where m_i has been replaced by m in the integrals.

The upper limit of the integral is not very critical, as $(1 - p)^{m_i}$ becomes very small for values of t or of m_i beyond small integers; moreover the contribution of the infrequent large m_i's to the value of the numerator (A3) is small. The upper limit could be taken as infinity, without great error, or as an arbitrary $N/2$, reflecting an average point of impossibility of loop continuance. A more accurate approximation would introduce a weighting factor of approximately triangular form to represent the lower likelihood of the longer loops. None of these changes would affect the entropy contribution by sensible amounts, and we proceed as indicated in (A4).

Performing the indicated integrations, we find

$$\overline{\ln(1 + 1/m_i)} = \frac{\begin{array}{r}\{\ln(q+1) - \ln q - \\ (1-p)^{N-(t+1)q}\ln[1 + 1/(N - tq)] - \mathrm{Ei}[(q+1) \times \\ \ln(1-p)]/(1-p)^{q+1} + \mathrm{Ei}[q\ln(1-p)]/(1-p)^q + \\ \mathrm{Ei}[(N - 2q + 1)\ln(1-p)]/(1-p)^{q+1} - \\ \mathrm{Ei}[(N - 2q)\ln(1-p)]/(1-p)^q\}\end{array}}{[1 - (1-p)^{N-(t+1)q}]} \qquad \text{(A5)}$$

where Ei is the exponential integral $\int_x^\infty e^x \,\mathrm{d}x/x$, and is read from tables, or computed in subroutine series, as the negative of the tabulated values of $-\mathrm{Ei}(-x)$, since all arguments thereof are negative.

We omit description of the integration, performed with standard substitutive and parts methods, but cite the results of the indefinite integration of the numerator Nu, and the denominator, De, of (A4)

$$\mathrm{Nu} = \frac{\begin{array}{r}(1-p)^m \ln(1 + 1/m) + \mathrm{Ei}[m\ln(1-p)] - \\ \{\mathrm{Ei}[(m+1)\ln(1-p)]\}/(1-p)\end{array}}{\ln(1-p)} \qquad \text{(A6)}$$

$$\mathrm{De} = (1-p)^m/\ln(1-p) \qquad \text{(A7)}$$

where Ei is here the indefinite form of the exponential integral. Substitution of limits and division of (A6) by (A7) gives (A5), and the correctness of the integration can be verified by differentiating to give (A4).

The quantity $\overline{\ln(1 + 1/m_i)}$, as given by (A5) and (A2), is the correction factor given in the main text in eq 9 and Table I. Computation thereof was programmed on Wang 380 calculator, for the same values of N, q, and t as given for the other entropy parameters in Table I. The two terms in the exponential integral of the upper limit, as well as the logarithmic term in the numerator containing the upper limit, in eq A5, were negligible, except in the case of $t = 2$, for which they were included in the calculation. The denominator of (A5) differs appreciably from unity only for t from 2 to 5, but was correctly included in the program for all values of t. Thus above $t = 5$, the existence of an upper limit to the loop size (with $N = 200$ and $q = 2$) could be totally ignored. Above $t = 2$, such limit only contributes a small factor to the denominator of (A5). Since the terms which are appreciably affected by an uncertainty in the upper limit of loop size only occur at a time when the whole correction is small, we feel the computed correction is a satisfactory representation of the contribution of single-loop branches to the entropy, and certainly more accurate than the uncertainty in the Monte Carlo method used would necessitate.

Thermodynamics of Equilibrium Polymerization in Solution. Effect of Polymer Concentration on the Equilibrium Monomer Concentration

J. Leonard

Département de Chimie, Université Laval, Québec 10, Canada.

Received May 27, 1969

ABSTRACT: Recently, it has been shown that for an equilibrium polymerization in solution, the equilibrium monomer volume fraction ϕ_m varies with the polymer volume fraction ϕ_p, in accordance with the linear relation $\phi_m = A + B\phi_p$. In this paper the relation between the constants A, B, ΔG_{lc}, the free-energy change upon the conversion of 1 mol of liquid monomer to 1 base-mol of long chain amorphous polymer, and the interaction parameters χ_{sp}, χ_{mp}, and χ_{ms} is emphasized, the subscripts m, p, and s referring to monomer, polymer, and solvent, respectively. Calculations show that, for a given monomer, the equilibrium position is predominantly determined by χ_{ms}, the monomer–solvent interaction parameter. Expressions for the variation of A with temperature and the effect of short chains on the value of ϕ_m are deduced. Results calculated from these expressions are in good agreement with those of the literature.

