

vestigation<sup>9</sup> on dilute solutions of GR-S fractions indicates an increase in  $\phi$  with increasing concentration. It may be significant that the  $\phi$  values for the GR-S solutions were two to three times higher than those for the present polyisobutylene solutions.

It is important to note that the ratio of  $\eta_{sp}/c$  at zero rate of shear to its value as ordinarily measured in a viscometer operating at a standard shearing stress increases as the concentration is decreased. This circumstance arises because  $\gamma$  decreases with increasing concentration owing to the increase in viscosity. Ordinary extrapolation to infinite dilution applied to measurements made with a single viscometer fails, therefore, to reduce the magnitude of the error arising from non-Newtonian flow. This is especially important for high molecular weight polymers in good solvents. Failure to correct for this non-Newtonian effect will, for example, distort the observed viscosity-temperature and viscosity-concentration relationships. In order to obtain an accurate value of the intrinsic viscosity, it is necessary to carry out a suitable extrapolation to zero rate of shear. Employing equations (5) and (6), it is now possible to make such extrapolations for solutions of polyisobutylene for which  $M < 2 \times 10^6$  and  $\eta_r < 2$ .

Certain qualitative observations concerning the dependence of  $\phi$  on  $[\eta]$  and  $M$  expressed in equation

(9) Unpublished results obtained in these laboratories.

(6) can be made. According to this equation, the departure from Newtonian behavior for solutions of a given polyisobutylene fraction is greater in a good than in a poor solvent,  $\phi$  increasing approximately as  $[\eta]^2$ . In the better solvent, the volume of the domain of a single polymer molecule is larger. The number of intrachain entanglements is thus diminished and hence the polymer is more deformable. Since the forces acting on the coiled polymer molecule increase as the volume of the domain increases, and since these forces presumably become more effective in distorting and orienting the polymer molecule in the flow field as the deformability increases, both of these factors may contribute toward the observed increase in  $\phi$ . On the other hand, if polyisobutylenes of different  $M$  are dissolved in different solvents so chosen that the intrinsic viscosities are equal, the value of  $\phi$  will be lower for the polymer of highest molecular weight. This may be explained by a higher concentration of intrachain entanglements in the more densely populated domain of the high molecular weight polymer, which therefore is rendered less deformable.

The above linear relationship between  $\ln \eta_{sp}$  and  $\gamma$  does not agree with the predictions of the theory of Kuhn and Kuhn<sup>10</sup> according to which  $\eta_{sp}$  should decrease initially with  $\gamma^2$ .

(10) W. Kuhn and H. Kuhn, *J. Colloid Sci.*, **3**, 11 (1948).

ITHACA, N. Y.

RECEIVED SEPTEMBER 22, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## Treatment of Intrinsic Viscosities<sup>1</sup>

By P. J. FLORY AND T. G. FOX, JR.

An improved derivation is given for the relationship between the configurational dimensions of a polymer molecule in solution and the thermodynamic interaction between polymer segments and solvent molecules. The connection between intrinsic viscosity and molecular configuration is discussed in the light of recent theories, and general procedures for treating intrinsic viscosity data are given. The root-mean-square end-to-end distance for the polymer molecule when the net thermodynamic interaction between segments and solvent is zero may be computed from suitable viscosity measurements. The influence of hindrance to free rotation on the polymer configuration, unperturbed by thermodynamic interactions with the solvent medium, is obtained directly from this dimension. The influence of thermodynamic interactions on chain dimensions is considered separately. Parameters expressing the heat and entropy of dilution of polymer segments with solvent may be deduced from intrinsic viscosity measurements at different temperatures.

