation.

Viscosity Average Molecular Weight.—Kraemer and Lansing[4] have shown that molecular weights of heterogeneous polymers calculated from intrinsic viscosities according to Staudinger's equation are weight averages. Since an equation of the form of (5) appears to be quite generally applicable to high polymer solutions, it is important to inquire concerning the type of average it yields. With Kraemer[39] we let $(\eta_r - 1)_i$ represent the viscosity increment of the i-th polymer component in the dilute solution. According to (5)

$$(\eta_r - 1)_i = Kc_iM_i^a$$

For the total viscosity increment

$$(\eta_r - 1) = \sum_i (\eta_r - 1)_i = K \sum_i c_iM_i^a$$

$$[\eta] \equiv [(\eta_r - 1)/c]_{c=0} = K \sum_i w_iM_i^a / \sum_i w_i$$

since c_i is proportional to the weight fraction w_i of the i-th species in the polymer. Hence

$$[\eta] = K\overline{M}_v^a \qquad (5')$$

where

$$\overline{M}_v = \left[\sum_i w_iM_i^a / \sum_i w_i\right]^{1/a} \qquad (6)$$

or

$$\overline{M}_v = \left[\sum_i N_iM_i^{a+1} / \sum_i N_iM_i\right]^{1/a} \qquad (6')$$

where N_i is the number of molecules of molecular weight M_i.

The term "viscosity average molecular weight" seems obviously satisfactory for $\overline{M}_v$.[40] When $a = 1$, $\overline{M}_v$ becomes identical with the weight average $\overline{M}_w$ and (5) reduces to Staudinger's equation. When $0<a<1$, it can be shown that for a heterogeneous polymer $\overline{M}_n < \overline{M}_v < \overline{M}_w$. Consequently, the actual viscosity–molecular weight relationship (5) gives an average molecular weight somewhat nearer the number average determined osmotically than would be obtained if Staudinger's equation were to apply.

In comparing number average molecular weights with intrinsic viscosities, as in Fig. 4, the heterogeneity of the samples obviously should be taken into account. Although all samples represented in Fig. 4 were carefully fractionated, the distribution curves for the fractions unquestionably are much broader than the range of precipitating conditions would indicate. The fractions probably overlap one another to a very marked degree. In the absence of any definitive evidence concerning the heterogeneity of the fractions, rough estimates have been made of the ratio $\overline{M}_v/\overline{M}_n$ for $a = 0.64$ for various types of distributions, and in particular for distributions of the type predicted for fractionated materials by Schulz.[30] In this way it has been concluded tentatively that the viscosity averages for the fractions probably are no more than 10% greater than their various number averages. On this basis the viscosity average molecular weight given by equation (4) may be as much as 10% too low. As there is no reason to expect variation in $\overline{M}_v/\overline{M}_n$ with the average molecular weight of the various fractions, the slope in Fig. 3, and hence a in (5), probably have not been vitiated appreciably by the heterogeneity of the fractions.

Structure of Polyisobutylene in Relation to Viscosity.—That polyisobutylene molecules are strictly linear is indicated by the complete solubility in hydrocarbons of even the highest molecular weight products obtainable. In general, an auxiliary process leading to random branching or

---

(39) E. O. Kraemer, *J. Franklin Inst.*, **231**, 1 (1941).

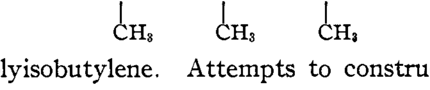
(40) E. O. Kraemer[39] has applied the term "viscosity average" in a totally different sense, not to be confused with our $\overline{M}_v$. It could be argued that $\overline{M}_v$ is not a simple average, but rather the a-th root of the ratio of the average of M^{a-1} to the (number) average molecular weight (See (6')).

cross-linking of the chains will cause partial insolubility if the process progresses far enough.[41] The extent of branching or cross-linking required for incipient insolubility when the chains are so long is exceedingly minute (of the order of one branch or cross-link per 500,000 units for the highest polymers). Consequently, appreciable deviation from linear polymer structure in the molecular weight range investigated experimentally is exceedingly unlikely. Staudinger's[6,7] frequent contention that deviation from (1) is due to a branched structure cannot be applied in the present instance.

