

For $X = OH$ strong internal hydrogen bonding has been found to exist for both II and III. This results in the stability of conformation d of Fig. 4 and, therefore, explains the fact that isotactic polyvinyl alcohol takes the TTT... form. Syndiotactic polyvinyl

alcohol also takes this form because the intermolecular hydrogen bonding is strong enough.

Thus, various conformations of linear high polymers can be explained satisfactorily by taking into account the energy of internal rotation in simple molecules.

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Dimensions of Polymer Molecules in Concentrated Solutions¹

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A concentration-dependent intermolecular potential previously derived from a fluctuation theory of polymer solutions is here used to obtain an analytic expression for the radial distribution function $g(r)$ in concentrated solutions. An approximate equation for $g(r)$ is used, either the Born-Green-Kirkwood or hypernetted chain equation; the two are equivalent under the applicable assumption: $g(r) - 1 \ll 1$. The excluded volume expansion factor α which minimizes the free energy is obtained in terms of $g(r)$ and is shown to decrease toward unity as the concentration is increased. The theory becomes valid in the low concentration region when extensive overlapping of polymer domains occurs and remains valid until the solvent volume fraction drops below *ca.* 10^{-1} – 10^{-2} , depending on the polymer molecular weight. The thermodynamic properties in this concentration range are those of a solution of randomly distributed polymer molecules.

I. Introduction

In earlier work^{2,3} the excluded volume expansion factor α of polymer molecules was calculated for moderately concentrated solutions by minimization of the free energy. The potential energy between polymer molecules was a gaussian function as was used by Flory and Krigbaum⁴ in their theory of the second osmotic virial coefficient. The radial distribution function was obtained by an approximate variational solution of the Born-Green-Kirkwood equation.^{2a} Subsequently, it was noted that the intermolecular potential could not properly be taken independent of polymer concentration, except in the dilute solution range.⁵ A model of polymer solutions was formed on the assumption that the local volume fraction of segments at any point in the system for a given configuration of polymer centers of mass would be close to the bulk volume fraction of segments, and from this assumption a concentration dependent intermolecular potential was derived. The potential was used to calculate the solvent chemical potential in polymer solutions, the same approximate determination of the radial distribution function being made as before. The present work has two purposes. The first is to evaluate the excluded volume expansion factor in concentrated solutions on the basis of the new concentration-dependent intermolecular potential rather than the old concentration-independent potential. The second purpose is to improve the method of calculation of the radial distribution function in concentrated solutions, and therefore also the calculation of the chemical potential and the expansion factor α .

The first stage of the calculation will be an improved version of the free energy minimization which determines α . For reasons not clear in retrospect the earlier calculation^{2b,3} was quite indirect. The osmotic pres-

sure was determined as a function of α and then integrated to obtain the free energy. However, the later work on thermodynamic functions in concentrated solution, using the improved intermolecular potential, gave the free energy as a configurational integral plus a self-energy term, and both of these terms are easy to vary directly with respect to α , to minimize the free energy. This is the procedure followed here. The result is an equation for α whose solution requires knowledge of the radial distribution function at the given concentration and for a given α which occurs implicitly as a scale factor in the segment density function of a single polymer molecule.

The approximate variational solution of the Born-Green-Kirkwood equation used in the earlier work is here replaced by an analytic solution valid when the radial distribution function $g(r)$ is close to unity for all values of the argument r . Our expectation was that this assumption would limit the validity of the analytic solution to very high polymer concentrations. The actual situation is more complicated. As the concentration is raised the approximation becomes valid at concentrations sufficiently high that the polymer domains fill the solution. The approximation then remains valid until some very high concentration is reached, a concentration which is higher the higher the polymer molecular weight. At these very high concentrations an effective repulsion between polymer molecules becomes more effective in causing a nonrandom distribution than is the increased polymer concentration effective in causing a random (or microscopically homogeneous) distribution. A lengthy but inconclusive discussion of this phenomenon is given. For most purposes the breakdown in the linearized theory of $g(r)$ has no importance since it occurs at solvent volume fractions of the order of 0.01 or lower, except for very low polymer molecular weights.

The results may be summed up as follows. The excluded volume factor α , which may be much greater than unity in good solvents, drops rapidly as the polymer concentration is increased in dilute solutions. The rate of decrease moderates during further increases

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(2) (a) M. Fixman, *J. Chem. Phys.*, **33**, 370 (1960); (b) *J. Polymer Sci.*, **41**, 91 (1960).

(3) M. Fixman, *Ann. N. Y. Acad. Sci.*, **89**, 657 (1961).