### Introduction

In the treatment of the properties of very dilute polymer solutions it is convenient to represent the molecule as a statistical distribution of chain elements, or segments, about the center of gravity. The average distribution of segments for a chain polymer molecule is approximately Gaussian<sup>2</sup>; its breadth depends on the molecular chain length and on the thermodynamic interaction between polymer segments and solvent. The intrinsic viscosity may be regarded as a measure of the ratio of the effective hydrodynamic volume  $V_e$  of the polymer in a given solvent to its

molecular weight  $M$ ; *i. e.*,  $[\eta] \propto R_e^3/M$ . The recent theories of Debye and Bueche,<sup>3</sup> Kirkwood and Riseman,<sup>4</sup> and of Brinkman<sup>5</sup> show that for sufficiently large chain lengths the effective hydrodynamic radius  $R_e$  must vary directly with a linear parameter of the Gaussian distribution characterizing the polymer in solution. Convenient linear parameters for this purpose are the root-mean-square distance  $\sqrt{r^2}$  between the ends of the polymer chain, or the root-mean-square distance  $\sqrt{s^2}$  of the segments from the center of gravity (*i. e.*, the radius of gyration of the dissolved molecule). The above conclusion had been anticipated previously by various authors<sup>6</sup> but the recent

(3) P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

(4) J. G. Kirkwood and J. Riseman, *ibid.*, **16**, 565 (1948).

(5) H. C. Brinkman, *Applied Sci. Res.*, **A1**, 27 (1947).

(6) W. Kuhn, *Kolloid Z.*, **68**, 2 (1934); W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **26**, 1394 (1943); P. J. Flory, *J. Chem. Phys.*, **13**, 453 (1945).

(1) This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

(2) P. Debye and I. M. Krieger (unpublished) have shown that the average distribution of each segment about the center of gravity is exactly Gaussian for a random chain unperturbed by intramolecular interactions.

theories<sup>3,4,5</sup> are more specific in regard to the conditions under which the above mentioned proportionality should prevail.

For a random chain devoid of intramolecular interactions between segments,  $\bar{r}^2$  (and  $\bar{s}^2$  as well) is proportional to the number of segments in the chain, and hence to the molecular weight  $M$ . This is true regardless of the steric restrictions due to interactions between neighboring segments and of other restrictions on rotations about bonds of the chain, provided that the chain possesses a degree of flexibility and that it is sufficiently long.<sup>7</sup> Intramolecular interactions between segments separated by many intervening segments along the chain (which are referred to here as "long range interactions" to distinguish them from the more specific steric "short range interactions" between near neighbor segments along the polymer chain) may be considered to alter the linear dimensions of the polymer by a factor  $\alpha$ .<sup>8</sup> Hence, the linear dimensions of the polymer coil will vary as  $\alpha M^{1/2}$ , from which it follows that the intrinsic viscosity  $[\eta]$  should vary as  $\alpha^3 M^{1/2}$ , provided that the effective hydrodynamic radius  $R_e$  varies as the linear dimensions of the coil. The intrinsic viscosity may be written

$$[\eta] = KM^{1/2}\alpha^3 \quad (1)$$

If the molecular chain length is large enough to assure that the above proportionality holds,  $K$  will assume a constant value independent of  $M$  and of the solvent; otherwise,  $K$  will vary (increase) with  $M$ .

The experimentally measured intrinsic viscosity of a chain polymer in a good solvent invariably is found to increase approximately with a power of  $M$  greater than one-half over a wide range in molecular weight; the exponent usually lies in the range from 0.6 to 0.8. According to equation (1), this enhanced dependence on molecular weight might be ascribed to an increase of either  $\alpha$  or  $K$  with increase in  $M$ . Debye and Bueche<sup>3</sup> and Kirkwood and Riseman<sup>4</sup> have chosen the latter alternative, according to which  $\alpha$  is tacitly assumed to be very nearly independent of  $M$  while  $K$  increases with  $M$ .<sup>9</sup> However, if reasonable values for the Stokes law radii of polymer segments are assumed, inspection of their expressions reveals that  $K$  should closely approach its asymptotic upper limit for polymers having molecular weights above about 10,000 to 50,000. In order to fit calculated values of  $KM^{1/2}$  to the observed intrinsic viscosity-molecular weight relationship for polystyrene in benzene under the assumption that  $\alpha^3$  is constant, it is necessary to assign to the polymer segment a Stokes law radius between one and two orders of magnitude lower than the mean radius of a chain unit.

