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about 2⅓ percent or 0.04A in the C−C bond. It is likely that the change in size of the molecule in passing to the triplet state is of the same order of magnitude. That there are, however, some fundamental differences in the shape of the lowest triplet and lowest excited singlet states is shown by the prominence of the 1178 and 1596 cm⁻¹ e_g^+ vibrations in the triplet emission, whereas the 606 and 1596 e_g^+ vibrations are prominent in the singlet emission.

The Configuration of Real Polymer Chains*

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The average configuration of polymer molecules in solution is markedly influenced by the obvious requirement, ordinarily disregarded in problems relating to molecular configuration, that two elements of the molecule are forbidden from occupying the same location in space. The influence of spatial "interferences" between different segments of the molecule on its average configuration has been investigated by statistical and thermodynamic methods.

It is shown that if the average linear dimension of a polymer chain is to be taken proportional to a power of the chain length, that power must be greater than the value 0.50 previously deduced in the conventional "random flight" treatment of molecular configuration. This power should approach 0.60 for long chain molecules in good solvents. With increase in size of the solvent molecule, the influence of interference on molecular configuration diminishes, vanishing entirely in the extreme case of a solvent which is also a high polymer. The effect of a heat of interaction between solvent and polymer may also be incorporated quantitatively in the theory. A positive heat of mixing (poor solvent) tends to offset the expansive influence of interference, and the exponent referred to above tends to approach 0.50. The results are of foremost significance in the interpretation of the intrinsic viscosity and its dependence on the polymer constitution and on the solvent. It is pointed out that the spatial dimensions of the irregularly coiled polymer molecule cannot be correlated directly with hindrance to rotation about chain bonds, unless the expansion of the configuration due to interference and the effects of the heat of dilution are first of all taken into account.

INTRODUCTION

THE spatial configuration of randomly coiled chain polymer molecules is customarily treated in the "random flight" approximation, according to which each element, or "segment," of the chain is considered to be free to choose any orientation with respect to its predecessor, independent of the locations of all other segments of the same molecule. Impossible configurations which would require two segments to occupy the same element of volume are not excluded from consideration. The effects of short range "interferences" of this nature between two segments situated in close proximity along the chain are readily taken into account approximately by merely enlarging the effective segment length somewhat, the form of the equation expressing the nature of the chain configurations being unaltered.[1] The influence of long range interferences between remotely related segments of the same chain is not so easily disposed of, however.

The average "density" of polymer within the region occupied by a chain of a thousand segments may be of the order of only one percent. The chance that a given segment will seek to occupy the site occupied by some other remotely connected segment will be relatively rare. It must not be inferred, however, that long range interferences are inconsequential under these conditions. A given "random flight" configuration for the molecule will be acceptable only in case *none* of its segments is assigned to a site occupied by another segment. The probability of compliance with this condition will be of the order of e^{-5} for a molecule of a thousand segments distributed at an average density of one percent. Only a very small fraction of the "random flight" configurations tacitly assumed in previous theories may be realized by the actual chain molecule. Interferences will be fewer on the average in more expanded configurations. Hence, a relatively larger fraction of the latter will be acceptable to the actual polymer chain and the average size of the randomly coiled molecule will be greater than that calculated by the usual procedures.

This fairly obvious influence of interference of actual chain molecules having finite lateral dimensions has been pointed out on various occasions[2-4] in the past, but it has not been investigated quantitatively. Direct treatment of the configuration problem in terms of the space coordinates for

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[1] W. Kuhn, Kolloid Zeits. **87**, 3 (1939).

[2] W. Kuhn, Kolloid Zeits. **68**, 2 (1934).
[3] M. L. Huggins, J. App. Phys. **10**, 700 (1939).
[4] R. Simha, J. Polymer Sci. **3**, 227 (1948).

each segment would be prohibitively difficult indeed. In the present paper an estimate of the effects of intra-chain interferences has been accomplished through the use of statistical methods. These lend themselves also to the taking into account of the effect on the molecular configuration of energy interactions between solvent and polymer. The results of this analysis are directly applicable to the treatment of intrinsic viscosity.

THE INFLUENCE OF LONG RANGE INTERFERENCE ON MOLECULAR CONFIGURATION

Consider a system containing N polymer molecules in a solution so dilute that the interactions between polymer molecules may be disregarded. We shall be concerned with the internal configurations of these molecules, their arrangement relative to one another throughout the solution being unimportant here. Let the state of the system be defined in terms of the numbers N_i of molecules having their ends separated by the distances r_i. Then the total number of internal configurations consistent with the given distribution of chain displacement lengths (r_i) may be written

$$\Omega = N! \prod_i (\omega_i)^{N_i}/N_i!, \tag{1}$$

where ω_i is the total number of configurations available to a chain having the "displacement length" r_i. If there were no interference, the probability W_i of a displacement length between r_i and r_i+dr_i would be given to a satisfactory approximation by the Gaussian function

