Intrinsic Viscosity, Diffusion, and Sedimentation Rate of Polymers in Solution

P. Debye and A. M. Bueche

Additional information on J. Chem. Phys.

Substitution of (A9) into (A10) yields

$$\varphi_k{}^* = f_k{}^* - [2\lambda\varphi_k{}^*/(\pi)^{\frac{1}{2}}] \int_{-\infty}^{+\infty}$$

$$\times [\beta^2 d\beta/(\pi^2 k^2 + \beta^4)]; \quad k \neq 0,$$

(A11)

$$\int_{-\infty}^{+\infty} [\beta^2 d\beta/(\pi^2 k^2 + \beta^4)] = (\pi/2|k|)^{\frac{1}{2}}; \quad k \neq 0,$$

$$\varphi_k{}^* = f_k{}^*/[1 + \lambda(2/|k|)^{\frac{1}{2}}]; \quad k \neq 0.$$

Since by definition, Eq. (A3), $\varphi_0{}^*$ vanishes, $f_k{}^*$ must also vanish, and

$$\varphi_0 = f_0/\mu_0,$$

$$\mu_0 = \frac{1}{2} \int_{-1}^{+1} \mu(x)dx = 1 + (8\sqrt{2}/3)\lambda,$$

(A12)

and the constant term in the Fourier series for

$\varphi(x)$ is determined. Writing $f_k{}^*$ as $f_k - \varphi_0\mu_k$, we obtain from Eqs. (A8), (A11), and (A12) the following Fourier series for $\varphi(x)$:

$$\varphi(x) = \frac{f_0}{1 + 8\sqrt{2}\lambda/3} + \sum_{\substack{k=-\infty \\ \pm 0}}^{+\infty}$$

$$\times [(f_k - \mu_k f_0/\mu_0)/(1 + \lambda(2/|k|)^{\frac{1}{2}})]e^{i\pi kx},$$

$$\mu_k = \frac{1}{2} \int_{-1}^{+1} [1 + 2\lambda(1+x)^{\frac{1}{2}}$$

(A13)

$$+ 2\lambda(1-x)^{\frac{1}{2}}]e^{-i\pi kx}dx,$$

$$f_k = \frac{1}{2} \int_{-1}^{+1} f(x)e^{-i\pi kx}dx,$$

which is the desired solution of Eq. (A1), employed in the foregoing theories of viscosity and diffusion.

Intrinsic Viscosity, Diffusion, and Sedimentation Rate of Polymers in Solution

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Intrinsic viscosity, diffusion and sedimentation rate of polymers in solution is calculated by a generalization of Einstein's theory for impermeable spheres. For the coiled polymer molecule a sphere is substituted which hinders the liquid flow through its interior only to a degree depending on the average density in space of the polymer molecule in solution. The amount of shielding of the liquid flow which is introduced in this way determines the exponent in the customary exponential relation between intrinsic viscosity, diffusion, or sedimentation rate and molecular weight. This relation is shown to have only the merits of an interpolation formula. It is shown how the dimensions of the molecular coil can be derived from the experimental data on viscosity, and these dimensions are compared with those derived from interference measurements. The point is stressed that the relation between intrinsic viscosity and molecular weight is rather indirect and depends essentially on the type of polymer molecule under consideration. In most cases polymer molecules are decidedly stiffer and therefore cover a larger space in solution than would be expected from models with free rotation around bonds.

IN the preceding paper Kirkwood and Riseman refer to some theoretical calculations concerning intrinsic viscosity of Debye and similar calculations of Bueche concerning diffusion and sedimentation. Since these papers are not readily available* it seems appropriate, in order to facilitate a comparison of the different lines of attack, to present here the main features of the theoretical approach as conceived by one of the authors of this paper.**

If the mutual interaction of the beads of a

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* The theory of viscosity was the subject of a report to the Office of Rubber Reserve presented in a meeting in Chicago, Oct. 31 and Nov. 1, 1946. A later report of A. M. Bueche dealt with sedimentation and diffusion. A paper containing the results concerning intrinsic viscosity as well as diffusion and sedimentation was submitted to Section 11 of the eleventh International Congress of Pure and Applied

Chemistry (London: July 17th–24th, 1947). This paper has not yet been printed. Two short notes appeared, one in Phys. Rev. 71, 486 (1947), the other in the Jan.–April issue of the Record of Chemical Progress, 1947.