Interactions between remotely connected segments of the given chain arise as consequences of

the finite volume of each segment from which all other segments are excluded, and of the net energy of interaction between segments which happen to be in contact. A calculation to take into account the spatial interference is equivalent to the calculation of the configurational probability of a mixture of solvent with polymer segments,<sup>8</sup> from which the entropy of mixing may be derived in the usual manner. The spatial interference may be dealt with, therefore, through consideration of the entropy of mixing, and the effect of the energy of interaction between polymer and solvent on polymer configuration may be treated simultaneously through introduction of the heat of mixing.<sup>8</sup> While the influence of the heat of mixing on polymer dimensions is widely recognized, spatial interference of segments, corresponding to the entropy of mixing, usually has been regarded as of minor importance. The entropy and heat of dilution ordinarily are similar in magnitude, and they depend on the segment concentration in the same manner in dilute solutions. Hence, it follows that spatial interference of segments should be comparable in importance to the energy of mixing in its influence on polymer dimensions, *i. e.*, on  $\alpha$ .

Expression of these concepts in approximate quantitative form has led to the following equation relating  $\alpha$  to  $M$  and thermodynamic factors<sup>8,10</sup>

$$\alpha^5 - \alpha^3 = C'(1 - \Theta/T)M^{1/2} \quad (2)$$

where  $C'$  and  $\Theta$  depend on the heat and entropy of dilution parameters characterizing the given polymer-solvent pair. According to this equation,  $\alpha$  should increase with  $M$  without limit,<sup>11</sup> which is contrary to conclusions reached by other investigators.<sup>12,13</sup> Experiments<sup>10</sup> have shown that the intrinsic viscosities of polyisobutylene fractions in cyclohexane, benzene, toluene and carbon tetrachloride depend on the molecular weight (from  $10^4$  to  $10^6$ ) and temperature (0 to  $90^\circ$ ) in close accordance with the predictions of equation (2) in conjunction with equation (1) assuming  $K$  to be constant. The same value was observed for  $K$  in different solvents, and the  $\Theta$ 's for the poor solvents, benzene and toluene, agreed (within  $5^\circ$ ) with the independently measured critical miscibility temperatures for high molecular weight polyisobutylene fractions in these solvents in accordance with theory. Furthermore, the observed dependences of  $[\eta]$  on *both*  $M$  and  $T$  could not be accounted for by ascribing to  $K$  a value less than its asymptotic limit, in which case  $K$  should increase with  $M$  and decrease with  $T$  in a poor solvent. There appears to be no necessity, from an experimental point of view, of postulating a variation in  $K$  within the molecular weight range ordinarily of interest. Hence, an unrealistic value for the

(10) T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949).

(11) Intrinsic viscosity measurements,<sup>10</sup> and measurements of the angular dissymmetry of scattered light as well, readily show that the ratio of the dimensions of a polymer molecule in a good and in a poor solvent increases steadily with  $M$ . (See E. D. Kunst, *Rec. trav. chim.*, **69**, 125 (1950), and P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).) Such experiments demonstrate in a most direct manner that  $\alpha$  depends on  $M$ .

(12) J. J. Hermans, *Rec. trav. chim. Pays-Bas*, **69**, 220 (1950).

(13) E. W. Montroll, *J. Chem. Phys.*, **18**, 734 (1950).

(7) See W. Kuhn, *Kolloid Z.*, **87**, 3 (1939).

(8) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

(9) It is to be noted that the  $K$  defined here and used henceforth includes the parameter ( $\phi$  of ref. (10)) expressing the departure of the hydrodynamic volume from proportionality to the cube of the dimension of the polymer coil for low  $M$ , or, in the language of Debye and Bueche,<sup>3</sup> the effect of flow permeation of the polymer coil. Thus,  $K$  of the present paper corresponds to  $K\phi$  of ref. (10).

Stokes law radius for the polymer segment is not required.

In the present paper a simplified derivation is given of the relationship, corresponding to equation (2), expressing  $\alpha$  as a function of  $M$ ,  $T$  and thermodynamic parameters. The latter are introduced in a more appropriate manner and  $C'$  is expressed in an improved form. Preferred methods of application of the theoretical relationships to experimental data are discussed.