$$W_i dr_i = (\beta^3/\pi^{\frac{3}{2}}) \exp(-\beta^2 r_i^2) 4\pi r_i^2 dr_i, \tag{2}$$

where

$$\beta^2 = 3/(2Zl^2), \tag{3}$$

Z being the number of segments and l the length of each segment for the "equivalent chain" composed of rigid segments connected by completely flexible bonds.[5] Consequently, in the absence of interference, ω_i would be given by $W_i\omega_0$ where ω_0 is the total number of all configurations available to the chain. Owing to interference, only a fraction f_i

of these random flight configurations for the chain displacement length r_i are acceptable. Hence

$$\omega_i = f_i W_i \omega_0, \tag{4}$$

and

$$\Omega = \Omega_0 N! \prod_i (f_i^{N_i} W_i^{N_i}/N_i!), \tag{5}$$

where Ω_0 is the total number of internal configurational arrangements given by

$$\Omega_0 = \omega_0^N.$$

It will be assumed that f_i may be replaced by its average value designated by f. On introducing Stirling's approximation, the logarithm of the relative number of configurations for a given chain displacement length distribution specified by the N_i's then becomes

$$\ln(\Omega/\Omega_0) = N \ln(fN) + \sum_i N_i \ln(W_i/N_i). \tag{6}[6]$$

For the purpose of estimating f, it is convenient to adopt the lattice model customarily employed in treating the configurational statistics of polymer mixtures and their solutions. The volume of a cell of the lattice will be expressed by V, and the number of segments *of this size* in the polymer molecule will be represented by x. These "lattice segments" will not ordinarily be identical with those employed in the specification of the configuration of the chain in space. The latter generally will be larger, depending on the flexibility of the chain and on local steric interactions; i.e., x generally will exceed Z, and $V^{\frac{1}{3}}$ will be less than l. With reference to the lattice scheme, the average random flight chain is represented by a probability distribution of occupied cells within a certain region of the lattice. Since the density distribution will be variable over this region, we may consider a small portion of the region in which the average density is uniform. If there are x_j segments in this volume composed of v_j cells, the probability that no two of the segments x_j are assigned to the same cell will be

$$f_j = \prod_{i=0}^{x_j-1} (1-i/v_j) \cong \exp(-x_j^2/2v_j)$$

from which it follows that

$$\ln f \equiv \sum_j \ln f_j = -\sum (x_j^2/2v_j). \tag{7}$$

The summation in Eq. (7) depends on the spatial distribution of segments of the polymer molecule. The exact character of this distribution is difficult to ascertain. Even in the case of a hypothetical

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[5] In the approximation that each bond between successive chain atoms is subject to a hindrance potential which is a function of the angle φ of rotation about that bond, and independent of other bond angles, β could be defined in accordance with the results of P. Debye (Report to the Office of Rubber Reserve, April 10, 1945) as follows:

$$\beta^{-2} = (2/3)l_0^2 n'[1+(\cos\varphi)_{Av}]/[1-(\cos\varphi)_{Av}] \times [1+\cos\theta]/[1-\cos\theta],$$

where l_0 is the length of a valence bond of the chain, n' is the number of chain bonds, and θ is the fixed valence angle (e.g. 109.5°). In general, polymer chains will not conform to this approximation (see subsequent discussion). Hence, the hypothetical chain of simply connected units, as referred to above and in other publications, is preferred here, notwithstanding the fact that the exact magnitude of l (and correspondingly of Z) remains beyond the scope of the treatment.

[6] If $f=1$ corresponding to no interference, and if the chain displacement length distribution is the most probable one specified by $N_i=NW_i$, W_i being given by Eq. (2), then $\Omega/\Omega_0=1$.

random flight chain, the distribution of segments about the center of gravity (unlike the chain displacement length distribution) cannot be expressed in closed form. The distribution for a real polymer chain, in addition to being expanded as a result of chain segment interference, probably will be distorted as well; the average concentration of segments near the center may be diminished relative to their concentration in outlying regions of the distribution.

Since the value of the sum in Eq. (7) is not critically dependent on the precise nature of the spatial distribution of segments, a satisfactory evaluation may be secured by arbitrarily expressing the average density of segments at a distance s from the center of gravity by a Gaussian function

$$W'(s) = (\beta'/\pi^{\frac{1}{2}})^3 \exp(-\beta'^2 s^2) 4\pi s^2, \qquad (8)$$

where the parameter β' is to be assigned a value such that the mean square distance, $\langle s^2 \rangle = 3/2\beta'^2$, of the segments from the center of gravity shall coincide with that for the actual distribution. For a random flight chain Debye[7] has shown that $\langle s^2 \rangle = \langle r^2 \rangle/6$ where r represents the distance between chain ends. According to Eqs. (2) and (3), $\langle r^2 \rangle = Zl^2$. Hence,

$$\langle s^2 \rangle = Zl^2/6$$

for the hypothetical random flight chain. Linear dimensions of the actual distribution of segments will be increased owing to the influence of long range interference by a factor designated by α. Hence, for a real polymer molecule

$$\langle s^2 \rangle = \alpha^2 Zl^2/6,$$

from which it follows that

$$\beta'^2 = 9/\alpha^2 Zl^2. \qquad (9)$$

Equation (9) specifies the value of β' which fulfills the requirement that the Gaussian distribution (8) shall yield the correct value for $\langle s^2 \rangle$.