(4) P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

(5) M. Fixman, *ibid.*, **35**, 889 (1961).

in concentration, and α approaches unity as ρ^{-1} , where ρ is the polymer number density. At extremely high concentrations α begins to increase, a behavior which is probably due to the breakdown of the linearized theory of $g(r)$, or more fundamentally, the breakdown of the gaussian model of the coil. The results for the solvent chemical potential are simpler. The deviation of the potential from its value in a microscopically homogeneous polymer solution is negligible throughout the concentration range in which the linearized theory of $g(r)$ is valid.

A few words should be said about the choice of equation for determining the radial distribution function.⁶ A wide variety of equations exists and a few of the more prominent ones have been examined. The hypernetted chain approximation agrees with the Born-Green-Kirkwood equation when both are linearized. Another equation, that of Percus and Yevick, was the first one chosen for investigation. The linearized Percus-Yevick equation gives entirely different predictions from those described here. The Percus-Yevick equation makes the total segment density in the vicinity of a given polymer center of mass very close to the macroscopic segment density, but only at the expense of a negative radial distribution function. This negative part of the radial distribution function is a δ -function at the origin, the same kind of unphysical behavior to which the solution of the linearized Born-Green-Kirkwood equation is tending as the concentration is raised. (The Percus-Yevick equation gives this unphysical behavior as an exact solution, while the Born-Green-Kirkwood equation gives it only when linearized.) Moreover, the Percus-Yevick equation shows this behavior at rather low concentrations (for typical choices of parameters in the intermolecular potential). We believe that the preferred position⁶ of the Percus-Yevick equation is established only for hard core potentials. For soft core potentials at concentrations high enough that great overlapping of molecules occurs and correlation functions are close to unity, the Born-Green-Kirkwood equation seems intuitively more acceptable, both in its derivation and in its predictions. It is possible that corrections to the hypernetted chain approximation could be explored in a useful way. The lines in the perturbation diagrams represent factors of $g(r) - 1$, and if this series will ever converge rapidly it should do so here, where $g(r) - 1$ is small and short-ranged.

II. Free Energy Minimization

The general theory of ref. 5 gave for the free energy A of the solution, relative to the infinitely dilute mixture of segments in solvent, the expression

$$A = A_0 + A_s - \frac{1}{2} \epsilon^{(2)} V v_2^2 - kT \ln Q_2 \quad (1)$$

Except for A_s , the symbols have the meaning previously given. Briefly, v_2 is the volume fraction of polymer, V is the total volume of the solution, $\epsilon \equiv \epsilon(v_2)$ is the free energy density of randomly mixing segments and solvent, and $A_0 = V\epsilon$

$$\epsilon^{(i)} \equiv d^{(i)} \epsilon(v_2) / dv_2^i$$

$\epsilon(v_2)$ is here presumed known; it could be obtained

(6) E. Helfand, *Ann. Rev. Phys. Chem.*, **14**, 117 (1963).

from either an approximate theory or experiment in which the polymer molecular weight is extrapolated to infinity.⁷ The Flory-Huggins approximation, for example, gives

$$\epsilon(v_2) = kT V_1^{-1} [v_1 \ln v_1 + \chi_0 v_1 v_2] \quad (2)$$

where V_1 is the partial molecular volume and v_1 the volume fraction of solvent. The goal is to use ϵ to predict results at finite molecular weight. The quantity A_s in eq. 1 is the total intramolecular free energy of N polymer molecules each with partial molecular volume V_2 .

$$A_s = \frac{1}{2} N \epsilon^{(2)} V_2^2 \int v^2(r) dr + NkT \left[-3 \ln \alpha + \frac{3}{2} (\alpha^2 - 1) \right] \quad (3)$$

where $nv(r)$ is the segment number density of a single polymer molecule at a distance r from its center of mass; the molecule has n segments. α is the excluded volume expansion factor and the term in brackets is the entropic contribution to A_s , which was previously suppressed because of lack of interest in the concentration dependence of α . Note that each molecule is assigned the same expansion factor. The remaining term in eq. 1 is

$$Q_2 = \int \dots \int \exp[-U\{\mathbf{R}\} / kT] d\{\mathbf{R}\} \quad (4)$$

$$U\{\mathbf{R}\} = \frac{1}{2} \sum_{i \neq j} E_{ij} \quad (5)$$

$$E_{ij} = V_2^2 \epsilon^{(2)} \int v(\mathbf{R}) v(\mathbf{r}_{ij} + \mathbf{R}) d\mathbf{R} \quad (6)$$

$$= V_2^2 \epsilon^{(2)} e(r_{ij}) \quad (7)$$

The problem is to minimize A with respect to α . The dependence of A on α arises from A_s and Q_2 , both terms depending on α through $v(r)$. Equation 1 yields from the equation $\partial A / \partial \alpha = 0$ the result

$$\frac{\partial A_s}{\partial \alpha} = kT \frac{\partial \ln Q_2}{\partial \alpha} \quad (8)$$