There is no evidence, such as Staudinger and Schulz[6] claim to have found in the case of polystyrene, for differences in polymer structure depending on the temperature or catalyst used in the preparation of the polymer. Fractions from polymers prepared in various ways (see Table I) fall on the same line in Fig. 4. The relationship[33] between volume of precipitant and intrinsic viscosity (or molecular weight) is precisely the same for all polyisobutylenes investigated.

Finally, the divergence from Staudinger's equation cannot be attributed to the particular solvent, diisobutylene, in which the intrinsic viscosities have been measured. Preliminary comparisons of intrinsic viscosities in various solvents indicate lower intrinsic viscosities the poorer the solvent, in accordance with results for other polymers.[21,42,43] However, the ratio of the intrinsic viscosity in diisobutylene to that in another solvent is roughly independent of molecular weight. Thus, the slope of a plot such as is shown in Figure 4 is approximately independent of the solvent.

Both chemical[14] and X-ray evidence[44] support the plausible chain structure



$$\begin{array}{cccccc} & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} \\ & | & & | & & | \\ -\mathrm{CH_2}- & \mathrm{C} & -\mathrm{CH_2}- & \mathrm{C} & -\mathrm{CH_2}- & \mathrm{C}-,\ \text{etc.} \\ & | & & | & & | \\ & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} \end{array}$$

for polyisobutylene. Attempts to construct the space model show that severe interference exists between the methyl groups of successive units, leading to compression of the hydrogens well below their kinetic theory diameters.[45] This very probably is the reason for the abnormally low heat of polymerization.[14] Possibly these interferences diminish the flexibility of the chains. Furthermore, the interferences are somewhat less for comparatively coiled-up configurations:[46] It should be expected, therefore, that the dimensions of the polyisobutylene molecule in solution probably are less than those of other polymers having the same number of carbon atoms in the chain. Intrinsic viscosities for polyisobutylenes should be correspondingly less than those for other polymers of the same chain length (contour length), according to current notions concerning polymer solution viscosities. That this is true can be shown by examination of results for rubber,[7,42] hydrorubber,[7] and polystyrene.[6]

The present results fail to confirm the theoretical treatment of polymer solution viscosities advanced by Huggins.[47] Considering that the solvent molecules move through the essentially rigid chain structure of random configuration, Huggins arrived at linear dependence of intrinsic viscosity on chain length. Kuhn,[48] on the other hand, considers that the solvent within the volume encompassed by the meandering chain moves with the chain. His calculations concerning chain configurations then lead to the conclusion that the intrinsic viscosity should depend on a power of the chain length which, though greater than one-half, should be less than unity. The present results are consistent with this hypothesis.

The theoretical implications of the results presented here will be presented in greater detail in another publication.

Acknowledgment.—The author wishes to acknowledge the assistance of Mr. John Thomas and Mrs. M. D. Robbins in securing the experimental data.

Summary

Experimental methods for fractionating polyisobutylene and for determining osmotic pressures have been described.

The ratio π/c of osmotic pressure to concentration has been found in the case of cyclohexane solutions of polyisobutylene to vary non-linearly with concentration, contrary to recent theories advanced by Huggins and the writer. The slope

---

(41) P. J. Flory, THIS JOURNAL, **63**, 3083, 3091, 3096 (1941); *J. Phys. Chem.*, **46**, 132 (1942).

(42) G. Gee, *Trans. Faraday Soc.*, **36**, 1171 (1940).

(43) T. Alfrey, A. Bartovics and H. Mark, THIS JOURNAL, **64**, 1557 (1942).

(44) C. S. Fuller, C. J. Frosch and N. R. Pape, *ibid.*, **62**, 1905 (1940).

(45) This was first pointed out to us by Dr. F. D. Rossini of the Bureau of Standards.

(46) Fuller and co-workers[44] have shown that X-ray results favor a spiral configuration in the crystallites obtained on stretching polyisobutylene.

(47) M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939); *J. Applied Phys.*, **10**, 700 (1939).