The number x_j of segments in a spherical shell of radius s_j and thickness Δs will be given by

$$x_j = xW'(s_j)\Delta s,$$

and the number of lattice cells in the same volume by

$$\nu_j = 4\pi s_j^2 \Delta s/V.$$

Substituting these expressions in Eq. (7) and evaluating the corresponding integral from $s_j = 0$ to ∞,

$$\ln f = -Vx^2\beta'^3/2^{5/2}\pi^{3/2}$$
$$= -(27/2^{5/2}\pi^{3/2}) Vx^2/(\alpha lZ^{1/2})^3. \qquad (10)$$

Letting the length l' of the lattice segment equal $V^{\frac{1}{3}}$ and noting that $xl' = Zl$, the above relationship

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

may be written

$$\ln f = -CZ^{\frac{1}{2}}/\alpha^3, \qquad (11)$$

where

$$C = (27/2^{5/2}\pi^{3/2})(l'/l) \qquad (12)$$
$$\cong (l'/l). \qquad (12')$$

It is obvious from the nature of the problem treated above that the actual average distribution of segments in space may be replaced by a uniform distribution of the x segments within a sphere of radius R_e so chosen as to give the required result.[8] The summation in Eq. (7) over the equivalent sphere is simply $x^2/2\nu$, where

$$\nu = (4\pi/3)R_e^3/V.$$

Hence,

$$\ln f = -3Vx^2/8\pi R_e^3.$$

Comparing this result with Eq. (10), the radius of the equivalent sphere is found to be given by

$$R_e = (\pi/2)^{1/6}(1/3)^{2/3}\alpha lZ^{1/2}$$
$$= 0.52\alpha lZ^{1/2} \cong \alpha lZ^{1/2}/2. \qquad (13)$$

Thus, R_e is very nearly half the root-mean-square distance between chain ends. This is about the same size as the equivalent sphere found by Debye and Bueche[9] to represent the hydrodynamic interaction of the chain with solvent in the limit of unperturbed velocity distribution ("free draining" chain) through the molecule.

In calculating the interference within the randomly coiled molecule according to the above procedure, no account is taken of the fact that segments comprising the molecule are connected to one another, and hence that these segments must occupy a contiguous set of lattice cells. The expectancy for the occurrence of a segment in a cell immediately adjacent to a cell known to be occupied has been tacitly assumed to equal the average concentration of segments at the given distance from the center of gravity. Actually, this expectancy is greater than the average concentration since the segment which occupies the given cell must be adjoined by two other segments of the same chain (assuming, of course, that the segment in question is not a terminal segment). Thus, the knowledge that a given cell is occupied by a polymer chain segment enhances the likelihood that other nearby cells are also occupied. "Short range" interferences between segments separated by only a few intervening segments are largely neglected in the above calculation. For this reason, Eqs. (10) and (11) must not be construed as

[8] This procedure is similar to that employed recently by Debye in the treatment of the hydrodynamic interaction of the polymer molecule with the solvent. The writer applied a similar simplification to the treatment of the thermodynamic behavior of dilute polymer solutions. (See reference 15.)

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

indicative of the *total* interference within the randomly coiled molecule. In this connection it should be noted that as a result of the above averaging procedure the interference according to Eq. (11) for a chain of $2Z$ segments is less than that for two chains of Z segments, i.e., $f_{2Z} > f_Z{}^2$. Obviously, the total interference for the chain of $2Z$ segments must exceed that for the separate chains.

The consequences of this deficiency of the above treatment are by no means as disastrous as might be supposed, for we are concerned here merely with that part of the total interference which is dependent on the volume occupied by the molecule; i.e., only the "long range" interferences between segments belonging to remotely connected portions of the chain are appreciably affected by moderate degrees of expansion of the average configuration. For this purpose, Eq. (11) appears to afford a legitimate approximation.