Equations 3, 4, and 8 give

$$-\rho V_2^2 \epsilon^{(2)} \int g(r) \left\{ \frac{\partial}{\partial \alpha} \int v(\mathbf{R}) v(\mathbf{r} + \mathbf{R}) d\mathbf{R} \right\} dr = \epsilon^{(2)} V_2^2 \frac{\partial}{\partial \alpha} \int v^2(r) dr + 6kT(\alpha - \alpha^{-1}) \quad (9)$$

where ρ is the number density of polymer molecules and $g(r)$ is the radial distribution function, a function

(7) $\epsilon(v_2)$ is described as a free energy of mixing segments with solvent, but it can be seen in two ways that the segments must be part of an infinite chain, rather than broken pieces or monomer units of the real molecule. In the first way one looks at the derivation of the theory and sees that ϵ is the free energy of mixing polymer and solvent in a small unit volume, much smaller on an edge than the mean dimensions of the polymer coil. Moreover, ϵ designates a free energy which has been partially averaged over segment positions, subject to fixed volume fraction in the small element of volume and fixed polymer centers of mass (and a few other constraints might be imagined to improve the theory, but we have not investigated them). For large chains it is very unlikely that the small volume element will contain an end segment, or that the partial averaging over orientation of the segments in the volume element will be perturbed by the gross constraints placed on the polymer molecules. Rather, the local free energy density should depend only on the polymer volume fraction in the volume element. The second way of arriving at the same conclusion requires only the results of the theory. We in fact find that $A \rightarrow V$ as $n \rightarrow 0$, where n is the number of segments per molecule.

of the distance r between two polymer centers of mass. As in the previous work, the segment density will be assumed gaussian.

$$v(r) = (3/2\pi\alpha^2 R_0^2)^{3/2} \exp(-3r^2/2\alpha^2 R_0^2) \quad (10)$$

where R_0 is some measure of average chain dimensions in the random-flight approximation (for example, the root-mean-square radius of gyration), and α is the associated expansion factor. Substitution of this expression into eq. 9 and evaluation of the derivatives and integrals gives

$$\alpha^5 - \alpha^3 = \frac{1}{2} (V_2^2 \epsilon^{(2)}/kT)(3/4\pi R_0^2)^{3/2} \times \\ \left\{ 1 - \rho \int h(r) \exp(-3r^2/4\alpha^2 R_0^2) dr + \right. \\ \left. (\rho/2\alpha^2 R_0^2) \int h(r) \exp(-3r^2/4\alpha^2 R_0^2) r^2 dr \right\} \quad (11)$$

where

$$h(r) = 1 - g(r) \quad (12)$$

Further progress with eq. 11 requires an explicit expression for $h(r)$; for this we turn to the Born-Green-Kirkwood-Yvon-Bogolubov (BGK) equation.⁸

III. Radial Distribution Function

In terms of the function

$$V(r_{ij}) \equiv E_{ij}/kT \quad (13)$$

the BGK equation is (with the notation $V(r_{ij}) = V(ij)$)

$$\nabla_1 \ln g(12) = -\nabla_1 V(12) - \rho \int g(23)g(13)\nabla_1 V(13) d3 \quad (14)$$

According to the expectations previously described, $g(r)$ should be very close to unity in the high concentration range. The substitution of $g(r) = 1 - h(r)$ into eq. 14 and suppression of nonlinear terms in h gives

$$-\nabla_1 h(12) = -\nabla_1 V(12) - \rho \int \nabla_1 V(13)[1 - h(23) - h(13)] d3 \quad (15)$$

$$= -\nabla_1 V(12) + \rho \nabla_1 \int V(13)h(23) d3 \quad (16)$$

since the spherical symmetry of $V(r)$ and $h(r)$ makes several terms vanish. Fourier transformation of eq. 16 gives

$$h_k = V_k(1 + \rho V_k)^{-1} \quad (17)$$

where

$$h_k = \int h(r)e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \quad (18)$$

$$V_k = \int V(r)e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \quad (19)$$