(48) W. Kuhn, *Kolloid Z.*, **68**, 2 (1934); *Angew. Chem.*, **49**, 858 (1936).

of this relationship appears to be independent of molecular weight. Reliable methods for extrapolating π/c to $c = 0$ have been established, enabling the determination of absolute molecular weights with satisfactory precision up to values of about 1,000,000.

Molecular weights of polyisobutylenes calculated from Staudinger's equation are too low; the discrepancy is more than ten-fold at high molecular weights.

On the basis of data for carefully fractionated samples covering a two-hundred-fold molecular weight range, the intrinsic viscosity is found to be proportional to the 0.64 power of the molecular weight. This decided deviation from Staudinger's "law" cannot in this instance be attributed to non-linear chain structure, as Staudinger has sought to do in other cases.

This dependence of molecular weight on intrinsic viscosity leads to the definition of a "viscosity average" molecular weight which is obtained when the relationship is applied to heterogeneous polymers. The viscosity average is less than the weight average molecular weight, which would be obtained if Staudinger's equation were applicable, and greater than the number average obtained by osmotic or cryoscopic methods.

ELIZABETH, N. J. RECEIVED NOVEMBER 18, 1942

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dielectric Dispersion and Absorption of Water and Some Organic Liquids

BY W. P. CONNER[1] AND C. P. SMYTH

The measurement of dielectric constants and the related loss factor of polar liquids at very high radio frequencies has long been a subject of investigation. Within recent years the improved experimental accuracy has made possible the determination of molecular size and shape, and of the potential barrier involved in dipole rotation from these data. This report records measurements carried out at 3.08×10^9 cycles with water from 0 to 100° and with sixteen organic compounds at 25°. The results are analyzed with regard to the existing theories.

Although numerous values[2-8] of the relaxation time of water for room temperature are found in the literature, the temperature coefficient has not been determined. It is expected that a knowledge of the barrier height for this relaxation time will aid in the differentiation of the molecular mechanism between actual rotation of a definite dipole and merely the jumping of a hydrogen atom from an equilibrium position near one oxygen atom to another equilibrium position near an adjacent oxygen atom.[9]

The Debye theory for the dispersion of the dielectric constant of polar liquids has been found unsatisfactory for relating the frictional torque opposing molecular rotation to the macroscopic viscosity. The application[10] of the absolute reaction rate theory to the rotational process indicates that its mechanism is very similar to that involved in viscous flow. This viewpoint is further discussed in the present paper.

Experimental

Materials.—The water used in this investigation was distilled in the usual way. Careful washing of the cell kept the direct current salt conductivity as low as possible. At the high frequency at which measurements were made, 3.08×10^9 cycles per second, both the elevation of the dielectric constant resulting from the Debye–Hückel effect and the increase in the loss factor from salt conductance are negligible. The organic compounds used had been previously carefully purified for low frequency dielectric constant measurements in this Laboratory. However, since they had been standing for some time in tightly stoppered bottles in the dark, small amounts of water may have been present and also slight decomposition may have occurred in the most unstable compounds.

Apparatus.—The frequency source will be discussed in a future publication. Suffice it to say that it was completely stable in its wave length (9.72 cm.) and power output except for sudden momentary thermal fluctuations. The dielectric constants were determined by measurement of the wave length of standing waves in coaxial tubes filled with the liquid to be investigated, the dielectric constant being

---

[1] Research Assistant on special funds from the Rockefeller Foundation.

[2] Tear, *Phys. Rev.*, **21**, 611 (1923).

[3] Ardenne, Groos and Otterbein, *Physik. Z.*, **37**, 535 (1936).

[4] Schmelzer, *Ann. Physik.*, **28**, 35 (1937).

[5] Hackel and Wien, *Physik. Z.*, **38**, 767 (1937).

[6] Bäz, *ibid.*, **38**, 774 (1937); **40**, 394 (1939).

[7] Slevogt, *Ann. Physik*, **36**, 141 (1939).

[8] Kebbel, *Z. Hochfr.*, **53**, 81 (1939).

[9] Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933); Pauling, "The Nature of the Chemical Bond," 2d ed., Cornell University Press, Ithaca, N. Y., 1940, p. 302.

[10] Powell and Eyring, "Advances in Colloid Science," Vol. I, edited by Kraemer, Interscience Publishers, Inc., New York, N. Y., 1942.