It remains to evaluate the second term on the right of Eq. (6). In the absence of interference the most probable chain displacement length distribution would be defined by

$$N_i = NW(r_i),$$

where $W(r_i)$ is the probability distribution (W_i) given by Eq. (2). The increase in the effective average volume of the randomly coiled molecule brought about by interference presumably will be accompanied by a similar distortion of the chain displacement length distribution. If this is the case, this distribution for the actual molecule can be expressed as follows

$$N_i = NW(r_i/\alpha),$$

or

$$N_i dr_i = N(\beta^3/\pi^{\frac{3}{2}}) \exp(-\beta^2 r_i{}^2/\alpha^2)(4\pi/\alpha^3)r_i{}^2 dr_i. \quad (14)$$

Thus, it is assumed that the distribution over r_i is uniformly shifted by the same factor α as applies to the average radial distribution of segments about the center of gravity. Substituting from Eq. (14) for N_i and from (2) for W_i in the latter term of Eq. (6)

$$\sum N_i \ln(W_i/N_i) = N \ln(\alpha^3/N)$$
$$- N(4\beta^5/\alpha^3\pi^{\frac{3}{2}})(1-1/\alpha^2) \sum_{r_i} \exp(-\beta^2 r_i{}^2/\alpha^2)r_i{}^4 dr_i.$$

Replacing the summation by the value of the corresponding integral over r_i from 0 to ∞,

$$\sum N_i \ln(W_i/N_i) = N \ln(\alpha^3/N) - 3N(\alpha^2-1)/2. \quad (15)$$

Substituting Eqs. (11) and (15) in (6) and expressing the results as an entropy $S(\alpha)$,

$$S(\alpha)/k = \ln(\Omega/\Omega_0)$$
$$= N[-CZ^{\frac{1}{2}}/\alpha^3 + 3 \ln\alpha - 3(\alpha^2-1)/2]. \quad (16)$$

The equilibrium expansion factor α for which $S(\alpha)$ is a maximum, obtained by differentiating and equating to zero, is specified by the relationship

$$\alpha^5 - \alpha^3 = CZ^{\frac{1}{2}}. \quad (17)$$

TREATMENT OF THE INTERACTION OF THE POLYMER MOLECULE WITH SOLVENT AS A SWELLING PHENOMENON

It is apparent from inspection of Eq. (16) and from its derivation that the last two terms correspond to the entropy of elastic deformation of a system of independent polymer chains subjected to uniform dilution. The first term can be shown to correspond to an entropy of dilution. Thus, the above treatment resembles that previously applied to the problem of swelling of cross-linked network structures.[10] The influence of long range interference on the average configuration of a system of independent polymer molecules dispersed in an abundance of solvent may, in fact, be treated as a swelling phenomenon. One may adopt the view that the polymer segments tend to dilute themselves with more solvent in order to achieve a higher entropy of mixing. This process of dilution of the segments is accompanied by an adverse expansion of the polymer chain configurations. Equilibrium is obtained when the attendant opposing forces are in balance. The influence of a heat of mixing of segments with solvent may be included in logical fashion. The following distinction from the problem of swelling in network structures must be borne in mind, however. The individual polymer chains are independent of one another in the present problem, whereas in the swelling of a network structure the ends of the chain elements are required to meet at the network junctions.[10]

The entropy of dilution of a system of polymer segments combined in a single continuous structure may be written[11,12]

$$\Delta S_{dil}/k = -n \ln v_1, \quad (18)$$

where n is the number of solvent molecules and v_1 is their volume fraction in that system. The entropy of elastic deformation of the molecule is given by

$$\Delta S_{el}/k = 3 \ln\alpha - 3(\alpha^2-1)/2, \quad (19)$$

derivation of which is obvious from the treatment given in the preceding section.[13] The effect of a

[10] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. 11, 521 (1943).
[11] M. L. Huggins, J. Phys. Chem. 46, 151 (1942); Ann. N. Y. Acad. Sci. 43, 1 (1942).
[12] P. J. Flory, J. Chem. Phys. 10, 51 (1942).
[13] W. Kuhn, R. Pasternak and H. Kuhn, Helv. Chim. Acta 30, 1705 (1947), have deduced Eq. (19) in an equivalent, though less direct, manner. They have applied it to the treatment of swelling of network structures, overlooking the fact that it does not take into account the requirement that the chain ends must meet at the network junctions. While Eq. (19) is applicable to the treatment of independent chains,

heat of mixing of polymer and solvent may be introduced through use of an expression of the van Laar form

$$\Delta H = Bx V v_1,$$

where B is the cohesive energy density constant characteristic of a given solvent-polymer pair. Employing the conventional procedure

$$\Delta H/kT = \mu x v_1, \qquad (20)$$

where μ is defined as

$$\mu = B V/kT, \qquad (21)$$

which differs from the usual definition of μ in that the volume V of the lattice cell replaces the molar volume of the solvent.

