Dimensions of Coiling Polymer Molecules from Viscosity and Light Scattering[1]

BY A. M. BUECHE

In a recent treatment[2] of the intrinsic viscosity of polymer solutions it was pointed out that viscosity data can be used to find the dimensions of polymer molecules in solution. It was shown that data relating the intrinsic viscosity to the molecular weight could be interpreted in terms of the radius of the molecular sphere and the permeability to solvent flow of the polymeric material inside this sphere.

The concept of the molecular sphere was introduced as an approximation in the viscosity theory so that the results could be expressed in closed form. The polymeric molecule was represented by a sphere of radius, R_s, having a constant average permeability and polymer density inside. Outside of the sphere the polymer density was taken as zero. The permeability of the molecule to solvent flow was characterized by a shielding length, L. R_s and L both depend on molecular weight for linear coiling molecules and are the two parameters evaluated when the suggested treatment of intrinsic viscosity data is followed.

When light is scattered by a molecule larger than about one-twentieth of the wave length it is not scattered symmetrically around the molecule. Due to interference of the light scattered from different parts of the molecule the scattered intensity is greater in the directions close to the direction of the primary beam. This dissymmetry of the scattered light has been shown to be a measure of the dimensions of the molecule.[3] In the case of linear coiling molecules the dissymmetry can be expressed in terms of R, the root mean square of the distance from the beginning to the end of the molecule and the wave length, λ, of the light in solution. The expression for the angular dependence of the relative intensity, I, after correction for the polarization of the light is

$$I \sim \frac{2}{x^2} [e^{-x} - (1 - x)] \qquad (1)$$

where

$$x = \frac{2\pi^2 s^2}{3} \left(\frac{R^2}{\lambda^2} \right)$$

and $s = 2 \sin(\theta/2)$. Here θ is the angle between the directions of the primary and scattered beams. If for measuring the scattering dissymmetry only the two angles, 45° and 135°, are used the expression for the quotient, I_{45}/I_{135}, of the intensities

of these angles can be closely approximated by

$$I_{45}/I_{135} = 1 + 6.556(R/\lambda)^2 \qquad (2)$$

for values of the quotient of the intensities up to 2. If R^2 is proportional[4] to the number of units in the molecular chain the quantity $(I_{45}/I_{135} - 1)$ will be proportional to the length of the extended molecule or, for a given polymer, to the molecular weight.

The relationship expressing proportionality between R^2 and the molecular weight was derived by Taylor and others on the assumption that parts of the coiling molecule do not interfere with one another in the course of its Brownian motion. This can never be strictly true for a coiling molecule. It seems to be a good approximation, however, for polymers dissolved in good solvents, as in the present case, where the molecules are rather highly extended. In poor solvents where the molecules are more compact the deviations from proportionality between R^2 and the molecular weight may be rather large.

In the limit of very permeable linear coiling molecules or low molecular weights it was shown theoretically that the diameter $2 R_s$ of the molecular sphere is approximately equal to R. They are related by the equation

$$2R_s = 1.056R \qquad (3)$$

The viscosity and light scattering experiments reported here were undertaken to determine the validity of equation (3) for polymer molecules of higher molecular weights and usual permeabilities. The experimental results obtained in the study of solutions of polystyrene in benzene also give information about the stiffness of the polystyrene molecule and indicate that the polystyrene fractions used are not branched or cross-linked as has been reported in some cases.[5]

Experimental

Six polystyrene fractions[6] were dried under vacuum and weighed amounts were dissolved in reagent grade benzene. Dust was removed from the solutions by filtration through a fine glass filter.

The polystyrene was prepared by thermal polymerization of styrene at an average temperature of 100°. It was fractionated by the method described by Badgely.[7] The essential feature of this method is that a precipitant is used which boils higher than the solvent, and the precipitant-solvent ratio is changed by distillation under reduced pressure. The fractionation procedure was carried out only once.