The inverse Fourier transformation of eq. 17 gives

$$h(r) = (8\pi^3)^{-1} \int V_k(1 + \rho V_k)^{-1} e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k} \quad (20)$$

V_k can be obtained from eq. 6 and 10, as follows

$$V(r) = (\epsilon^{(2)}V_2^2/kT)(3/4\pi\alpha^2 R_0^2)^{3/2} \exp(-3r^2/4\alpha^2 R_0^2) \quad (21)$$

which will be written in the form

$$V(r) = \beta \exp(-r^2) \quad (22)$$

the unit of length being temporarily chosen so that

(8) T. L. Hill, "Statistical Mechanics," McGraw-Hill Book Co., New York, N. Y., 1956.

$4\alpha^2 R_0^2/3 = 1$. Therefore

$$V_k = \beta \pi^{3/2} \exp\left(-\frac{1}{4}k^2\right) \quad (23)$$

where

$$\beta = (\epsilon^{(2)}V_2^2/kT)(3/4\pi\alpha^2 R_0^2)^{3/2} \quad (24a)$$

or

$$\beta = (\epsilon^{(2)}V_2^2/kT)\pi^{-3/2} \quad (24b)$$

in the special units.

It is now important to note that $\beta \rightarrow \infty$ as $v_1 \rightarrow 0$, since this fact has a major and perhaps dire effect on $g(r)$. A Flory-Huggins choice of $\epsilon(v_2)$

$$\epsilon(v_2) = kTV_1^{-1}[v_1 \ln v_1 + \chi_0 v_1 v_2] \quad (25)$$

gives

$$\epsilon^{(2)} = kTV_1^{-1}(v_1^{-1} - 2\chi_0) \quad (26)$$

The growth of $\epsilon^{(2)}$ must be as v_1^{-1} for sufficiently small v_1 in any theory. The consequence of $\beta \rightarrow \infty$ in eq. 17 is that

$$h_k \rightarrow \rho^{-1} \quad (27)$$

or

$$h(r) = 1 - g(r) = \rho^{-1}\delta(r) \quad (28)$$

where $\delta(r)$ is a Dirac δ -function. Equation 28 satisfies the assumption that $h(r)$ is small almost everywhere, but where the assumption is made, it is very, very bad. The resulting eq. 28 is unsatisfactory only in that it makes $g(r)$ negative at the origin, and $g(r)$ as defined is a positive quantity. In another respect the result makes physical sense, namely in respect to the average segment density at a distance r from the center of mass of one molecule. Call this segment density $n\rho(r)$. Addition of contributions from the specified molecule and all the others gives

$$n\rho(\mathbf{r}) = nv(\mathbf{r}) + n\rho \int v(\mathbf{r} - \mathbf{R})g(\mathbf{R}) d\mathbf{R} \quad (29)$$

$$= n\rho + nv(\mathbf{r}) - n\rho \int v(\mathbf{r} - \mathbf{R})h(\mathbf{R}) d\mathbf{R} \quad (30)$$

Equation 28 gives $\rho(\mathbf{r}) = \rho$; in words, the distribution of segments around the center of mass of one molecule becomes random as $v_1 \rightarrow 0$. We believe the result to be correct in general and as a consequence of the gaussian model. The inference from eq. 30, that $h(r) = \rho^{-1}\delta(r)$ if $\rho(\mathbf{r}) \equiv 1$, is straightforward. What must be incorrect is the model of the polymer chain on which eq. 29 is based, a model in which the chain is a spherically symmetric cloud of segments that can distort only through expansion or contraction of a scale factor. If the actual chain-like nature of the molecule were taken into account in eq. 29 (as it is in the intuitive assertion that $\rho(\mathbf{r}) \rightarrow \rho$ as $v_1 \rightarrow 0$), $v(\mathbf{r} - \mathbf{R})$ in the integral would not be the same function as $v(r)$ and would depend on r and \mathbf{R} separately since it would be a conditional segment density.

Because the model can give a physically realistic result ($\rho(\mathbf{r}) = \rho$) in the limit $v_1 \rightarrow 0$ only at the expense of an impossible $g(r)$, we will not attempt to improve on the linearization of eq. 14, but rather recognize that when v_1^{-1} is so large that the linearization fails, the model of the polymer molecule must also fail. To set

more precisely the limits of validity of the calculation, the maximum value of $h(r)$ must be known.