Combining Eqs. (18), (19) and (20), there is obtained for the free energy of dilution

$$\Delta F/kT = n \ln v_1 + \mu x v_1 + 3(\alpha^2 - 1)/2 - 3 \ln \alpha. \qquad (22)$$

Adopting the previously employed equivalent sphere within which the polymer segments are considered to be uniformly distributed

$$n = [(4\pi/3)R_e{}^3 - x V]/x_s V,$$

where x_s is the number of lattice cells occupied by a molecule of solvent. In this way, the effect of the size of the solvent molecule is included. Substituting from Eq. (13) for R_e, and using the previous substitutions $V^{\frac{1}{3}} = l'$ and $xl' = Zl$,

$$n = (x/x_s)(x\alpha^3/2CZ^{\frac{1}{2}} - 1), \qquad (23)$$

where C is defined by Eq. (12), or to a satisfactory approximation by Eq. (12'). Similarly,

$$v_1 = nx_s/(nx_s + x) = 1 - 2CZ^{\frac{1}{2}}/x\alpha^3. \qquad (24)$$

Substituting these expressions for n and v_1 in Eq. (22) and expanding the logarithmic term in series

$$\Delta F/kT = -(1/x_s)(x - CZ^{\frac{1}{2}}/\alpha^3 - \cdots)$$
$$+ \mu(x - 2CZ^{\frac{1}{2}}/\alpha^3) + 3(\alpha^2 - 1)/2 - 3 \ln \alpha. \qquad (25)$$

Terms beyond the first two in the series expansion may be neglected. On equating to zero the derivative of ΔF with respect to α, there is obtained

$$C(1/x_s - 2\mu)Z^{\frac{1}{2}} = \alpha^5 - \alpha^3 \qquad (26)$$

which replaces Eq. (17) of the previous development. Equation (26) reduces to (17) for the case: $x_s = 1$ and $\mu = 0$.

If the solvent and polymer mix without heat effect, $\mu = 0$ and

$$CZ^{\frac{1}{2}}/x_s = \alpha^5 - \alpha^3. \qquad (26')$$

If the solvent is itself polymeric such that x_s is very large, the term on the left approaches zero and α approaches unity. Thus, a polymer molecule situated in a medium consisting of other polymer molecules of the same kind, or in a medium of unlike polymer molecules with which it mixes athermally, will occupy spatial configurations coinciding with those calculated in the random flight approximation, undistorted by interference effects. To understand the basis for this deduction, it is necessary to observe that while an expansion of the dissolved molecule decreases its interference with itself, "interference" with surrounding polymer molecules is correspondingly increased. Expansion of the molecule achieves no net improvement in the configurational freedom of the system as a whole. This deduction is important for it justifies use of the random flight approximation in the treatment of concentrated polymer systems, e.g., in the treatment of rubber elasticity.

If the solvent is of low molecular weight, x_s may be set equal to unity. It is preferable, however, to express the relationship (26) as follows:

$$C_1(1 - 2\mu_1)Z^{\frac{1}{2}} = \alpha^5 - \alpha^3, \qquad (27)$$
where
$$C_1 = C/x_s \quad \text{and} \quad \mu_1 = \mu x_s.$$

It is to be noted that μ_1 ($= B V_1/RT$ where V_1 is the molar volume of the solvent) is the analog of the μ defined in previous treatments of polymer solvent interactions.[11,12,14] The present μ_1 may not be numerically equivalent to the μ deduced from thermodynamic measurements on the same polymer-solvent system. In particular, the value of μ_1 applicable here should not correspond to the μ obtained from thermodynamic measurements on *dilute* solutions.[15] The former applies to the energy interaction of an individual polymer molecule with its immediate environment; the energy contribution to the latter depends on the over-all polymer concentration in quite a different manner owing to the discontinuous nature of the solution.[15] Furthermore, the latter μ contains contributions from sources other than the interaction energy.[15]

It has often been suggested[3,12,16] that an endothermic heat of interaction between solvent and polymer should cause the randomly arranged polymer chain to contract so that it occupies a smaller volume. This expectation is abundantly confirmed by the lower intrinsic viscosity values observed in poorer solvents. Similarly, in good solvents configurations for which there are fewer polymer-to-polymer contacts will be preferred, and the molecule will therefore choose larger configurations. The

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an additional term (given by $-(3/2) \ln \alpha$ for a tetrafunctionally connected network) must be included in the elastic entropy of dilution of a network structure.

[14] P. J. Flory, J. Chem. Phys. **12**, 425 (1944).
[15] P. J. Flory, J. Chem. Phys. **13**, 453 (1945).
[16] T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. **64**, 1557 (1942).

present theory gives quantitative form to these ideas. If μ_1 is positive (but less than $\frac{1}{2}$),[17] the value of the expansion factor is diminished according to Eq. (27). If μ_1 is negative, representing a favorable heat of mixing, α is increased.

The interaction energy term obviously could have been introduced in the treatment given in the preceding section. The effect of the size of the solvent is not so easily incorporated in that development. To indicate the manner in which it would enter, it may be sufficient to point out that a solvent comprised of more than one segment may assume any one of a number of internal configurations; i.e., its situation is no longer specified by merely assigning it a location in the lattice. The interference term cannot be expressed in terms of the polymer molecule alone, for the arrangement of the polymer molecule affects the configurations available to the solvent molecules. The total configurations available to the system as a whole must be considered. In this way the influence of solvent size as expressed in Eq. (26) may be deduced.