** Calculations along the same line were made independently by H. C. Brinkman, Proc. Amsterdam Acad. 50, No. 6 (1947); App. Sci. Res. A1, 27 (1947). Brinkman's results coincide with ours.

pearl string, which is substituted for a linear chain molecule with more or less free rotation, is neglected, the intrinsic viscosity is represented by the following relation:[***]

$$[\eta] = \frac{1}{36} \frac{f/\eta}{m} R^2. \qquad (1)$$

$[\eta]$ is the intrinsic viscosity expressed in cc/gr (which is 100 times the value expressed in customary units); f the friction factor of one bead, defined in such a way that in order to drag one single bead through the liquid with a velocity v a force fv is needed; η is the viscosity of the solvent, m the mass of one bead, and R^2 the average square of the distance between the two ends of the chain. Since R^2 is proportional to the degree of polymerization, the relation confirms Staudinger's rule.

I

The assumption that the interaction can be neglected obviously cannot be accepted. As a matter of fact, each individual bead will move in a velocity field which deviates from the original undisturbed field because of the superposition of the disturbances caused by all the other beads. The situation is analogous to a case in which a dielectric medium is placed in an electric field and in which we find that in a point in the dielectric the field is distorted because of the disturbances caused by the polarization of all the other parts of the medium. In an attempt to formulate this idea such that care is taken of the essential features and at the same time the mathematical complications are reduced to a minimum, Debye comes to the following scheme.

In a homogeneous liquid, considered incompressible and with a viscosity η, the velocity $\bar{v}$ can be determined from the fundamental equations

$$\eta \, \text{curl curl} \bar{v} + \text{grad} p = 0, \quad \text{div} \bar{v} = 0, \qquad (2)$$

in which p denotes the pressure. The first equation merely expresses that equilibrium exists between the frictional force on an element of volume and the force caused by local variations in pressure. As soon, however, as parts of the polymer molecule are situated in the element of

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[***] P. Debye, J. Chem. Phys. **14**, 636 (1946).

volume under consideration, we have to take account also of the frictional force between the beads and the liquid. If we call the relative velocity of the liquid with respect to the molecule at the point in question, $\bar{v}_r$, the average value of this force acting on the liquid in an element of volume $d\tau$ will be

$$-\nu f \bar{v}_r d\tau,$$

provided the average number of beads contained in $d\tau$ is $\nu d\tau$. Adding this force to the forces already considered in (2) we arrive at a new set of equations, namely,

$$\eta \, \text{curl curl} \bar{v} + \nu f \bar{v}_r + \text{grad} p = 0, \quad \text{div} \bar{v} = 0. \qquad (3)$$

From the statistics of the chain molecule we know the bead density ν as a function of the distance from the center of gravity. For the relative velocity $\bar{v}_r$ we can substitute the actual velocity of the liquid $\bar{v}$ minus a velocity $\bar{v}_0$ corresponding to the proceeding and rotating molecule. In this way the problem of finding the velocity of the liquid everywhere, inside and outside of the space occupied in the average by the polymer molecule, is now reduced to finding the appropriate solution of the set of Eqs. (3). And, of course, as soon as we know this velocity distribution, the additional heat developed due to the immersion of one polymer molecule can be found, and the intrinsic viscosity can be calculated along familiar lines.