**Treatment of Long Range Intramolecular Interactions.**—The free energy change for the process of mixing  $x$  segments (the number per molecule) with solvent to yield a distribution equivalent to the average spatial distribution of a polymer molecule will be considered. In the absence of intramolecular interactions this distribution would be given by

$$x_j = x(\beta'/\pi^{1/2})^3 \exp(-\beta_0'^2 s_j^2) 4\pi s_j^2 \Delta s_j \quad (3)$$

where  $x_j$  is the number of segments occurring in the spherical shell of radius  $s_j$  from the center of gravity and of thickness  $\Delta s_j$ , and

$$\beta_0' = \sqrt{3/2\bar{r}_0^2} = 3/\sqrt{\bar{r}_0^2} \quad (4)^{14}$$

where  $\bar{r}_0^2$  is the mean-square distance between the ends of the polymer chain in the absence of intramolecular interactions. The spatial distribution of segments in the actual molecule wherein intramolecular interactions are operative is assumed to be uniformly expanded by a factor  $\alpha$ . It is convenient for present purposes to focus attention on a given set of segments, namely, those  $x_j$ , which would occur within the region  $s_j$  to  $s_j + \Delta s_j$  if  $\alpha$  were equal to unity. In the equilibrium configuration of the polymer molecule they will occupy the spherical shell between  $\alpha s_j$  and  $\alpha(s_j + \Delta s_j)$ . Let  $\Delta F_j$  represent the free energy of mixing the  $x_j$  segments with  $4\pi\alpha^3 s_j^2 \Delta s_j (1 - v_{2j}) \mathbf{N}/v_1$  solvent molecules, where  $v_{2j}$  is the volume fraction of polymer,  $v_1$  is the molar volume of the solvent and  $\mathbf{N}$  is Avogadro's number, to form the  $j$ -th shell of the domain occupied by the polymer molecule. The total free energy of mixing is

$$\Delta F = \sum_j \Delta F_j$$

We require the quantity

$$\partial \Delta F / \partial \alpha = \sum_j (\partial \Delta F_j / \partial \alpha) = (1/\mathbf{N}) \sum_j (\mu_{1j} - \mu_1^0) (\partial n_{1j} / \partial \alpha) \quad (5)$$

where  $\mu_{1j}$  and  $\mu_1^0$  are the chemical potentials of solvent in the  $j$ -th shell and of pure solvent, respectively, and  $n_{1j}$  represents the number of solvent molecules in the shell  $j$ .

The partial molal entropy of dilution for a dilute solution of polymer segments located in an assigned region of space (*e. g.*, situated with respect to a fixed center of gravity) may be assumed to be proportional to the square of the polymer concentration. Thus<sup>15</sup>

$$\Delta \bar{S}_1 = \psi_1 R v^2 \quad (6)$$

where  $v_2$  is the volume fraction of polymer and

(14) The second equality follows from the fact that  $\bar{r}_0^2 = \bar{r}_g^2/6$ . See P. Debye, *J. Chem. Phys.*, **14**, 636 (1946).

(15) P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950).

$\psi_1$  is a parameter characterizing a given polymer-solvent pair. According to earlier theories based on the idealized lattice model<sup>16,17</sup>  $\Delta \bar{S}_1 = R v_2^2/2$ , *i. e.*,  $\psi_1 = 1/2$ , irrespective of the polymer and solvent. It has become apparent, both in the treatment of the results reported in a following paper<sup>18</sup> and from osmotic investigations,<sup>19</sup> that the entropy of dilution differs widely for a given polymer in different solvents. The empirical parameter  $\psi_1$  has been introduced for this reason.

The partial molal heat of dilution may be written in the familiar form

$$\Delta \bar{H}_1 = B v_1 v_2^2 = RT \kappa_1 v_2^2 \quad (7)$$

where  $\kappa_1 = B v_1 / RT$  replaces the former  $\mu_1$  (not to be confused with chemical potential)<sup>20</sup> and  $B$  is the usual parameter characterizing the net heat of interaction for the polymer-solvent pair. From equations (6) and (7)

$$\mu_{1,j} - \mu_1^0 = RT(\kappa_1 - \psi_1) v_{2j}^2 \quad (8)$$

The volume fraction of polymer in the  $j$ -th layer is

$$v_{2j} = x_j V / 4\pi\alpha^3 s_j^2 \Delta s_j \\ = x V (\beta_0' / \alpha \pi^{1/2})^3 \exp(-\beta_0'^2 s_j^2) \quad (9)$$

where  $V$  is the volume of a segment. Also

$$\partial n_{1j} / \partial \alpha \cong 12\pi\alpha^2 s_j^2 \Delta s_j \mathbf{N} / v_1 \quad (10)$$