The light scattering measurements were made using an

(1) The work reported in this paper was done in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

(2) P. Debye, paper presented at the International Congress of Chemists, London, 1947; P. Debye and A. M. Bueche, J. Chem. Phys., 16, 573 (1948).

(3) P. Debye, J. Phys. and Colloid Chem., 51, 18 (1947).

(4) W. J. Taylor, J. Chem. Phys., 16, 412 (1947).

(5) T. Alfrey, A. Bartovics and H. Mark, THIS JOURNAL, 65, 2319 (1943).

(6) Kindly supplied by Dr. R. S. Spencer of The Dow Chemical Company, Midland, Mich.

(7) W. Badgely, Doctoral Dissertation, Polytechnic Institute of Brooklyn.

instrument designed by P. P. Debye.[8] The phototube below the stage was used in conjunction with the travelling mirror dipping into the solutions. The solutions were held in a rectangular glass cell having a volume of about 300 cc. All measurements were made using the mercury blue line (λ = 4358 Å.) as isolated by Corning filters. The scattered light was measured at the three angles, 45, 90 and 135°. The meter readings were converted to absolute scattering values by comparing them with readings obtained from a benzene solution of polystyrene whose turbidity had been determined by the "absolute camera" method.[3]

The refractive index differences between solutions and solvent were measured in a differential refractometer similar to that described by P. P. Debye.[8] This refractive index difference, $\mu - \mu_0$, was a linear function of the concentration in the range 0 to 0.01 g./cc. and independent of the molecular weight. For polystyrene in benzene and λ = 4358 Å. the difference can be expressed by

$$\mu - \mu_0 = 0.1151C$$

where C is the concentration in g./cc.

The molecular weights of the fractions were obtained from the 90° scattering values by the usual extrapolation of the concentration divided by the turbidity to infinite dilution. Since some dissymmetry of scattering was observed for each fraction the molecular weights obtained by 90° scattering alone were too low. They were multiplied by the necessary correction factors[3] obtained from equation (1). The corrected molecular weights were found to range from 135,000 to 895,000.

To avoid a direct extrapolation of the dissymmetries to infinite dilution the quantities C/I_{45} and C/I_{135} were plotted as functions of the concentration. These plots were linear at low concentrations. The dissymmetries were obtained by forming the quotients of the intercepts at $C = 0$. The instrument itself was responsible for a dissymmetry, $I_{45}/I_{135} = 1.10$ because the primary beam was not symmetrical around the center of the scattering cell. The dissymmetries as calculated from the intercepts were corrected by dividing by this number.

Flow times, t and t_0, of solutions and solvent were measured in an Ostwald viscometer at 38°. The kinetic energy correction was found to be negligible. The intrinsic viscosities were obtained from the intercepts at $C = 0$ of the ln (t/t_0) vs. C plots. Account was taken of the difference in concentration of the solutions at room temperature and 38°.

The experimental data are given in Table I and the extrapolated quantities obtained from it are given in Table II.

Results and Discussion

The dissymmetries are plotted as a function of the molecular weights, M, in Fig. 1. The equation of the least squares straight line through the points is

$$I_{45}/I_{135} = 1 + 9.66M \cdot 10^{-7} \tag{4}$$

This linear dependence of dissymmetry on M is what would be expected from a linear coiling molecule in a good solvent as previously discussed. If the molecules were highly branched or cross-linked this linear dependence would not exist. This can be seen in an approximate way by the following considerations.

Suppose the molecule were so highly cross-linked that for light scattering measurements it acted as a sphere of constant density. The diameter of the molecule would then be proportional to the cube root instead of the square root of the molecular weight. It is to be expected that for

(8) P. P. Debye, *J. Applied Phys.* **17**, 392 (1946).