The main point to consider before proceeding with the solution of Eq. (3) is the average density in space of the beads. From a consideration of the statistics of the chain it is found that this density is a maximum around the center of gravity of the polymer molecule, and with increasing distance r of this point ν decreases gradually. The function $F(r)$ which represents this density has a shape which resembles a Gaussian probability curve. At this stage I have not considered it worth while to go ahead and solve our problem using the exact representation of the density. It is more than probable that the essential features of the final result will depend only in minor details on the exact form of $F(r)$. Instead I propose to substitute as a picture for the average space occupied by the polymer molecule a sphere of radius R_s in which the bead density ν is supposed to be constant throughout,

whereas outside of this sphere $\nu=0$. If N is the total number of beads of the string, we then have inside the sphere

$$\nu=(3/4\pi)(N/R_s{}^3). \qquad (4)$$

In this formulation we have to find solutions of Eq. (3), one for the outside of the sphere of radius R_s with $\nu=0$, another for the inside with ν equal to the constant value given by Eq. (4). The constants appearing in these solutions have to be adjusted in such manner that at large distances we have the original undisturbed velocity distribution. At the surface of the sphere the velocities inside and outside must be the same as well as the stresses.

The mathematical method which leads to this goal is a generalization of a method derived by *G. Kirchhoff*, formerly used by *A. Einstein* in his well-known but simpler problem of calculating the effect of a number of immersed *impermeable* spheres on the over-all viscosity.†

The angular velocity of the whole molecule can be left indeterminate at the outset, but using the condition, as in the simpler case in which no interaction was considered, that the average total torque on the molecule must be zero, it turns out that just as before this angular velocity still is equal to half the gradient of the velocity of the liquid.

Accepting the form which has now been given to the problem, it is readily seen that apart from the number of beads, N, only two constants each of the dimension of a length enter into it. The first is, of course, the radius R_s of the substituted spherical space occupied in the average by the polymer molecule. The second is a length L defined by the relation

$$1/L^2=\nu(f/\eta), \qquad (5)$$

in which ν is the bead density according to Eq. (4). I would like to call L the "*shielding length*" for the following reason. Consider a much simpler case in which a liquid is flowing free in the x direction with a velocity having a gradient α in the z direction everywhere above the plane $z=0$, whereas below this plane the flow is hindered by an accumulation of beads, distributed with constant density ν. Using Eq. (3), we find that in

this latter part, that is for negative values of z, the velocity v_x decreases exponentially and is proportional to $\exp(z/L)$. The lower part of the medium is therefore shielded by the accumulated effect of the beads, and the distance in this part over which the velocity decreases by a factor $1/e$ is our shielding length L. I understand that the same formulation as expressed by Eq. (3) is used by engineers in discussing the flow of water through sand.

The advantage of using the approximation of constant bead density in our problem of the rotating sphere is that all the functions which have to be introduced as solutions of the equations can be expressed by elementary functions. By a queer coincidence the fundamental equation which has to be satisfied is of the same type as that describing the potential around an ion in a strong electrolyte.

Skipping now all further mathematical details, the final result for the intrinsic viscosity appears in the following form:

$$[\eta]=(\Omega_s/M)\phi(\sigma)\cdots\sigma=R_s/L. \qquad (6)$$

$\Omega_s=(4\pi/3)R_s{}^3$ is the spherical volume occupied by the sphere substituted for the polymer molecule, M is its actual mass, and $\phi(\sigma)$ is a function of a number $\sigma=R_s/L$, which I would like to call the "shielding ratio."†† This function is represented by Eq. (7):

$$\phi(\sigma)=\frac{5}{2}\frac{(1+(3/\sigma^2)-(3/\sigma)\,\mathrm{cotgh}\,\sigma)}{1+(10/\sigma^2)(1+(3/\sigma^2)-(3/\sigma)\,\mathrm{cotgh}\,\sigma)}. \qquad (7)$$

For small values of the shielding ratio σ we have

$$\phi(\sigma)=\sigma^2/10[1-(2/35)\sigma^2+\cdots]. \qquad (8)$$

Substituting the first approximation of ϕ for small values of σ in Eq. (6) and remembering the definition of ν and L as expressed by Eqs. (4) and (5), we find in the limit for $\sigma=0$

$$[\eta]=1/10(f/\eta m)R_s{}^2. \qquad (8')$$

This relation should be compared with Eq. (1), which was derived directly (without using the approximation of the substituted sphere with constant bead density) for the case of infinitely small shielding effect. If we do this we see that in

† A. Einstein, Ann. d. Physik (4) **19**, 289 (1906); **34**, 591 (1911).