Equation 20 gives, on angular integration over \mathbf{k} ,

$$h(r) = (2\pi^2)^{-1} \int_0^\infty V_k (1 + \rho V_k)^{-1} [(\sin kr)/kr]^2 dk \quad (31)$$

The function V_k is positive and $|(\sin kr)/kr| \leq 1$, so the maximum value of $h(r)$ occurs at $r = 0$.

$$h(0) = (2\pi^2)^{-1} \int_0^\infty V_k (1 + \rho V_k)^{-1} k^2 dk \quad (32)$$

$$= (2\pi^2\rho)^{-1} \int_0^\infty \exp\left(a^2 - \frac{1}{4}k^2\right) \times \left[1 + \exp\left(a^2 - \frac{1}{4}k^2\right)\right]^{-1} k^2 dk \quad (33)$$

where

$$a^2 = \ln(\rho\beta\pi^{1/2}) \quad (34)$$

The substitution

$$k = 2ay$$

gives

$$h(0) = 4(\pi^2\rho)^{-1} a^3 \int_0^\infty \{1 + \exp[a^2(y^2 - 1)]\}^{-1} y^2 dy \quad (35)$$

$h(0)$, and $h(r)$ generally, can be evaluated analytically if $a^2 \gg 1$. The behavior of β , as given in eq. 24 and 26, indicates that this condition holds for the concentration range of interest. For $a^2 \gg 1$ the function

$$f(y) \equiv \{1 + \exp[a^2(y^2 - 1)]\}^{-1} \quad (36)$$

passes very rapidly from unity to zero as y increases through unity. Therefore, $[-f'(y)]$ has approximately the properties of a δ -function, and

$$\int_0^\infty y^2 f(y) dy = - \int_0^\infty \frac{y^3}{3} f'(y) dy \sim \frac{1}{3}$$

or

$$h(0) \sim \frac{4}{3} a^3 (\pi^2\rho)^{-1} \quad (37a)$$

Here ρ must be measured in units of $(3/(4\alpha^2 R_0^2))^{3/2}$. In ordinary units

$$h(0) \sim \frac{4}{3} a^3 (\pi^2\rho)^{-1} (3/4\alpha^2 R_0^2)^{3/2} \quad (37b)$$

Equations 24, 26, and 34 give, with the following estimate at small v_1

$$\begin{aligned} V_1 &\sim b^3 \\ V_2 &\sim nb^3 \\ a^2 R_0^2 &\sim nb^2 \\ \rho &\sim V_2^{-1}. \end{aligned}$$

the results

$$\begin{aligned} a &\sim [\ln(nv_1^{-1})]^{1/2} \\ h(0) &\sim 0.1n^{-1/2} [\ln(nv_1^{-1})]^{3/2} \end{aligned} \quad (38)$$

As v_1 decreases $h(0)$ gets larger. This estimate is ob-

viously very crude; the important thing shown by eq. 38 is that the theory may be carried to quite high concentrations, for reasonable values of n , without violation of the assumption $h(r) \ll 1$. Note also that $h(0)$ vanishes with increasing n as $n^{-1/2}$.

IV. Expansion Factor

The integrals in eq. 11 can now be evaluated. Again in units such that $3/(4\alpha^2 R_0^2) = 1$

$$\rho \int h(r) \exp(-r^2) dr = 4a^3 \pi^{-1/2} \int_0^\infty f(y) \exp(-a^2 y^2) y^2 dy \quad (39)$$

where $f(y)$ is defined in eq. 36. Similarly

$$\rho \int r^2 h(r) \exp(-r^2) dr = 4a^3 \pi^{1/2} \int_0^\infty f(y) \left(\frac{3}{2} - a^2 y^2\right) \exp(-a^2 y^2) y^2 dy \quad (40)$$

Substitution of eq. 39 and 40 into eq. 11, introduction of the variable β from eq. 24, and continued use of units such that $3/(4\alpha^2 R_0^2) = 1$ gives

$$\alpha^2 - 1 = \frac{1}{2}\beta \left[1 - \frac{8}{3} a^5 \pi^{-1/2} \int_0^\infty y^4 f(y) \exp(-a^2 y^2) dy\right] \quad (41)$$