A state of equilibrium between monomer and "living" polymer may be attained in the course of an anionic or cationic polymerization. Ivin and Leonard[1] have recently observed that in the case of the equilibrium anionic polymerization of α-methylstyrene in tetrahydrofuran (THF), at certain temperatures, the equilibrium monomer concentration decreased linearly with increasing concentration of polymer.

Taking into consideration the effect of polymer concentration on the equilibrium monomer concen-

---

[1] K. J. Ivin and J. Leonard, *Eur. Polym. J.*, in press.

TABLE I

THERMODYNAMIC PARAMETERS USED FOR THE COMPUTATION OF ϕ_m

T, °C	ϕ_m^{0a}	B^a	$-(\Delta G_{lc}/RT)$	β	a^b	B^b	a^c	B^c
−20	0.030	−0.044	4.08	−1.65	0.031	−0.058	0.031	−0.061
0	0.100	−0.133	2.68	−1.52	0.102	−0.165	0.103	−0.177
+20	0.279	−0.299	1.34	−1.38	0.282	−0.363	0.288	−0.400

[a] Experimental data.[1] [b] With $\chi_{mp} = 0.3$. [c] With $\chi_{mp} = 0.4$.

tration, they derived an expression for the free energy of polymerization. From the Flory–Huggins expression[2] for the partial molar free energy of monomer and polymer in a ternary system, they obtained

$$\Delta G_{lc}^* = RT[\ln \phi_m + 1 + (\chi_{ms} - \chi_{sp}(V_m/V_s))\phi_s + \chi_{mp}(\phi_p - \phi_m) - (\ln \phi_p + 1)/n] \quad (1)$$

where ΔG_{lc}^* is the free-energy change upon conversion of 1 mol of liquid monomer to 1 base-mol of liquid amorphous polymer, R is the gas constant, T is the temperature, n is the average number of segments in a chain, and V_m and V_s are the molar volumes of monomer and solvent, respectively. ϕ is the volume fraction of any component in the system under equilibrium conditions, and χ is the free energy parameter between any two components, the subscripts m, s, and p referring to monomer, solvent, and polymer, respectively. If n is large and ϕ_p is not too small, the last term of eq 1 is negligible and one obtains

$$\Delta G_{lc} = RT[\ln \phi_m + 1 + (\chi_{ms} - \chi_{sp}(V_m/V_s))\phi_s + \chi_{mp}(\phi_p - \phi_m)] \quad (2)$$

ΔG_{lc} represents the free-energy change upon the polymerization of 1 mol of liquid monomer to 1 base-mol of liquid amorphous polymer of infinite chain length.

The observed variation of ϕ_m illustrates the effect of the environment on the behavior of the polymerization. Since this effect is not obvious from eq 1 and 2, both equations can be transformed in order to relate ϕ_m directly to the thermodynamic properties of the medium.

Chains of Infinite Length. In their work on the polymerization of α-methylstyrene, Ivin and Leonard[1] found that the monomer concentration varies linearly with the polymer concentration. Experimentally, it is found that the variation of ϕ_m can be expressed by

$$\phi_m = \phi_m^0 + B\phi_p \quad (3)$$

where ϕ_m^0 is the value of ϕ_m when ϕ_p approaches zero and B is the slope obtained from a plot of ϕ_m against ϕ_p. In all cases n is quite large. For example for the four points on the 20° isothermal shown in Figure 1, reading from left to right, n is estimated to be 210, 190, 570, and greater than 1000; therefore, the assumption of chains of infinite length is a valid approximation.