Substituting equation (9) in (8), and (8) and (10) in (5), replacing the summation by an integral and integrating over  $s_j$  from 0 to  $\infty$ , there is obtained

$$\partial \Delta F / \partial \alpha = 3\beta_0'^2 (2\pi)^{-3/2} (x^2 V^2 \mathbf{N} / v_1) k T (\kappa_1 - \psi_1) / \alpha^4$$

where  $k$  is Boltzmann's constant. Replacing  $xV$ , the molecular volume of the polymer molecule, with  $M\bar{v}/\mathbf{N}$  where  $\bar{v}$  is the specific volume (or partial specific volume) of the polymer, and substituting from equation (4) for  $\beta_0'$ ,

$$\partial \Delta F / \partial \alpha = 6 C_M k T (\kappa_1 - \psi_1) M^{1/2} / \alpha^4 \quad (11)$$

where

$$C_M = (27/2^{3/2} \pi^{3/2}) (\bar{v}^2 / \mathbf{N} v_1) (M/\bar{r}_0^2)^{3/2} \quad (12)$$

The configurational entropy  $S_{el}$  of the chain may be treated according to the methods employed in the theory of rubber elasticity. Assuming that the average end-to-end distance for the chain and the root-mean-square distance of the segments from the center of gravity are distorted by the same factor  $\alpha$ , the change in the configurational entropy with deformation is<sup>8</sup>

$$\partial S_{el} / \partial \alpha = -3k(\alpha - 1/\alpha) \quad (13)$$

Since the internal energy of the chain (apart from the energy of interaction of the chain with its environment) is assumed to be unaffected by deformation, at equilibrium

$$(\partial \Delta F / \partial \alpha) - T(\partial S_{el} / \partial \alpha) = 0$$

Hence, according to equations (11) and (13)

$$\alpha^5 - \alpha^3 = 2 C_M (\psi_1 - \kappa_1) M^{1/2} \quad (14)$$

(16) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **48**, 1 (1942).

(17) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(18) T. G. Fox, Jr., and P. J. Flory, *THIS JOURNAL*, **73**, 1909 (1951).

(19) M. J. Schick, P. M. Doty and B. H. Zimm, *ibid.*, **72**, 530 (1950).

(20) P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949).

Or

$$\alpha^5 - \alpha^3 = 2C_M\psi_1(1 - \Theta/T)M^{1/2} \quad (15)$$

where  $\Theta = \kappa_1 T / \psi_1$  is the critical temperature for total miscibility for a polymer homolog of infinite molecular weight in the same solvent.<sup>10,21</sup> This follows from the fact that at  $T = \Theta$  the second virial coefficient is equal to zero<sup>15,20</sup> (and higher coefficients also are very nearly zero), while the first virial coefficient,  $1/M$ , vanishes as  $M \rightarrow \infty$ . The parameter  $C_M$  is identical with the  $C_M$  which enters in the theory of intermolecular interactions developed for the treatment of the thermodynamic behavior of dilute polymer solutions.<sup>15,20</sup>

**Short Range Interactions and Polymer Chain Dimensions.**—The above treatment is concerned only with interactions between pairs of segments which in general are remotely situated along the polymer chain. Short range steric interactions between neighboring, or near neighboring, segments or distortion due to hindrance to free rotation enter only as they affect the value of  $\bar{r}_0^2$ . Both  $K$  of equation (1) and  $C_M$  depend on  $\bar{r}_0^2$ , hence determination of these parameters may lead to information concerning the intrinsic configurational character of a given polymer chain.