The δ -function property of $f(y)$ cannot be used immediately in eq. 41 because $\exp(-a^2 y^2)$ is a rapidly varying function of y . However, the right-hand side of the identity

$$f(y) \equiv 1 - f(y) \exp[a^2(y^2 - 1)]$$

provides a substitution for $f(y)$ which leaves it multiplied, in eq. 41, by a simple power of y . The application of $f'(y) \cong -\delta(y)$ then gives

$$\alpha^2 - 1 = (4\beta/15\sqrt{\pi}) a^5 \exp(-a^2) \quad (42)$$

and eq. 34 and 37a allow this to be rewritten as

$$\alpha^2 - 1 = \frac{1}{5} a^2 h(0) \quad (43)$$

Mathematical approximations made in the derivation of eq. 43 require for their validity that $h(0)$ is small and a^2 is large (for sufficiently small v_1 , a^2 becomes so large that it is impossible for $h(0)$ to be small). In practice the result ought to be a good approximation at concentrations sufficiently high that $a^2 \geq 5$, $\rho \geq 2$ (in units of $3/(4\alpha^2 R_0^2)$) and up to a v_1 of a least 0.8-0.9 (or higher v_1 for very large molecular weights). Equation 43 may be compared with the result valid at infinite dilution

$$\alpha_0^2 - 1 = \frac{1}{2}\beta_0 \quad (44)$$

according to eq. 11 and 24, where β_0 is β evaluated at $v_1 = 1$, and similarly for α_0 . The assumptions made in the derivation of eq. 43 make it impossible to connect smoothly eq. 43 onto eq. 44. But eq. 43, together with the earlier work on α in moderately concentrated solutions, allows a nearly complete picture of α vs. v_2 to be given. α decreases first rapidly and then gradually from α_0 as v_2 increases, the dominant behavior being $\alpha^2 - 1 \sim \rho^{-1}$. This behavior continues until the theory breaks down ($v_1 < 0.1$ to 0.001) and probably beyond.

V. Thermodynamic Properties at High Concentration

The expression previously given for the solvent chemical potential \bar{A}_1 involved integrals over $h(r)$ (previously designated $G(r)$). The result was presented in the form

$$\bar{A}_1 = \bar{A}_{01} - V_1 kT\rho + \bar{A}_{s1} + v_2^2 \Gamma \quad (45)$$

where the first two terms on the right-hand side of eq. 45 give the chemical potential at infinite molecular weight (or for a random distribution of polymer molecules).

$$\bar{A}_{01} \equiv \left\{ \partial [V\epsilon(v_2)] / \partial N_1 \right\}_{N_2, T, P} \quad (46)$$

\bar{A}_{s1} is the partial molecular "self-energy" and was calculated to be

$$\bar{A}_{s1} = -\frac{1}{2} V_1 V_2 v_2^2 \pi^{-3/2} \epsilon^{(3)} \quad (47)$$

in units such that $3/(4\alpha^2 R_0^2) = 1$.

$$\Gamma = \frac{1}{2} V_1 \epsilon^{(2)} \pi^{-3/2} \left\{ \frac{2}{3} \int r^2(r) \exp(-r^2) dr + v_2 [\epsilon^{(3)}/\epsilon^{(2)}] \int h(r) \exp(-r^2) dr \right\} \quad (48)$$

The same integrals appear as in eq. 39 and 40. The method there described gives

$$\rho \int h(r) \exp(-r^2) dr = 1 - \beta^{-1} h(0) \quad (49a)$$

$$\rho \int r^2 h(r) \exp(-r^2) dr = -\frac{3}{2} \beta^{-1} h(0) \left(1 - \frac{2}{5} \alpha^2 \right) \quad (49b)$$

Substitution of these expressions into eq. 48 gives

$$\Gamma = \frac{1}{2} V_1 \epsilon^{(2)} \pi^{-3/2} h(0) \rho^{-1} \beta^{-1} \left[\frac{2}{5} \alpha^2 - 1 \right] + v_2 (\epsilon^{(3)}/\epsilon^{(2)}) [\rho^{-1} - h(0) \rho^{-1} \beta^{-1}] \quad (50)$$

The important question regarding eq. 45 is the magnitude of $(\bar{A}_{s1} + v_2^2 \Gamma)$ relative to the magnitude of $(\bar{A}_{01} - V_1 kT\rho)$. Suppose that a Flory-Huggins expression for $\epsilon(v_2)$ is used, as in eq. 25. Then

$$\bar{A}_{01} - V_1 kT\rho = kT [\ln v_1 + \chi_0 v_2^2 + v_2(1 - V_1/V_2)] \quad (51)$$

is the chemical potential according to the Flory-Huggins theory, while $(\bar{A}_{s1} + v_2^2 \Gamma)$ is a correction due to the nonrandom distribution of polymer centers of mass. On substitution for β its definition in eq. 24, eq. 47 and 50 give

$$\bar{A}_{s1} + v_2^2 \Gamma = -\frac{1}{2} kT V_1 \rho h(0) \left[v_2 (\epsilon^{(3)}/\epsilon^{(2)}) - \left(\frac{2}{5} \alpha^2 - 1 \right) \right] \quad (52)$$