Equation 2 can be transformed in order to obtain an expression which can be compared with eq 3. First, $\ln \phi_m$ is expanded in a series; that is

$$\ln \phi_m = \ln a + (\phi_m - a)/a - (\phi_m - a)^2/2a^2 + (\phi_m + a)^3/3a^3 - \ldots \quad (4)$$

where $0 < \phi_m < 2a$. If the value of the constant is such that $(\phi_m - a)^2/2a^2$ is negligible with respect to the first two terms of eq 4, one can then write

$$\ln \phi_m = \ln a + \phi_m/a - 1 \quad (5)$$

Then, with $\phi_s = 1 - \phi_m - \phi_p$ and substituting eq 5 for $\ln \phi_m$, after rearranging eq 2, the following expression for the variation of ϕ_m with ϕ_p is obtained

$$\phi_m = \frac{-(\Delta G_{lc}/RT) + \ln a + \beta}{\beta + \chi_{mp} - 1/a} + \frac{\chi_{mp} - \beta}{\beta + \chi_{mp} - 1/a}\phi_p \quad (6)$$

where $\beta = \chi_{ms} - \chi_{sp}(V_m/V_s)$. With the exception of ϕ_m and ϕ_p, all the terms appearing in eq 6 are assumed to be constant at a given temperature.

Comparing eq 3 and 6, it then follows that

$$B = (\chi_{mp} - \beta)/(\beta + \chi_{mp} - 1/a) \quad (7)$$

From this relation, the variation of the equilibrium monomer concentration with the polymer concentration may be explained in terms of the constant a and the interactions between the components of the system measured by the thermodynamic parameters β and χ_{mp}. Since ϕ_m^0 is a constant for a given polymerization at a given temperature, a can therefore be replaced by ϕ_m^0 in eq 5. If values of ϕ_m^0, obtained for the polymerization of α-methylstyrene in tetrahydrofuran, are entered in eq 5, the latter yields values of $\ln \phi_m$ which are within 3% of those obtained for concentrations of polymer as high as 2.5 base-mol/l. This is a fairly good approximation and, ideally, values of a and ϕ_m^0 should coincide. From the above considerations and by comparing eq 3 and 6, one finally obtains

$$\phi_m^0 = \frac{-(\Delta G_{lc}/RT) + \ln a + \beta}{\beta + \chi_{mp} - 1/a} = a \quad (8)$$

Using this definition of a, eq 6 may be rewritten to give

$$\phi_m = a + (\chi_{mp} - \beta)/(\beta + \chi_{mp} - 1/a)\phi_p \quad (6')$$

If $(\Delta G_{lc}/RT)$, β and χ_{mp} are known, eq 8 can be solved for a. Once a is known, it is then possible to calculate the variation of ϕ_m with ϕ_p using eq 6′ and compare it with experimental results. Table I gives experimental values of ϕ_m^0 and B obtained for the anionic polymerization of α-methylstyrene in tetrahydrofuran[1] at various temperatures and the corresponding values calculated by means of eq 6′ and 8. Values of $(\Delta G_{lc}/RT)$ are computed from the data of Ivin and Leonard using eq 2 but these could be obtained from any other source since $(\Delta G_{lc}/RT)$ is essentially independent of the system. THF and the monomer being good solvents for the polymer, a value of 0.3 is assumed for χ_{sp} and $\chi_{mp} \cdot \phi_s'$ is computed from the experimental data and the value of χ_{ms} deduced from Figure 2. With

---

(2) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XIII.

$(V_m/V_s) = 1.60$, β is computed from its definition given with eq 6. As can be seen from Table I, the value of χ_{mp} at $-20°$ has little or no effect on B and a; however, the effect is far from being negligible at higher temperatures. This is expected since at low temperature values of $(\Delta G_{lc}/RT)$ and $1/a$ are large and are decreasing rapidly with increasing temperature. The variation of ϕ_m with ϕ_p is shown in Figure 1 where a good agreement is obtained between experimental curves and curves computed using eq 6′ and 8.

As one can see, the effect of monomer–polymer interactions is not predominant, and the same assertion can be made for the solvent–polymer interactions. On the other hand, a change in the monomer–solvent interactions can bring about a pronounced change in the position of equilibrium for the polymerization of a given monomer. This can be shown by comparing the polymerization of α-methylstyrene in tetrahydrofuran and in cyclohexane at a given temperature. Since the Θ temperature for the poly-α-methylstyrene–cyclohexane system is 37°,[3] both polymerizations are therefore compared at 40°. Experimental data are not available for any of the two polymerizations but the variation of ϕ_m with ϕ_p at this temperature can be calculated using successively eq 8, 7, and 6′.