According to equation (1) and the discussion preceding it,  $K$  is proportional to  $V_e/M^{3/2}\alpha^3$ . Since for sufficiently high molecular weights  $V_e$  assumes proportionality to the cube of the linear dimensions of the polymer coil, it is convenient to introduce a quantity  $\Phi$  defined by the relationship

$$K = \Phi(\bar{r}^2/M\alpha^2)^{3/2} = \Phi(\bar{r}_0^2/M)^{3/2} \quad (16)$$

When  $M$  is large,  $\Phi$  (which includes the hydrodynamic factor of previous papers<sup>3,9,10</sup>) should attain a constant (maximum) value; failure of the proportionality between  $V_e$  and  $(\bar{r}^2)^{3/2}$  at lower molecular weights will manifest itself as a decrease in  $\Phi$  with decrease in  $M$ . For chains consisting of more than a few segments,  $\bar{r}_0^2/M$  is a constant characteristic of a given chain structure. According to experimental data previously published,<sup>10</sup>  $K$  for polyisobutylene is a constant independent of molecular weight for  $M > 50,000$ . It follows that  $\Phi$  possesses a value substantially equal to its asymptotic upper limit throughout the molecular weight range of interest. This circumstance greatly simplifies the treatment of intrinsic viscosity data.

Knowledge of the value of  $\Phi$  would at once permit deduction of the structure parameter  $\bar{r}_0^2/M$  from  $K$  obtained in viscosity studies. Experimental evaluation of  $\Phi$  should be feasible using the following relationship derived from equations (1) and (16)

$$\Phi = [\eta]M/(\bar{r}^2)^{3/2} \quad (17)$$

The mean-square end-to-end distance  $\bar{r}^2$  may be determined from measurements on the angular

(21) Equation (14) with  $\psi_1 = 1/2$  is exactly equivalent to equation (27) of reference (8). Thus  $C_1$  of the former paper reduces to  $C_M M^{1/2}/Z^{1/2}$ , where  $Z$  is the number of equivalent configurational segments (see ref. (8)) the introduction of which has been avoided here. Equation (15) is similarly equivalent to equation (6) of ref. (10) which appears here as equation (2). The symbol  $\kappa_1$  is used here in place of the former  $\mu_1$  as mentioned above.

dissymmetry of scattered light<sup>22</sup>;  $[\eta]$  must be measured in the same solvent at the same temperature. If the molecular weight also is known,  $\Phi$  may be calculated from (17).

According to the hydrodynamic treatment of Kirkwood and Riseman,<sup>4</sup> the intrinsic viscosity expressed in  $(\text{g./100 cc.})^{-1}$  is given by

$$[\eta] = 0.0588(\pi/6)^{3/2} N(\bar{r}_0^2)^{3/2} M^{-1} \quad (18)$$

provided that  $M$  is sufficiently large for  $V_e$  to be proportional to  $(\bar{r}_0^2)^{3/2}$ . Introducing the factor  $\alpha^3$  neglected by Kirkwood and Riseman and comparing with equations (1) and (16),  $\Phi = 3.6 \times 10^{21}$ .<sup>23</sup> Approximations employed in the development of their theory cast doubt on the literal validity of the numerical factor in equation (18), and hence also on this value for  $\Phi$ . The empirical expression derived by Kuhn and Kuhn<sup>24</sup> from experiments on models yields a similar result,  $\Phi = 3.4 \times 10^{21}$ , in the limit of large  $M$ .

Whatever the exact numerical value of  $\Phi$  may be, it is clearly evident that it should be the same for all polymers regardless of the solvent and temperature. Differences in the  $K$ 's for various polymers must reflect differences in  $(\bar{r}_0^2/M)^{3/2}$ , which may be written  $(\bar{r}_0^2/nM_0)^{3/2}$  where  $n$  is the number of chain bonds and  $M_0$  is the molecular weight per bond. Thus,  $K$  for any given polymer will be determined solely by  $M_0$  and the "natural" degree of extension of the chain  $(\bar{r}_0^2/n)$  in the absence of thermodynamic interaction. From knowledge of  $K$  and bond dimensions, information is at hand concerning the influence on chain configuration of hindrances to rotation about the chain bonds. Since the effect of hindrances to rotation will change with temperature,  $K$  should, in general, depend somewhat on temperature. Conversely, it should be possible to secure information concerning the barriers to free rotation from the magnitude of  $K$  and its temperature coefficient. On the other hand, at a given temperature  $K$  should be independent of the solvent according to equation (16), since  $\bar{r}_0^2$  is the chain dimension in the absence of interactions between chain segments and their environment.