TABLE I

Sample	C (g./100 cc.)	$H\dfrac{c}{\tau_{45}} \times 10^7$	$H\dfrac{c}{\tau_{90}} \times 10^7$	$H\dfrac{c}{\tau_{135}} \times 10^7$	$\dfrac{\ln t/t_0}{c}$
D-1	1.00	40.5	160	44.0	0.438
	0.667	32.4	129	33.8	0.451
	.445	28.2	113	29.2	.465
	.296	24.4	99.4	28.2	.473
	.197	22.6	92.7	25.6	.473
	.132	21.6	87.1	22.9	...
D-2	1.0	38.4	193	64.7	.732
	0.667	29.4	139	45.2	.753
	.445	23.8	111	35.4	.755
	.296	19.6	90.6	29.1	.770
	.197	17.6	86.9	27.4	.773
	.132	15.1	65.2	25.6	.788
	.088	15.8	71.3	23.2	.773
D-3	1.0	19.1	121	44.0	.955
	0.667	15.5	95.6	32.8	.996
	.445	13.2	72.7	24.6	1.03
	.296	11.0	56.2	18.6	1.05
	.197	9.59	52.7	15.9	1.07
	.132	8.60	48.5	14.4	1.07
	.088	7.96	45.0	13.1	...
D-4	.794	16.2	93.2	35.2	1.18
	.530	12.3	66.6	23.3	1.25
	.352	9.86	52.0	17.1	1.31
	.234	8.10	43.1	13.8	1.35
	.157	7.20	39.4	12.0	1.38
	.105	6.33	35.0	10.3	1.37
D-5	.296	6.90	44.4	13.84	1.70
	.197	5.76	37.2	11.32	1.78
	.132	5.07	31.6	9.75	1.84
	.088	4.73	29.9	8.76	1.87
	.0586	4.44	29.0	8.27	1.93
	.0391	3.89	26.6	7.97	...
D-6	.667	13.8	67.0	32.0	1.85
	.445	10.1	52.4	22.2	2.02
	.296	8.02	39.9	17.1	2.17
	.197	6.56	34.0	13.9	2.29
	.132	5.74	30.2	12.3	2.27
	.088	4.70	24.9	10.4	2.31
	.059	3.98	20.9	8.85	2.39
	.039	3.60	20.2	8.21	2.44

TABLE II

$M \times 10^{-5}$	I_{45}/I_{135}	$[\eta]$, cc./g.
8.95	1.90	244
6.01	1.60	195
4.55	1.43	143
3.28	1.27	109
2.59	1.24	78.6
1.35	1.04	49.8

lesser degrees of cross-linking the diameter would be proportional to an intermediate power. Although there are a number of difficulties to be overcome such data may be useful in making an estimation of the degree of cross-linking.

The dependence of R on the molecular weight can be found from equations (2) and (4) to be

$$R = 1.11M^{1/2} \tag{5}$$

For a molecular weight of 1,000,000 this leads to $R = 1110$ Å. R. H. Ewart[9] and P. Doty[10] have obtained values of R for polystyrene in other solvents. Ewart investigated a range of molecular weights in carbon tetrachloride and found $R = 1050$ Å. for $M = 1,000,000$. Doty investigated a polystyrene sample having $M = 4.8 \cdot 10^6$ in toluene. Making use of the proportionality between R and $M^{1/2}$ his value leads to $R = 1080$ Å. The agreement among the three values is better than was expected when the experimental errors are considered.
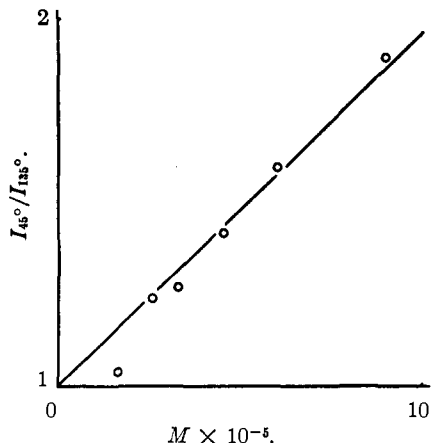
Fig. 1.—Dissymmetries of polystyrene fractions vs. molecular weight.