The extrapolation of values of $\Delta G_{lc}/RT$, computed by means of eq 2, yields a value of -0.26 for $\Delta G_{lc}/RT$ at 40°. For the monomer–polymer, tetrahydrofuran–polymer, and cyclohexane–polymer systems, respective values of 0.3, 0.3, and 0.5 are assumed for the interaction parameters χ. Since experimental data are not available for the computation of χ_{ms} in terms of the excess molar free energy of mixing, the excess entropy of mixing is assumed to be nil and χ_{ms} is computed by means of the relation[4]

$$\chi_{ms} = \Delta \bar{H}_M / x_m' RT\phi_s' \qquad (9)$$

where $\Delta \bar{H}_M$ is the integral heat of mixing of α-methylstyrene with solvent; x_m' is the monomer mole fraction in a binary mixture of monomer and solvent; ϕ_s' is the solvent volume fraction in the same mixture. With respect to the polymerization system, ϕ_s' is equal to the ratio $V_s'/(V_s' + V_m')$ where V_s' and V_m' are the volumes occupied by the solvent and the monomer, respectively, in the polymerization system and thus $\phi_s' = \phi_s/(\phi_s + \phi_m)$. From the experimental values of ϕ_m and B given in Table I, one can verify that at a given temperature, ϕ_s' is remarkably constant for the range of ϕ_p covered here.

Integral heats of mixing of α-methylstyrene in both solvents were measured at 26.9° by Cottam, Cowie, and Bywater.[5] From their data and eq 9, χ_{ms} is computed for different values of ϕ_s', and the variation of χ_{ms} with ϕ_s' is shown in Figure 2. The ratio $\Delta \bar{H}_M/T$ is assumed to be independent of temperatures and the curves shown in Figure 2 are used as such for the determination of χ_{ms} at 40°.

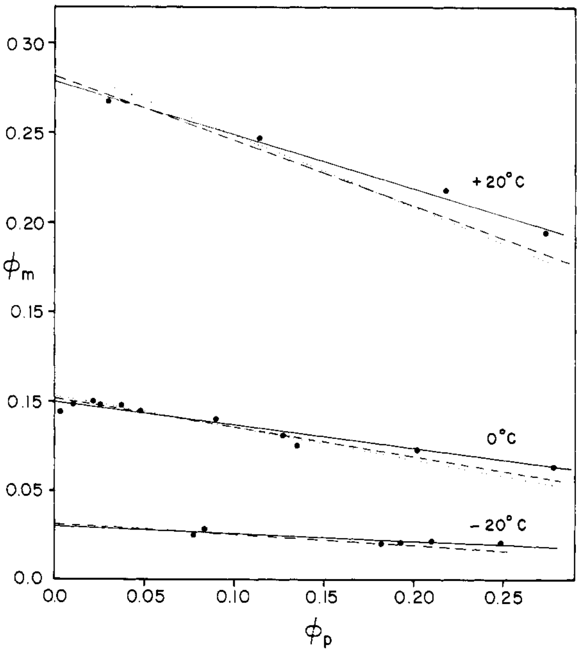

Figure 1. Variation of ϕ_m, the equilibrium monomer volume fraction, with ϕ_p, the equilibrium polymer volume fraction, for the anionic polymerization of α-methylstyrene in the THF at +20, 0, and −20°: solid lines, experimental data; dotted lines and dashed lines, values calculated using $\chi_{mp} = 0.4$ and $\chi_{mp} = 0.3$, respectively.

Since the value of ϕ_s' at 40° is unknown (and so is χ_{ms}), eq 8 cannot be used in a straightforward manner for the computation of a and one has to proceed through successive approximations. First, an arbitrary value of χ_{ms} is selected and β is computed accordingly. β is then substituted into eq 8 which is then solved for a. At infinite dilution $a = 1 - \phi_s = 1 - \phi_s'$, and a new value of ϕ_s' is then obtained from a. With this new value of ϕ_s', χ_{ms} is determined from Figure 2. From this new value of χ_{ms} a new value of a is obtained and the procedure described above is repeated until a constant value of a is attained. Then B is calculated by means of eq 7 using the final value of a. Starting with χ_{ms} equal to 1.0 and -1.0 for the cyclohexane–monomer and tetrahydrofuran–monomer systems, respectively, one finally obtains