In the special case of a simple chain comprised of  $n$  equivalent valence bonds each of length  $l_0$  joined at a fixed valence angle  $\theta$

$$\bar{r}_0^2 = nl_0^2 [(1 - \cos \theta)/(1 + \cos \theta)][(1 + \cos \phi)/(1 - \cos \phi)] \quad (19)^{25}$$

where  $\phi$  is the angle of rotation of a given bond measured from the plane defined by the two preceding bonds in the chain, and  $\cos \phi$  designates the average value of  $\cos \phi$ ; the potential hindering free rotation is assumed to be symmetric about

(22) P. Debye, *J. Phys. Colloid Chem.*, **51**, 18 (1947).

(23) It is interesting to note that the radius of the spherical domain which is the hydrodynamic equivalent of an Einstein rigid sphere is approximately  $\sqrt{s^3}$  according to the results of Kirkwood-Riseman. Thus, if we assume that  $R_e = \sqrt{s^3}$

$$[\eta] = 2.5 \times 10^{-2} N V_e / M = N(\pi/30)\alpha^3(\bar{r}_0^2)^{3/2} / M$$

and  $\Phi = 4.3 \times 10^{21}$  in virtual agreement with the above value.

(24) W. Kuhn and H. Kuhn, *J. Chem. Phys.*, **16**, 838 (1948); *Helv. Chim. Acta*, **30**, 1233 (1947).

(25) P. Debye, unpublished; W. J. Taylor, *J. Chem. Phys.*, **15**, 412 (1947); H. Kuhn, *ibid.*, **16**, 843 (1947).

$\phi = 0$ . For such a chain according to equation (16)

$$K = \Phi(l_0/M_0^{1/2})^3 [(1 - \cos \theta)/(1 + \cos \theta)]^{1/2} \times [(1 + \cos \phi)/(1 - \cos \phi)]^{1/2} \quad (20)$$

For a simple chain made up of identical bonds of length  $l_0$  and angle  $\theta$ , the value of  $\overline{\cos \phi}$  may be deduced from  $K$ , provided  $\Phi$  is known.

The constant  $C_M$  depends on  $(M/\bar{r}_0^2)^{1/2}$  and on  $\bar{v}^2/v_1$ . Since the latter factor is relatively insensitive to temperature,  $C_M$  may be assumed to vary inversely as the change in  $K$  with temperature.  $C_M$  is specifically dependent on the solvent through the molar volume  $v_1$ , but it should be possible to calculate the  $C_M$  for one solvent from that for another (at the same temperature) knowing their molar volumes.

#### Methods for Treating Experimental Data.—

Equations (1) and (15), together with  $C_M$  as defined by (12), provide the essential basis for the treatment of intrinsic viscosity. Eliminating  $\alpha$  between equations (1) and (15) and considering  $T$  and  $M$  to be known quantities, three parameters  $K$ ,  $\Theta$ , and the product  $\psi_1 C_M$  remain to be determined from suitable experimental data. Since  $K$  is dependent only on the structure of the polymer and to some extent on  $T$ , its evaluation is a logical first objective; the other two parameters may then be determined readily for each solvent.

The most straightforward determination of  $K$  requires only the measurement of the intrinsic viscosity of a polymer of known  $M$  in a poor solvent at the temperature  $T = \Theta$ . It follows from equation (15) that  $\alpha^3 = 1$  at  $T = \Theta$ , hence according to equation (1),  $K$  at this temperature is equal to  $[\eta]/M^{1/2}$ . The value of  $\Theta$  is determined by extrapolation of the linear relationship<sup>17</sup> between the critical miscibility temperature  $T_c$  and  $M^{-1/2}$  to  $M = \infty$ , the precipitation measurements being carried out on a series of fractionated polymers. By choosing solvents with suitably differing  $\Theta$ 's, it is possible to determine  $K$  as a function of temperature in this manner.