The intrinsic viscosity, $[\eta]$, of a polymer in solution can be expressed as

$$[\eta] = (\Omega/m)\, \phi\, (R_s/L) \tag{6}$$

where Ω is the volume of the molecular sphere, m is the mass of one molecule and $\phi(R_s/L)$, a function of the shielding ratio, R_s/L, ranges from 0 to 2.5. In utilizing this equation to obtain the size of the molecular sphere a scheme proposed in the original paper[2] was followed.

Figure 2 is a plot of log $[\eta]$ vs. log M. The slope, ϵ, of the best straight line through the points is 0.850. Values of $R_s/L = 2.85$ and $\phi = 0.560$ corresponding to this slope are found from the table in reference (2). The average molecular weight of the range studied is 384,000 and the corresponding value of the intrinsic viscosity is 116 cc./g. Substitution of these values into equation (6) leads to a value $2R_s = 606$ Å. This is equivalent to the value $2R_s = 1030$ Å. for $M = 1,000,000$. Fig. 3 is a plot of $[\eta]$ vs. M. The solid line is that predicted by equation (6) using the quantities determined above. The data agree with the theoretical curve within experimental error.

The value of $2R_s = 1030$ Å. from viscosity is to be compared with $1.056R = 1170$ Å. as deter-

(9) R. H. Ewart, U. S. Rubber Company, Passaic, N. J., private communication.
(10) P. Doty, W. Affens and B. Zimm, Trans. Faraday Soc., XLIIB, 66 (1946).
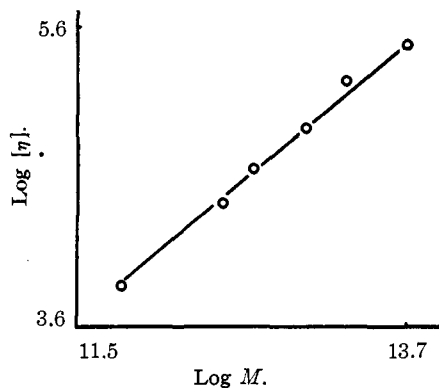

Fig. 2.—Natural logarithmic plot of the intrinsic viscosities of polystyrene fractions vs. molecular weight.

mined by light scattering. The two differ by 13%. Since this is about the precision expected from the experiments the diameter of the molecular sphere and the root mean square of the distance between the ends of the molecule can be said to be equal within experimental error.
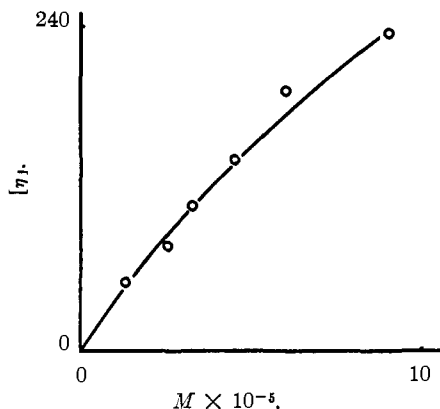

Fig. 3.—Intrinsic viscosities of polystyrene fractions vs. molecular weight.

The diameter of the molecular sphere as calculated from these measurements is in some disagreement with that obtained by R. H. Ewart[9] by the same method for polystyrene in benzene. Ewart's measurements lead to $2R_s = 880$ Å. for $M = 1,000,000$. We are unable to account for the discrepancy between his value and ours of 1030 Å. except for the fact that the samples are not the same. Both values are less than the value of R found by light scattering. This might indicate that the average distance between the ends of the molecule is slightly larger than the diameter of the molecular sphere.

Taking the average of all the measurements the distance between the ends of the polystyrene molecule is about 3.4 times larger than the distance calculated supposing free rotation in the molecular chain. The polystyrene molecule, therefore, shows a considerable degree of stiffening[4] which would correspond to an oscillation

around each bond of 200°, calculated from Debye's modification of the Kuhn equation, instead of the 360° for free rotation. Since the intrinsic viscosity is proportional to $R_s{}^3$ it is about 39 times larger than would be expected for a polystyrene molecule having free rotation.