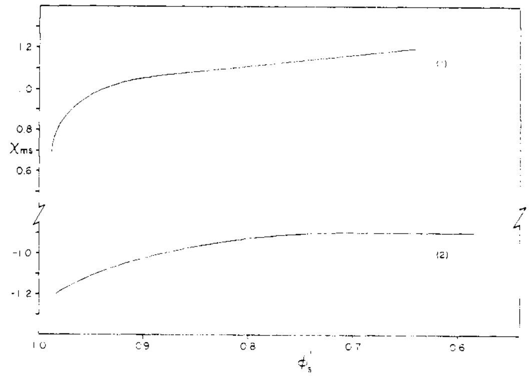

Figure 2. Variation of the monomer solvent interaction parameter χ_{ms} with the solvent volume fraction ϕ_s': (1) for the α-methylstyrene–cyclohexane system; (2) for the α-methylstyrene–THF system.

---

(3) J. M. G. Cowie, D. J. Worsfold, and S. Bywater, *Polymer*, **8**, 105 (1967).

(4) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Dover Publications, Inc., New York, N. Y., 1964, Chapter VII.

(5) B. J. Cottam, J. M. G. Cowie, and S. Bywater, *Makromol. Chem.*, **86**, 116 (1965).

$$\phi_m = 0.60 - 0.61\phi_p \text{ in tetrahydrofuran}$$

and

$$\phi_m = 0.20 + 0.051\phi_p \text{ in cyclohexane}$$

Here the solvent effect on the equilibrium position is obvious. Changing the solvent from cyclohexane to tetrahydrofuran should increase ϕ_m^0 threefold. From the above results, it can be seen that the monomer concentration will decrease rapidly upon the addition of polymer in tetrahydrofuran, whereas it will have little or no effect in cyclohexane, except for a slight depolymerization which will occur upon the addition of polymer.

Temperature Effect. As can be seen from Figure 1, values of ϕ_m corresponding to a given value of ϕ_p vary considerably with T. This temperature effect can be estimated from the variation of a and B with temperature. The variation of a with T is obtained by differentiating a, given by eq 8, with respect to T. Using the Gibbs–Helmholtz relation, one finally obtains

$$\left(\frac{\partial a}{\partial T}\right) = (\Delta H_{lc}/RT^2)/(\beta + \chi_{mp} - 1/a) + \left[\left(\frac{\partial \beta}{\partial T}\right) - a\left\{\left(\frac{\partial \beta}{\partial T}\right) + \left(\frac{\partial \chi_{mp}}{\partial T}\right)\right\}\right] \Big/ (\beta + \chi_{mp} - 1/a) \quad (10)$$

with $(\partial\beta/\partial T) = (\partial\chi_{ms}/\partial T) - (V_m/V_s)(\partial\chi_{sp}/\partial T)$.

The order of magnitude of the variation of all the χ parameters with T is $1/T$ or smaller. With such small variations, the last term of eq 10 can be neglected with respect to the first term on the right-hand side of the equation for most of the polymerizations and eq 10 can be integrated assuming all the χ parameters are constant.

If the temperature varies from T_1 to T_2, a will then vary from a_1 to a_2. Integrating eq 10 from T_1 to T_2, the variation of a will be expressed by the equation

$$(\beta + \chi_{mp})(a_2 - a_1) - \ln\left(\frac{a_2}{a_1}\right) = (\Delta H_{lc}/R)\left(\frac{T_2 - T_1}{T_2T_1}\right) \quad (11)$$

Equation 11 can be verified by computing values of a_2 with reference to the value of a at 0°. With $\Delta H_{lc} = -10$ kcal[1] and $\beta = -1.52$, one obtains values of a equal to 0.280 and 0.026 at +20 and −20°, respectively. These values are in good agreement with those given in Table I.