DISCUSSION

The exact value to be assigned to C, or to C_1, cannot be deduced from theory because of the difficulty of bridging the gap between the actual polymer chain in solution on the one hand and the idealized chain model composed of Z segments arranged in the hypothetical lattice on the other. In general l' will be less than l. Values of C in the range from 0.1 to 1.0 are anticipated, depending on the cross-sectional dimensions of the chain and its flexibility. For a very high polymer, Z will be of the order of 10^4. Hence, $\alpha^5 - \alpha^3$ may assume values of the order of 10 to 100, corresponding to $\alpha = 1.7$ to 2.5 for high polymers in athermal solvents. The predicted influence of long range interference on the dimensions of the random polymer chain is by no means trivial, therefore.

The factor α may be incorporated directly in previous formulas expressing the dimensions of polymer molecules in terms of bond angles and the potential energy function associated with rotation about the bonds. Thus, the mean square distance between the ends of a tetrahedrally bonded chain may be expressed approximately as follows:[5, 18, 19]

$$\langle r^2 \rangle \cong 2\alpha^2 l_0^2 n'(1 + \langle \cos\varphi \rangle)/(1 - \langle \cos\varphi \rangle), \quad (28)$$

where l_0 is the length of each bond, n' is the number of bonds and φ represents the angle of rotation

about a bond measured from the trans (or planar zig-zag) configuration, $\langle \cos\varphi \rangle$ indicating the average value of the cosine. Alternatively, this may be expressed in terms of the equivalent hypothetical freely jointed chain as follows:

$$\langle r^2 \rangle = \alpha^2 l^2 Z, \quad (29)$$

where compliance with Eq. (28) together with the condition $Zl = n'l_0$ would require that l and Z be related to l_0 and n' as follows

$$l = 2l_0(1 + \langle \cos\varphi \rangle)/(1 - \langle \cos\varphi \rangle),$$

and

$$Z = (n'/2)(1 - \langle \cos\varphi \rangle)/(1 + \langle \cos\varphi \rangle).$$

Dimensions of high polymer molecules in solution, as deduced from the angular dissymmetry of scattered light, are known to be appreciably larger than would be calculated assuming free rotation about every bond and neglecting the interference effect.[9, 20] Debye and Bueche[9] noted for example that the value of $\langle r^2 \rangle^{\frac{1}{2}}$ deduced from light scattering dissymmetry measurements on a polystyrene of molecular weight 10^6 was $3.5(\langle r^2 \rangle_0)^{\frac{1}{2}}$, where $\langle r^2 \rangle_0$ represents the mean square distance between the ends of a chain possessing free rotation and devoid of interference; according to Eq. (28), $\langle r^2 \rangle_0 = 2l_0^2 n'$. If the difference between the observed $\langle r^2 \rangle$ and $\langle r^2 \rangle_0$ is to be ascribed entirely to hindrance to free rotation, it follows from Eq. (28) that the average value of $\cos\varphi$ must be 0.85 corresponding to $\varphi = \pm 32°$. In terms of the freely jointed hypothetical chain (Eq. (29))

$$\langle r^2 \rangle_{\text{obs.}}/\langle r^2 \rangle_0 = \alpha^2 l/2l_0. \quad (30)$$

If $\alpha = 1$, the result of Debye and Bueche requires that $l/l_0 = 24$, i.e., the equivalent chain must consist of about twelve structural units. This seems unreasonably large to be attributed entirely to hindered rotation.

Recent calculations by Taylor[21] show that the potential barrier to free rotation about the bonds of a polymethylene chain is capable of accounting for an increase in linear dimension by a factor of only 1.5 to 2.0. The phenyl substituents of polystyrene doubtless increase the hindrance to free rotation. Some of these steric interactions may oppose the planar zig-zag arrangement of adjacent chain atoms, however, and it does not follow that the average of $\cos\varphi$ will be much increased by the presence of bulky substituents. Short range interferences between nearby, but not consecutive, units will increase the length of the chain somewhat. It seems unlikely, however, that the aggregate influence of hindrance to free rotation about the carbon-

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[17] Precipitation probably will set in for values of the μ_1 near $\frac{1}{2}$. It is readily seen that as $1 - 2\mu_1$ approaches zero, Eq. (27) acquires multiple solutions in α. At $\mu_1 = \frac{1}{2}$, solutions are $\alpha = 1$ and 0. The indicated collapse of the molecule will be preceded by mutual interaction of polymer molecules resulting in the formation of a new phase.

[18] W. J. Taylor, J. Chem. Phys. **15**, 412 (1947).