†† The intrinsic viscosity is again expressed in cc/g.

order to obtain coincidence we should take $R_s^2/10$ equal $R^2/36$, and this means that the diameter $2R_s$ of our spherical volume should be taken equal to $1.054R$. This diameter is therefore very nearly equivalent to R, the square root of the average square of the distance between ends of the chain.

For large values of the shielding ratio we have

$$\phi(\sigma) = 5/2[1-(3/\sigma)-\cdots], \qquad (9)$$
and
$$[\eta] = 5/2(\Omega_s/M) = 5/2(\Omega_s/Nm). \qquad (9')$$

This is Einstein's relation for rigid impenetrable spheres, as it should be.

It is of interest to observe that the important features which determine the intrinsic viscosity are *not* primarily concerned with the molecular weight. They are, as seen from (6): firstly, the specific volume of the material of the polymer molecule as distributed over the average space occupied by this molecule in the liquid; secondly, the shielding ratio σ. However, if we know the structure of the molecule we can connect both these quantities with the degree of polymerization N (or the molecular weight). So for linear chains we know that R or R_s is proportional to $N^{\frac{1}{2}}$, and we see immediately from (8') and (9') that in this case we can find anything between proportionality with N to proportionality with $N^{\frac{1}{2}}$ depending on the shielding ratio. However, if the chain is not linear, if, for instance, the molecule is highly cross-linked, a very different dependence on the molecular weight will prevail. Under such circumstances we can have very high molecular weights combined with relatively small intrinsic viscosities.

It remains to be seen how the customary formula for the intrinsic viscosity with an exponent of the molecular weight between 1 and $\frac{1}{2}$ has to be interpreted.

If we assume a linear chain $(R_s\sim N^{\frac{1}{2}})$ and draw according to Eq. (6) a curve for the intrinsic viscosity as a function of the degree of polymerization, we will find that it begins proportional to N and that its slope gradually decreases with increasing N until for very large N we end up with a proportionality to $N^{\frac{1}{2}}$. At any point of this curve for a given value $N=N_0$ we can approximate the curve by its tangent, repre-

senting it by the linear function

$$[\eta] = \alpha+\beta(N-N_0) \qquad (10)$$

with two constants α and β. This would be the usual procedure. But of course this procedure is arbitrary inasmuch as we decided arbitrarily on the outset that a linear approximation was what we wanted to use. We can just as well decide that in the vicinity of $N=N_0$ we want to approximate the curve by an expression of the form

$$[\eta] = AN^\epsilon \qquad (10')$$

with two other constants A and ϵ. If we take the logarithm on both sides of (10'), we see that the meaning of this second form of approximation is to draw a curve for $\log[\eta]$ as a function of $\log N$ and to approximate this new curve by its tangent. Fundamentally and from a purely mathematical point of view, there is no difference between the two procedures, but in our special case the exponential approximation according to (10') has a peculiar advantage. We know that our formula, as well as any other formula which might be proposed, makes $[\eta]=0$ for $N=0$. The exponential approximation formula (10') does this also, automatically, whereas the linear approximation (10) does not. In this way it turns out that the exponential approximation has really 3 points in common with the actual curve, whereas the linear approximation has only 2. We will therefore expect that the exponential approximation will not usually deviate much from the actual curve over a large range of values N. This is actually what is observed. We have here before us a case in which a special formula fits the experimental data very well, and still it would be wrong to conclude that its special form has any fundamental importance.