Once the value of a is obtained in that manner, B can be computed directly using eq 7. This is the simplest way of getting values of B since differentiating eq 7 with respect to T does not lead to a simple expression for the variation of B with T. It would be worthwhile to note here that, with the help of the present set of equations and thermodynamic parameters, very little experimentation has to be performed in order to get the complete diagram of ϕ_m *vs.* ϕ_p at various temperatures. If χ_{sp}, χ_{mp}, ΔH_{lc}, and $\Delta\bar{H}_M$, the integral heat of mixing of monomer with solvent, are known, only one determination of ϕ_m and the corresponding ϕ_p at a given temperature is then required. Since ϕ_m and ϕ_p are known, ϕ_s' is computed by means of the relation $\phi_s' = (1 - \phi_m - \phi_p)/(1 - \phi_p)$. Values of $\Delta\bar{H}_M$ and ϕ_s' are then substituted in eq 9, and χ_{ms} is computed accordingly. Equation 2 yields the value of $\Delta G_{lc}/RT$ which is then substituted in eq 8, together with the other thermodynamic parameters, to give a. After computing B from eq 7, it is then possible to write $\phi_m = a + B\phi_p$ for a given temperature. The variation of ϕ_m with ϕ_p at any other temperature can be obtained by means of eq 11 and 7. If the value of $(\Delta G_{lc}/RT)$ is known at a given temperature, it is then possible, by using the procedure described above, to obtain the entire diagram of ϕ_m *vs.* ϕ_p at various temperatures without having to perform a single determination of ϕ_m and ϕ_p.

Short Chain Effect. If the polymer chain length is taken into consideration, then an expression for the variation of ϕ_m with ϕ_p can be derived from eq 1. The expression is obtained in the same way as described above by making use of eq 5 and the relation $\phi_s = 1 - \phi_m - \phi_p$. The final expression is

$$\phi_m = \frac{-(\Delta G_{lc}^*/RT) + \ln a + \beta}{(\beta + \chi_{mp} - 1/a)} + \frac{\chi_{mp} - \beta}{(\beta + \chi_{mp} - 1/a)}\phi_p - \frac{(\ln \phi_p + 1)/n}{(\beta + \chi_{mp} - 1/a)} \quad (12)$$

By making the analogy with eq 6 and 6′, eq 12 can then be written as

$$\phi_m = a + \frac{\chi_{mp} - \beta}{(\beta + \chi_{mp} - 1/a)}\phi_p - \frac{(\ln \phi_p + 1)/n}{(\beta + \chi_{mp} - 1/a)} \quad (13)$$

The first two terms of eq 13 are identical with eq 6′. Since a is independent of the chain length, ΔG_{lc} and χ_{ms} used in eq 13 are parameters for a polymer of infinite chain length. The correction for short chains comes solely from the last term of eq 13. This term becomes important when the number of segments in a chain is small. Such a situation occurs when the concentration of polymer is low and the number of chains is large. However, one has to keep in mind that the Flory–Huggins treatment applies when the density of segments is uniform throughout the solution and that its use at very low concentration in the case of a good solvent is questionable. Assuming $n = [P]/[C]$, where [P] is the concentration of polymer in base-moles per liter and [C] is the concentration of chains in moles per liter, the number of segments n, may then be expressed as

$$n = \phi_p/[C]\bar{V}_p \quad (14)$$

where $\bar{V}_p$ is the volume of 1 base-mol of polymer in solution. Substituting eq 14 in eq 13, the latter becomes

$$\phi_m = a + \frac{\chi_{mp} - \beta}{(\beta + \chi_{mp} - 1/a)}\phi_p - \frac{(\ln \phi_p + 1)[C]\bar{V}_p/\phi_p}{(\beta + \chi_{mp} - 1/a)} \quad (15)$$

When there is only one "living end" per chain, [C] is identical with the concentration of "living ends" [L.E.]. Thus, eq 15 expresses the variation of the equilibrium monomer concentration through ϕ_m in terms of the variables ϕ_p and [L.E.]. The variation of ϕ_m with ϕ_p is computed for different concentrations of "living ends" in the case of the anionic polymerization of α-methylstyrene in tetrahydrofuran at 20°. Using the values given in Table I and with $\bar{\Gamma}_p = 0.107$ l./base-mol of polymer[1] and [C] = [L.E.]/2, the variation of ϕ_m can be expressed by the following equation

$$\phi_m = 0.282 - 0.363\phi_p + 1.16 \times 10^{-2}[\text{L.E.}](\ln \phi_p + 1)/\phi_p$$

Calculations are then carried out for three concentrations of "living ends" (10^{-4}, 10^{-3}, and 10^{-2} *M*) and the results are shown in Figure 3. The straight line represents the variation of ϕ_m for chains of infinite length. For concentrations of "living ends" smaller than 10^{-3}, values of ϕ_m computed either from eq 6′ or eq 15 coincide down to very low value of ϕ_p. However, the discrepancy between the two curves becomes important for concentrations greater than 10^{-2} *M*. It can readily be seen from eq 14 that for [L.E.] = 10^{-2}, *n* increases very slowly with increasing value of ϕ_p. Because of this short chain effect, the extrapolation of values of ϕ_m will yield a too low value of $\phi_m{}^0$ when the concentration of "living ends" is too high.