[19] H. Kuhn, J. Chem. Phys. **15**, 843 (1947).

[20] P. M. Doty, W. A. Affens, and B. H. Zimm, Trans. Faraday Soc. **42B**, 66 (1946).

[21] W. J. Taylor, J. Chem. Phys. **16**, 257 (1948).

carbon single bonds, steric interactions between substituents, and short range interferences may be sufficient to account for the observed disparity between $\langle r^2 \rangle$ and $\langle r^2 \rangle_0$. This difficulty disappears if α is assigned a value in the range predicted above. The length l of the equivalent segment (see Eq. (30)) then assumes a reasonable value, and extraordinary hindrance to free rotation need not be postulated. In any event, molecular dimensions should not be related directly to chain stiffness; the effect of long range interference on the molecular dimensions must first of all be taken into account. It is important to note that whereas l in Eq. (29) (or l_0 and the function of $\langle \cos \varphi \rangle$ in Eq. (28)) should be independent of molecular weight, α increases with the chain length.

In the above discussions both the polymethylene chain model with hindered rotation (Eq. (28)) and the hypothetical freely jointed chain (Eq. (29)) have been employed. Clearly the short range steric interactions—steric interactions between substituents and what have been called short range interferences—are too complex to justify literal application of Eq. (28); in particular, the potential energy associated with rotation about a given bond will depend also on the rotation angle prevailing for other nearby bonds. Interpretation of chain configurations in terms of the hypothetical freely jointed equivalent chain (Eq. (29)) widely used by Kuhn is to be preferred.

The expansion in chain configuration resulting from long range interference is also of importance in the interpretation of the viscosities of dilute polymer solutions. Kuhn[2] long ago pointed out that solvent within the domain of an irregularly coiled polymer molecule of sufficient size would move with the molecule when the dilute solution is subject to shear.[22] In effect, then, the molecule and associated solvent would behave like an Einstein sphere and the specific voscosity of the solution should be 2.5 times the total *effective* volume of all these spheres. Translated to intrinsic viscosity expressed in $(g/cc)^{-1}$

$$[\eta] = 2.5(4\pi/3)R_e{}^3/M, \qquad (31)$$

where R_e is the radius of the equivalent sphere.[23] For the random flight chain R_e will be proportional to $M^{\frac{1}{2}}$. Hence, the intrinsic viscosity should be proportional to $M^{\frac{1}{2}}$. However, Kuhn[2,22] recognized that the "volume filling effect" (equivalent to long

range interference) would increase the molecular configuration dimension, and for reasons not made clear he concluded that the augmentation in the effective volume could be introduced as a factor proportional to a low power of M. He suggested, therefore, that the intrinsic viscosity should depend on the molecular weight according to the relationship[2]

$$[\eta] = KM^a, \qquad (32)$$

where a lies in the range from 0.6 to 0.9. This conclusion regarding the exponent a appeared to be contradicted by such experimental data as were available at that time (1934) but it has since proved to be remarkably correct.

The recent treatments of the hydrodynamic interaction of a randomly coiled polymer molecule with the solvent medium advanced by Debye and Bueche[9] and by Kirkwood and Riseman[24] in effect permit the factor 2.5 to be replaced by a function (designated by φ in the D-B treatment) representing the effective permeation of the flowing solvent through the domain of the polymer chain. Making this replacement in Eq. (31) and substituting from Eq. (13) for R_e,

$$[\eta] = \text{const.} (l^3 Z^{\frac{3}{2}}/M)\alpha^3 \varphi$$
$$= \text{const.} (l^3/M_0)Z^{\frac{1}{2}}\alpha^3 \varphi, \qquad (33)$$

where M_0 is the molecular weight per segment and φ varies with chain length, approaching an upper limiting value (2.5 in the D-B treatment) for sufficiently long chains. Debye and Bueche,[9] and also Kirkwood and Riseman,[24] attribute the almost universal apparent dependence of intrinsic viscosity (in a good solvent) on a power of the chain length which is greater than one-half to the variation of the hydrodynamic factor φ with M.

According to Eqs. (26), or (27), α in a good solvent should approach proportionality to $Z^{1/10}$ in the high molecular weight range. As the molecular weight decreases, or if a poorer solvent is used, the dependence of α on Z must be approximated by a lower power of Z. Hence, the product $Z^{\frac{1}{2}}\alpha^3$ in Eq. (33) should vary as Z raised to a power between 0.5 and 0.8, being near the upper limit in a good solvent if the chain length is great. Virtually all reliable experimental results on the relationship of intrinsic viscosity to molecular weight require a values for Eq. (32) which are in this range. This fact together with other experimental observations to be discussed elsewhere[25] lead to the conclusion that the hydrodynamic factor φ is substantially independent of M within the molecular weight range ordinarily covered; apparently φ approaches

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[22] See also W. Kuhn, and H. Kuhn, Helv. Chem. Acta. **26**, 1394 (1943).