Having established the value of  $K$  for the given series of polymer homologs at a given temperature, both  $\Theta$  and  $\psi_1 C_M$  for any given solvent may be evaluated from data on the dependence of  $[\eta]$  on  $T$  in that solvent. From such data values of  $\alpha^3$ , and hence  $\alpha^5 - \alpha^3$ , at each temperature are readily calculated by equation (1), employing the relationship of  $K$  to  $T$  established previously. According to equation (15) plots of  $K_T/K_0$  ( $\alpha^5 - \alpha^3$ )/ $M^{1/2}$  vs.  $1/T$  should be linear; the ratio ( $K_T/K_0$ ) of  $K$  at  $T$  to its value at a reference temperature  $T_0$  is introduced in view of the temperature dependence of  $C_M$  noted previously. The reciprocal of  $\Theta$  is given by the intercept of the straight line with the  $1/T$  axis, and the product  $\psi_1 C_M$  at  $T_0$  may be determined from the slope of this line, the latter being equal to  $2\psi_1 C_M \Theta$ .

In cases where it is difficult to obtain accurate

values of  $\Theta$  or where it is inconvenient to carry out viscosity measurements at temperatures near  $\Theta$ , values of  $K$  may be established from the relationship of  $[\eta]$  to  $M$  in a given solvent at a given temperature. Solution of equation (1) for  $\alpha$  and insertion of the result into equation (15) yields the expression

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + K^{5/3} C_T M / [\eta] \quad (21)$$

where

$$C_T = 2\psi_1 C_M (1 - \Theta/T) = (\alpha^5 - \alpha^3)/M^{1/2} \quad (21a)$$

Hence, a plot of  $[\eta]^{2/3}/M^{1/3}$  vs.  $M/[\eta]$  in a given solvent at a particular temperature will be linear;  $K$  and  $C_T$  are determined by the intercept at  $M/[\eta] = 0$ , and by the slope, respectively.<sup>26</sup> If the  $[\eta]$  vs.  $M$  data are available for several temperatures, the dependence of  $K$  and of  $C_T$  on temperature may be deduced. Values of  $\Theta$  and  $\psi_1 C_M$  can be computed exactly as described in the preceding paragraph.

It is noteworthy that the thermodynamic parameters governing the interaction of polymer segments with solvents,  $\psi_1$  and  $\kappa_1$ , may be determined, at least in principle, solely from the measurement of an irreversible kinetic process, the viscous flow of the polymer solution through a capillary tube. Thus, values of  $\psi_1$  and  $\kappa_1$  may be calculated from  $\psi_1 C_M$  and  $\Theta$  determined by the procedure described above, and the relationship  $\Theta = \kappa_1 T / \psi_1$ , provided that the value of  $C_M$  is known. The latter may be calculated from equation (12) and the value of  $\bar{r}_0^2/M$ , assuming that the numerical factor in this equation, based on approximate theory, is sufficiently accurate for this purpose. In principle,  $\bar{r}_0^2/M$  may be calculated from viscosity data alone by equation (16) employing the theoretically estimated value of  $\Phi$  given above. Values of  $C_M$ ,  $\psi_1$  and  $\kappa_1$  obtained in this manner must, of course, be considered provisional until  $\Phi$  and the numerical coefficient of equation (12) are established with certainty. One of the sources of uncertainty, but not both, can be eliminated if the value of  $\bar{r}_0^2$  is determined independently from the dissymmetry of scattered light for a dilute solution of a polymer of known  $M$ .<sup>22</sup> In either case, the value of  $\psi_1$  and  $\kappa_1$  for various solvents should be correct relative to one another. Absolute values of these parameters may be determined from viscosity data if the value of  $\psi_1$  for one of the solvents is determined independently from thermodynamic studies of dilute solutions of the polymer, e. g., from osmotic pressure or turbidity measurements at different temperatures. Viscosity and thermodynamic measurements afford mutually supplementary data for the elucidation of parameters pertaining to polymer-solvent interactions in dilute solutions.<sup>15</sup>

ITHACA, N. Y.

RECEIVED SEPTEMBER 22, 1950

(26) This graphical procedure was suggested by Dr. J. R. Schaefgen of The Goodyear Research Laboratory. An analogous analytical method was employed in reference (10).