Equation 25 makes $(\epsilon^{(3)}/\epsilon^{(2)})$ diverge as $(-v_1^{-1})$ for small solvent concentration so it is clear once more that the present theory becomes invalid at very small v_1 . An estimate of how large (52) is relative to (51) can be obtained by putting the coefficient ρv_2 of $(\epsilon^{(3)}/\epsilon^{(2)})$ equal to its maximum value, namely, V_2^{-1} , and $(\epsilon^{(3)}/\epsilon^{(2)})$ equal to $(-v_1^{-1})$. The term $(2/5 \alpha^2 - 1)$ is relatively

small. Then

$$(kT)^{-1} [\bar{A}_{s1} + v_2^2 \Gamma] \sim \frac{1}{2} (V_1/V_2) h(0) v_1^{-1} \quad (53)$$

It has already been shown that $h(0) \ll 1$ for quite small v_1 ; see eq. 38. It follows that the right-hand side of eq. 53 is much less than unity if v_1^{-1} is less than n , the number of segments, since $(V_2/V_1) \sim n$. We may conclude that (53) forms a negligible correction to (51) within the concentration range for which $h(0) \ll 1$, or in other words, within the domain of the linearized theory of $h(r)$.

VI. Discussion

The validity of the theory of $h(r)$ has so far been examined mainly at small v_1 . A few comments on the theory for dilute or moderately concentrated solutions are necessary to round out the picture. It is clear from eq. 32 that the theory is valid into the very dilute solution range if the solvent is poor, for then V_k is small and $h(0) \ll 1$. However, the theory will become invalid in very dilute solutions if the solvent is very good (say $\beta \gg 1$ in eq. 23 for V_k). Equation 34 shows that a is rather insensitive to the exact value of $(\rho\beta)$ and we can take $a \simeq 1$. Then eq. 37a indicates that the lower bound of ρ for which $h(0) \ll 1$ and the theory is valid occurs at $\rho \simeq 1$, that is, at a concentration such that the polymer domains just begin to fill the solution. The amount of polymer overlap required to make the theory valid will increase very slowly with β .

A second question for discussion is the nature of the breakdown in the theory at high concentrations. It is conceivable that the model, based on a pairwise additive concentration dependent intermolecular potential, remains valid at high concentration. Equation 31 for $h(r)$ predicts an oscillation of $g(r)$ around unity at high concentrations, an oscillation of $g(r)$ vs. r which increases in amplitude and decreases in wave length as the concentration is increased. Specifically, the development used in eq. 32-36 gives, when applied to eq. 31

$$h(r) = 2(\pi^2 \rho)^{-1} a^2 r^{-1} \int_0^\infty f(y) \sin(2ayr) y dy \quad (54)$$

$$\cong 2(\pi^2 \rho)^{-1} a^2 r^{-1} \int_0^1 y \sin(2ayr) dy \quad (55)$$

if $r \ll a$. Or

$$h(r) = 2(\pi^2 \rho)^{-1} a^2 r^{-1} \left\{ (2ar)^{-2} \sin(2ar) - (2ar)^{-1} \cos(2ar) \right\} \quad (56)$$

Note that $ar > 1$ is permitted; the condition $r \ll a$ does not preclude oscillations. It is difficult to explain away the oscillatory behavior of $h(r)$ as an erroneous consequence of the approximations since the oscillations occur and are increasing with concentration in a concentration range such that $h(r)$ is everywhere small. This oscillation presents a picture of incipient crystallization in the solution. The polymer molecules, which become randomly mixed at intermediate concentrations, begin to expand and separate at very high concentrations. Unfortunately, the analysis cannot be carried to a conclusion because as the oscillations increase the potential on which the calculation is based becomes inadequate.

The intermolecular potential was derived on the assumption that the free energy of mixing the solution for a given configuration of polymer centers is an integral of $\epsilon[f(R)]$ over the solution volume, where $f(R)$ is the local volume fraction of segments. It was further assumed that $\epsilon(f)$ could be expanded in powers of $(f - v_2)$ and that terms higher than quadratic could be suppressed. The last assumption is responsible for the existence of a pair potential. If cubic and higher powers of $(f - v_2)$ were retained, not only would the concentration dependence of the pair potential be modified, but three-body and, in general, n -body potentials would be introduced. The concept of interacting polymer molecules would become useless and a return to explicit consideration of segment-segment interactions would be necessary. The unfortunate failure of $h(r)$ to stay near unity makes probable the

failure of the quadratic expansion, but the neglect of fluctuations in the gaussian segment distribution must also become serious at very high concentrations as follows from the analysis of the segment concentration after eq. 30. We know of no experiments to test directly the theory of α . Some related possibilities are light scattering studies of a polymer A in a solution of polymer B, such that B and the solvent have the same refractive index,⁹ and studies of polymer solutions in the critical region,¹⁰ where the theory of intermolecular interference might be simple enough to allow extraction of polymer dimensions. The former experiment would require minor and the latter experiment major extensions of the theory.