From what has been said about the meaning of the exponential approximation, it follows immediately that *for a linear chain*

$$\epsilon = \frac{d\log[\eta]}{d\log N} = \frac{N}{[\eta]}\frac{d[\eta]}{dN} = \frac{1}{2}+\frac{1}{4}\frac{\sigma}{\phi}\frac{d\phi}{d\sigma}. \qquad (11)$$

To every value N of the degree of polymerization belongs a definite exponent ϵ, which can be calculated from (11) as a function of the shielding ratio σ. The following table gives corresponding

values of the shielding ratio σ, the function ϕ (which for reasons apparent from Eq. (6) is called the volume factor), and the exponent ϵ.

In order to illustrate the use of this table, we can take some measurements of R. H. Ewart on polystyrene in benzene. Ewart represents his results by the interpolation formula

$$[\eta] = 7.54 \cdot 10^{-3} \, (MW)^{0.783} \qquad (12)$$

in which the intrinsic viscosity is measured in cc/g. and MW indicates the customary molecular weight. The measurements covered a range from $MW = 50000$ to $MW = 800000$. The average molecular weight of this interval (the average being taken in the logarithmic diagram) is $MW = 200000$. We will assume that the exponent 0.783 corresponds exactly to this average MW. Now assuming that polystyrene is a linear polymer, we find by interpolation in Table I that $\epsilon = 0.783$ corresponds to $\sigma = 3.92$ and $\phi = 0.836$. At the same time Ewart's relation (12) gives for $MW = 200000$ the value $[\eta] = 107$ cc/g. From Eq. (6) it follows that the specific volume of the polymer substance within the substituted sphere is $\Omega_s/M = 128$ cc/g. Since we know the mass of the polymer molecule, we now can calculate the volume Ω_s and the diameter $2R_s$ of this sphere and find $2R_s = 431$A. If we decide that the relation $2R_s = 1.054R$, which holds for the limiting case $\sigma = 0$, can be used, we will conclude that for a linear polystyrene molecule in benzene of $MW = 200000$ the root mean square distance between ends $R = 409$A, which is 3 times as large as the theoretical value of a $C-C$ chain with absolutely free rotation.

II

A. M. Bueche has applied the same line of reasoning to the problem of diffusion and sedimentation. If a polymer molecule is dragged through a liquid with the velocity v, a force Fv will have to be applied. The friction constant F is the essential quantity in sedimentation experiments; the diffusion constant D follows from Einstein's relation

$$D = kT/F. \qquad (13)$$

For the friction constant F Bueche finds

$$F = 6\pi\eta R_s\psi(\sigma) \qquad (14)$$

TABLE I. (Linear polymers) $[\eta] = (\Omega_s/M)\phi$.

Shielding ratio σ	Volume factor ϕ	Exponent ϵ
0	0	1.000
1	0.0947	0.973
2	0.327	0.910
3	0.600	0.839
4	0.857	0.778
5	1.07	0.731
6	1.25	0.693
7	1.40	0.664
8	1.52	0.642
9	1.62	0.625
10	1.70	0.611
15	1.96	0.569
20	2.10	0.549
∞	2.50	0.500

in which ψ is again a function of the shielding ratio σ analogous to ϕ. It is defined by the relation

$$\psi(\sigma) = \frac{(1 - (1/\sigma)Tgh\sigma)}{1 + (3/2\sigma^2)(1 - (1/\sigma)Tgh\sigma)}. \qquad (15)$$

For small σ we have

$$\psi = (2/9)\sigma^2[1 - (4/15)\sigma^2 + \cdots], \qquad (16)$$

which leads in the limiting case $\sigma = 0$ to

$$F = Nf, \qquad (16')$$

remembering the definition of the shielding length L by Eq. (5). This is exactly what has to be expected since, if we neglect all interaction, the force on N beads is N times as large as that on a single bead.