The short chain effect can be checked from the work of Vrancken, Smid, and Szwarc[6] on the anionic polymerization of α-methylstyrene in tetrahydrofuran at 0°. These authors measured the equilibrium monomer concentrations for high concentrations of "living ends"; under these conditions a short chain effect is expected. The variation of ϕ_m with ϕ_p is computed from their plot of $[M]_e$, the equilibrium monomer concentration, against $[M]_0$, the initial monomer concentration, both concentrations being expressed in moles per liter. ϕ_m is obtained through the relation $\phi_m = [M]_e\bar{\Gamma}_m$, where $\bar{\Gamma}_m$ is taken as 0.1273[7] l./mol. ϕ_p is further obtained by calculating n_p, the number of base-moles of polymer obtained from 1 l. of a monomer–solvent mixture having a monomer concentration of $[M]_0$. n_p is given by

$$n_p = ([M]_0 - [M]_e)/(1 - [M]_e\,dV)$$

where d*V* is the change in volume upon the polymerization of 1 mol of monomer. With $\bar{\Gamma}_p = 0.106$ l./mol,[1] d*V* is then equal to 0.0213 l./mol at 0°. n_p is related to ϕ_p through the equation

$$\phi_p = \bar{\Gamma}_p[P]_e = \bar{\Gamma}_p n_p/(1 - n_p\,dV)$$

Figure 4 shows the variation of ϕ_m with ϕ_p for different concentrations of "living ends." The solid straight line (curve 1) represents the variation of ϕ_m as determined experimentally for chains of infinite length. The curves 2 and 3 are from the results obtained by Szwarc and coworkers for [L.E.] = 0.014 and 0.068 (in moles per liter), respectively. The curves 4 and 5 represent the variation of ϕ_m computed by means of eq 15 and using the parameters given in Table I. All calculations were performed for $n > 4$.

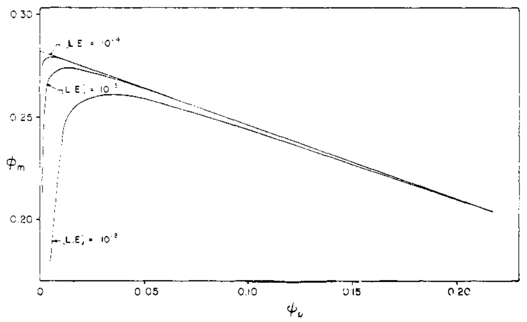

Figure 3. Anionic polymerization of α-methylstyrene in THF at +20°. Variation of ϕ_m with ϕ_p according to eq 15 for [L.E.] = 10^{-4}, 10^{-3}, and 10^{-2} mol/l.

From eq 15 and Figure 3, it is expected that the equilibrium monomer concentration will be lowered in the presence of a high concentration of "living ends." This general trend is confirmed by experimental results given in Figure 4. As can be seen from this figure, the agreement between experiment and theory is excellent for [L.E.] = 0.068 (curves 3 and 5). In the case of [L.E.] = 0.014 (curves 2 and 4), the first part of the experimental curve behaves as expected; however, it falls below the curve for [L.E.] = 0.068 at a high value of ϕ_p. At present this peculiar behavior remains inexplicable, and more experimental data are needed in order to throw some light on the subject. Nevertheless, eq 15 predicts a rapid falloff of ϕ_m at high concentration of "living ends" and low values of ϕ_p, which is confirmed by the experimental data presently available.

Acknowledgment. The author thanks the National Research Council of Canada for financial assistance.