(9) Preliminary attacks on this difficult experiment were made some time ago by W. H. Stockmayer, private communication.

(10) P. Debye, B. Chu, and D. Woermann, *J. Chem. Phys.*, **36**, 1803 (1962).

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Irradiation Cross Linking of Polyethylene. The Temperature Dependence of Cross Linking in the Crystalline and Amorphous States¹

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The irradiation cross linking of molecular weight fractions of polyethylene has been studied as a function of the temperature and state of the system. In general it is found that a definite distinction must be made between the temperature and the state of the system since the irradiation temperature has a different effect on the crystalline and amorphous regions. At low temperatures there is essentially no difference in the cross-linking efficiency of a highly crystalline bulk specimen when compared with one in which the crystallinity is not as well developed. However, at temperatures exceeding 100° the efficiency of cross linking the highly crystallized specimen increases by a factor of two while the efficiency for the other specimen remains essentially constant. An explanation of these results is offered in terms of the onset of molecular motion among the chain units in the crystalline sequences at this temperature. In addition, it is found that at temperatures where a direct comparison can be made, intermolecular cross linking is much more easily accomplished in the highly crystalline specimen than in a completely amorphous one. Experiments on the partitioning between sol and gel subsequent to the irradiation of crystals formed from dilute solution are interpreted in terms of these results.

Although the effect of high energy ionizing irradiation on polyethylene has been extensively studied many fundamental questions still remain unresolved.² The problems of concern include the efficiency of the cross-linking process, particularly as it depends on the state of the system, the partitioning between sol and gel, the elastic and thermodynamic properties of the resulting network structures, as well as the mechanistic details of the radiation chemistry involved. These difficulties in interpretation still are present even if consideration is limited to linear polyethylene. One major reason for these problems can be attributed to the very broad molecular weight distribution in the samples that have been studied which in turn makes difficult any detailed interpretation of the sol-gel curve. In addition, the crystallization of polyethylene at the usual irradiation temperatures introduces into the sample distinctly different coexisting chain configurations as a result of the polycrystalline and partially crystalline character of the system. Since it can be anticipated³⁻⁶ that the efficiency of the cross-linking

process as well as the properties of the resultant isotropic network will depend on the chain configuration and hence the state of the system at the time cross links are introduced, obviously complication in analyses will inherently exist unless the level and type of crystallization can be quantitatively described. This requirement involves, as a minimum condition, the controlled crystallization of samples prior to irradiation as well as the control of the sample temperature during the irradiation process.

In an effort to sort out these various complexities, we have investigated the effects of high energy ionizing radiation on molecular weight fractions of linear polyethylene. The samples were prepared under prescribed crystallization conditions with an attempt being made to take advantage of other investigations involving a description and analysis of the thermodynamics of the fusion process⁷ as well as the crystallization kinetics from the melt of fractions.^{8,9} We have reported¹⁰

(4) L. Mandelkern, D. E. Roberts, J. C. Halpin, and F. P. Price, *ibid.*, **82**, 46 (1960).

(5) D. E. Roberts and L. Mandelkern, *ibid.*, **80**, 1289 (1958).

(6) J. C. Halpin and L. Mandelkern, *J. Polymer Sci.*, **2B**, 139 (1964).

(7) R. Chiang and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 2857 (1961).

(8) W. Banks, M. Gordon, R. J. Roe, and A. Sharples, *Polymer*, **4**, 61 (1963).

(9) J. Fatou and L. Mandelkern, to be published.

(10) R. Kitamaru, L. Mandelkern, and J. Fatou, *J. Polymer Sci.*; in press.

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(2) A. Chapiro, "Radiation Chemistry of Polymer Systems," Interscience Publishers, Inc., New York, N. Y., 1962, pp. 385-405.

(3) L. Mandelkern, D. E. Roberts, A. F. Diorio, and A. S. Posner, *J. Am. Chem. Soc.*, **81**, 4148 (1959).