For large σ we have

$$\psi(\sigma) = 1 - (1/\sigma) - \cdots, \qquad (17)$$

which leads to Stokes' formula

$$F = 6\pi\eta R_s. \qquad (17')$$

TABLE II. (Linear polymer) $F = 6\pi R_s\psi$.

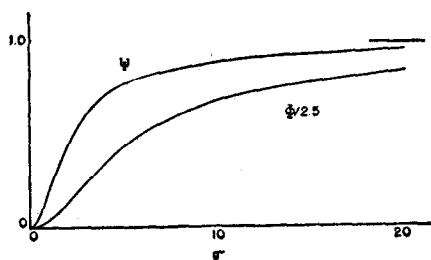| Shielding ratio σ	Volume factor ψ	Exponent ϵ
0	0.000	1.000
1	0.176	0.899
2	0.432	0.752
3	0.600	0.661
4	0.701	0.610
5	0.770	0.574
8	0.858	0.544
10	0.890	0.532
∞	1.000	0.500

FIG. 1. Volume factor Φ and radius factor Ψ as functions of the shielding ratio σ.

Again as in the case of the intrinsic viscosity, the friction constant F can be represented by an exponential formula of the type

$$F = A N^\epsilon$$

over a limited range of molecular weights and again there will exist a one-to-one correspondence between ϵ and σ, according to the relation

$$\epsilon = \frac{1}{2} + \frac{1}{4} \frac{\sigma}{\psi} \frac{d\psi}{d\sigma}. \tag{18}$$

Table II contains corresponding values of the shielding ratio σ, the "radius factor" ψ, and the exponent ϵ for the case of linear polymers. In Fig. 1 the two functions $\phi/2.5$ and ψ are shown plotted as functions of the shielding ratio σ.

III

We now have two theoretical representations of the intrinsic viscosity and two of the friction constant, one type attributable to Kirkwood and Riseman, which we will indicate by the letters
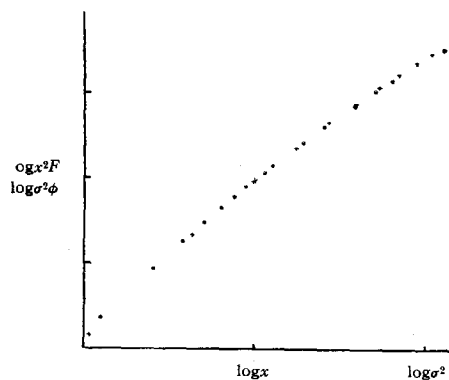

FIG. 2. Comparison of the Kirkwood-Riseman representation of intrinsic viscosity with that of Debye-Bueche. Circles for K.R., cross for D.B.

K.R., and one type discussed in this paper to be indicated by the letters D.B.

In making the calculations of the K.R. type a pearl string with small beads is substituted for the polymer and it is assumed that the links connecting the beads do not experience any friction. The very interesting mathematical treatment cannot be carried out quite rigorously; interchanges of averaging processes have to be introduced. In the calculations of the D.B. type a permeable sphere is substituted for the polymer, and its permeability is connected with the monomer number in the polymer. Once the problem has been formulated mathematically, it is solved rigorously.

The question now arises as to which of the two types of representation is better as compared with the experimental facts. Confirming our attention to the intrinsic viscosity alone, K.R. as well as D.B. are satisfied with the performance in the few examples for which sufficiently accurate data are available. It seems, therefore, that we should ask how much difference exists between the two types when each of them is used to represent a definite set of experimental values.

In the K.R. case the intrinsic viscosity is represented by a formula of the type

$$[\eta] = A x^2 F(x), \quad x = B N^{\frac{1}{2}}, \tag{19}$$

in which A and B are adjustable constants and N is the degree of polymerization. The function F and the variable x are those used in the K.R. paper. In the D.B. case the intrinsic viscosity is represented by a formula of the type

$$[\eta] = A^* \sigma^2 \phi(\sigma), \quad \sigma^2 = B^* N^{\frac{1}{2}}, \tag{19'}$$

with two adjustable constants A^* and B^*. The function ϕ and the variable σ are those used in this paper.