Summary

Molecular dimensions for polystyrene fractions in benzene have been obtained from viscosity and light scattering data. It was found that the root mean square of the distance between the ends of the molecule is approximately equal to the diameter of the molecular sphere needed for the explanation of viscosity. Evidence for the absence of appreciable branching or cross-linking in the polystyrene fractions was obtained. Polystyrene molecules in benzene were found to be much stiffer than would be expected from a free rotation model. This stiffness is responsible for the relatively high viscosities of polystyrene solutions.

Properties of Electrolytic Solutions. XXXVIII. The Distribution of Hexadecylpyridonium Chloride between Water and Nitrobenzene at 25°

By Philip F. Grieger[1] and Charles A. Kraus

I. Introduction

The purpose of the present investigation was to determine the distribution of a long chain electrolyte between water and a slightly soluble organic liquid of relatively high dielectric constant, and thereby to test (by a method apparently hitherto untried) the validity of certain ideas which are currently held to be true, concerning aqueous long chain electrolyte solutions. Hexadecylpyridonium chloride was chosen as the salt because its critical concentration in water is convenient for the purpose of this work. Nitrobenzene was chosen as the reference liquid because its solubility in water is low (about 0.2% by weight), its dielectric constant is relatively high (34.5) and especially because considerable information was available on the conductance of long chain salts in this solvent.

Previous measurements made in this Laboratory on long chain electrolytes in nitrobenzene indicate that the activity product of simple ions can be evaluated from a knowledge of the conductance of these solutions.[2] Then, from distribution and conductance measurements, the activity product of simple ions in water saturated with nitrobenzene can be established and, in turn, the concentration product of simple ions in the aqueous solvent can be approximated. In the light of this information, another test can be made of the two leading hypotheses on long chain electrolyte solutions: (I) complete dissociation of the electrolyte at concentrations less than critical; (II) association of the electrolyte (to form one or more polyionic species) at concentrations greater than critical. The experimental results presented here are consistent with these two hypotheses.

In the distribution experiments concentrations were determined conductometrically; it was

(1) Lalor Foundation Fellow, Brown University, 1947–1948. Present address: Department of Chemistry, University of Illinois, Urbana, Ill.

(2) H. L. Pickering, Thesis, Brown University (1947).

found that significantly precise measurements could be made at concentrations approaching 10^{-4} N, or well below the critical concentration, 5.8×10^{-4} N.

Although the solubility of nitrobenzene in water is low, the conductance of hexadecylpyridonium chloride in water saturated with nitrobenzene differs significantly in the neighborhood of the critical concentration (and below) from the conductance of this salt in pure water. Hence, the distribution results reported here must be regarded as appertaining specifically to the solvent: water saturated with nitrobenzene.

Conventions.—Salt concentrations are given in moles per liter of solution, exclusively. Quantities that refer to the water phase are designated by primes, while quantities that refer to the nitrobenzene phase are not specially marked. In some instances where only the water phase is under consideration (and no ambiguity can result), the water phase quantities have not been primed.

II. Experimental

The distribution measurements were made in a cell similar to those used in previous conductance work in this Laboratory, except that a side chamber (large enough to hold all the nitrobenzene in the system) was sealed to the cell near its base. By manipulating the cell, it was possible to place either the water or nitrobenzene layer in contact with the electrodes. It was found that equilibrium could be established (as judged by the constancy of the resistances of the separate phases) within a reasonable time, usually one or two days, by moving the cell in such a way that the liquids were caused to pass slowly through each other. By careful mixing, foam and emulsion formation were practically eliminated. The electrodes of the cell were lightly platinized.

The distribution experiments were carried out simply, as follows: after weighing the cell dry, nitrobenzene and then

(3) Evers and Kraus, This Journal, 70, 3049 (1948); Pickering, Thesis, Brown University, 1947.