[23] The equivalent sphere entering into Eq. (31) may differ in size from that employed above in the treatment of the interference effect. Actually they are similar in size, although the use of the same symbol R_e here and above is not meant to imply that they are identical. For present purposes it is sufficient to note that the one R_e should be proportional to the other.

[24] J. G. Kirkwood and J. Riseman, J. Chem. Phys. **16**, 565 (1948).

[25] T. G. Fox, Jr. and P. J. Flory, to be published.

its upper limit for negligible solvent flow permeation of the equivalent sphere. The difference between the value of a observed to apply in Eq. (32) and 0.50 should be ascribed primarily to the influence of long range interference and to the heat of dilution of the polymer segments with solvent molecules.

At sufficiently low molecular weights the decrease in φ with further decrease in chain length must become significant. On the other hand, α^3 varies as Z raised to a power which diminishes as the chain length becomes small (see above). The dependences of these two factors (φ and α^3) on Z are such as to compensate (partially at least) one another so as to preserve the empirical relationship (32) with a fixed exponent a down to lower molecular weights than would be possible if either of the two factors alone entered in Eq. (33).

Theory of the Thermal Diffusion of Electrolytes in a Clusius Column

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A theory is presented which accounts approximately for the apparently anomalous difference between the thermal diffusion coefficients of an ion in the presence and in the absence of other electrolytes; the theory is based on the existence of an electric field parallel to the thermal gradient in the electrolyte as a consequence of the variation in mobility among the various ions present. It is pointed out also that some data on the behavior of electrolytes in a Clusius column are at variance with the Debye exponential law concerning the steady-state distribution of solute.

AN apparent anomaly in the thermal diffusion of electrolytes was reported by Gillespie and Breck[1] and by Hirota[2] in 1941. In experiments with the Clusius column[3] these workers found that one[4] of a mixture of two electrolytes was transported into the upper reservoir, contrary to its behavior when it was the only solute; the other electrolyte of the mixture was transported as usual into the lower reservoir, but to a greater extent than when it was the only solute. Prior to this work no instances of the thermal diffusion of an electrolyte against the temperature gradient had been recorded in the literature.

A similar but less striking effect has long been known to occur in the ordinary diffusion of mixtures of electrolytes:[4,5] the more mobile of two mixed electrolytes diffuses more rapidly, the less mobile more slowly, than each diffuses alone. Vinograd and McBain[6] accounted for the effect quantitatively in terms of an electrostatic field set up by the diffusion of ions of different mobilities. It occurred to one of us (G.G.) that the results of Gillespie and Breck and of Hirota could be similarly explained.

We present herewith approximate treatments of the behavior of the mixed electrolytes in the pure Soret effect and in the Clusius column; the analysis accounts approximately for the anomalies referred to above.

THE SORET EFFECT

Let the thermal gradient lie along the x axis. At the steady state the flux f_i of the i'th ionic species across any plane in the solution normal to x will vanish, i.e.

$$f_i = -D_i dc_i/dx - D_i' c_i dT/dx + \nu_i u_i c_i E = 0 \quad (1)$$

where D_i is the ordinary diffusion coefficient, D_i' is the thermal diffusion coefficient, c_i is the concentration in equivalents per unit volume, u_i is the equivalent mobility, ν_i is the sign of the ionic charge, and E is the local field postulated to arise from the difference in ionic mobilities. Let us substitute $RTu_i = FD_i$, where F is the Faraday; multiply Eq. (1) by ν_i/D_i and sum over all ions. Applying the approximate neutrality condition $\sum \nu_i dc_i/dx = 0$ we obtain

$$(EF/RT)\sum c_i = (dT/dx)\sum \nu_i c_i D_i'/D_i, \quad (2)$$

and

$$\frac{d \ln c_i}{dx} = \left(-\frac{D_i'}{D_i} + \frac{\nu_i \Sigma \nu_i c_i D_i'/D_i}{\Sigma c_i} \right)\frac{dT}{dx}. \quad (3)$$

For non-electrolytes the Soret coefficient, σ, is equal to the ratio $-D'/D$. We shall call this ratio for individual ions the intrinsic Soret coefficient $\sigma_i{}^*$.

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[1] L. J. Gillespie and S. Breck, J. Chem. Phys. 9, 370 (1941).
[2] K. Hirota, Bull. Chem. Soc. (Japan) 16, 232 (1941).
[3] K. Clusius and G. Dickel, Naturwiss. 26, 546 (1938).
[4] In these experiments the two electrolytes have a common ion.
[5] T. Graham, Phil. Trans. Roy. Soc. (London) 805 (1850); J. W. McBain and C. R. Dawson, J. Am. Chem. Soc. 56, 52 (1934).
[6] J. R. Vinograd and J. W. McBain, J. Am. Chem. Soc. 63, 2008 (1941).