A comparison of the two types can most easily be carried out, without any reference to specific experimental values, by plotting on one sheet of paper $\log(x^2 F)$ as a function of $\log x$, and on another transparent sheet $\log(\sigma^2 \phi)$ as a function of $\log \sigma^2$. After superimposing the two sheets, the transparent sheet is moved until the two curves are estimated to coincide as well as possible, always keeping the corresponding axes of the two sheets parallel. This has been done using the

F values from the K.R. table and the ϕ values from the D.B. table. The result of this superposition is represented in Fig. 2, the circles are K.R. points, the crosses D.B. points. The length of the decades is indicated on the axes. Since the horizontal axis covers 2 decades, which means a factor 10^4 in the degree of polymerization, and the vertical axis comprises 3 decades, which means a factor 10^3 in the intrinsic viscosity, it seems that only one conclusion can be drawn. Both types of representation show such exceedingly small deviations from each other that with proper adjustment of the constants, *A* and *B* in the one case, A^* and B^* in the other, no preference can be given to either. It is, of course, still possible that a set of experimental data may deviate, but if it does so, we have to expect that these deviations will be just as serious in the one case as in the other.

We now come to the interpretation of the constants in terms of the fundamental molecular quantities. One of these quantities is the friction factor of the monomer: ζ in the K.R. paper, *f* in the D.B. paper. The four authors agree that no theory exists which links this factor adequately with the structure of the monomer and that an attempt to represent it by a Stokes sphere turns out to be very unsatisfactory indeed. The other quantity appears in two forms, in the K.R. theory it is the root mean square distance *R* of the ends of the linear chain, in the D.B. theory it is the diameter $2R_s$ of the substituted sphere. In this last case a comparison with the *R* value of a linear chain can only be made for the limiting case of small shielding and then it is found that $2R_s = 1.054R$. It is evident that further progress can only be made if the *R* value can be determined by some other independent method. As such we now have the interference method based on the difference of the intensity of the light scattered by the solution in different directions,[†††] for which in appropriate cases also the dependence of the scattered intensity on the

wave-length of the light can be substituted. The theory of the interference effect is decidedly more reliable than a theory of viscosity can ever expect to be.

Three sets of dissymmetry measurements performed on polystyrene are known to us. Reducing the experimental sets of data which have been obtained with polymers of different molecular weights to a common molecular weight of 10^6, the following values of *R* in A units have been found: Doty for polystyrene in toluene 1080, Ewart for polystyrene in carbon tetrachloride 1050, Bueche for polystyrene in benzene 1110. I believe that the very close agreement is accidental to some degree. In the K.R. paper *R* is found from viscosity measurements equal to 1125, in this paper we found as a result from our discussion of one set of measurements 914. It seems, therefore, that the experimental evidence from light scattering favors the K.R. representation. However, viscosity measurements of Bueche on the same samples on which he measured the light scattering, discussed according to the D.B. schedule, lead to $R = 1030$. Taking the average of all the values without any preference and disregarding the use of different solvents in the interference measurements, since all 3 liquids are good solvents, we arrive at $R = 1050$. As far as the experimental evidence goes we have to conclude that we do not yet have a clear-cut case.

There is general agreement about the one point that polystyrene is much more extended than we would calculate from the usual formula in which free rotation is assumed, since this formula leads to $R = 300$ which is 3.5 times smaller than the average experimental value.

Another final point has to be considered which happens to be in favor of the D.B. treatment. The K.R. treatment is restricted to a linear chain. Many of the polymers may be branched or cross-linked. If this is so or if we do not definitely know from the beginning that the polymer is linear, the substitution of the sphere of the D.B. treatment seems to be indicated.

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††† P. Debye, J. Phys. a. Coll. Chem. **51**, 18 (1947).