Appendix I

Calculation of the parameters of Table I.

$$T = +20°$$

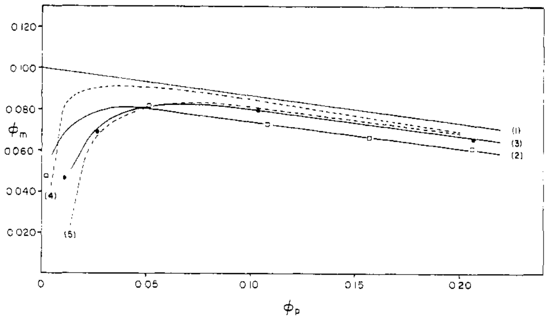

Figure 4. Short chain effect for the anionic polymerization of α-methylstyrene in THF at 0°: solid lines, experimental data; broken lines, values computed using eq 15; curve 1, with chains of infinite length; curves 2 (open squares) and 4, with [L.E.] = 0.014; curves 3 (full circles) and 5, with [L.E.] = 0.068 mol/l.

---

[6] A. Vrancken, J. Smid, and M. Szwarc, *Trans. Faraday Soc.*, 58, 2036 (1962).

[7] R. H. Boundy and R. F. Boyer, "Styrene," Reinhold Publishing Corp., New York, N. Y., 1952, p 698.

A value of 0.3 is assumed for χ_{mp} and χ_{sp}, α-methylstyrene and THF being considered as "good solvents" for the polymer.

From Figure 1, the variation of ϕ_m with ϕ_p is expressed by $\phi_m = 0.279 - 0.299\phi_p$. With $\phi_p = 0.1$, ϕ_m is equal to 0.249 and $\phi_s' = \phi_s/(\phi_s + \phi_m) = 0.725$. The corresponding value of -0.90 for χ_{ms} is deduced from Figure 2. Then

$$\beta = \chi_{ms} - \chi_{sp}(V_m/V_s) = -0.90 - 0.3 \times 1.60 = -1.38$$

Entering these values in eq 2, a value of 1.34 is obtained for $-(\Delta G_{1c}/RT)$.

$-(\Delta G_{1c}/RT)$, β and χ_{mp} being known, eq 8 is solved for a and yields $a = 0.282$. Finally, B is obtained from eq 7.

The Correlated Chain. A Statistical Model for Macromolecules[1]

Isaac C. Sanchez and Carl von Frankenberg

Department of Chemistry, University of Delaware, Newark, Delaware 19711.

Received July 8, 1969

ABSTRACT: A new model chain for macromolecules is constructed by employing standard Fourier transform techniques. It is shown that the links of the model chain are directionally correlated; a measure of the correlation is expressed in terms of a chain flexibility parameter C_F. When $C_F = 1$, the model chain behaves like an uncorrelated random flight chain; as $C_F \rightarrow 0$ correlation increases until the model reduces to a rigid or rodlike chain. The intramolecular light scattering function $P(\mu)$ is evaluated for the model chain; $P(\mu)$ reduces to the usual expressions for flexible and rodlike chains for the limiting values of C_F.

I. Introduction

A problem of interest in macromolecular science is the characterization of the statistical properties of a real macromolecular chain; macromolecular solution properties (light scattering, intrinsic viscosity, etc.) are sensitive to the kind of configurational statistics obeyed by the chain.

A model chain that has been successful in interpreting the solution properties of flexible macromolecules in ideal (Θ) solvents is a random flight chain where the link vectors have identical, spherically symmetric, Gaussian distributions. However, this model and simple modifications of this model have enjoyed less success in describing the solution properties of flexible macromolecules in good solvents and for some nonflexible or "stiff" macromolecules in any solvent.

By employing Fourier transform techniques (Markoff's method[2]), a new statistical model for macromolecules is formulated in the present paper. The model is characterized by only two parameters: the mean square radius of gyration $\langle S^2 \rangle$ and the chain flexibility C_F, or equivalently, $\langle S^2 \rangle$ and the persistence length α. The model behaves like an uncorrelated random flight chain in one limit ($C_F = 1$) and like a rigid or rodlike chain in the other limit ($C_F = 0$) of chain flexibility. If a model is capable of describing both extremes of random flight chain behavior, then it may also be useful in simulating the statistical behavior of chains with intermediate statistical characteristics—the so-called "non-Gaussian" chains. The present model is an instructive alternative to several such models that have recently been proposed.[3-7]

II. Definition of the Model Chain

The reader is forewarned that the model to be described is not an attempt to describe explicitly the statistical behavior of a real macromolecular chain with fixed bond angles, hindered rotation, etc. Instead, an ideal chain will be defined that possesses the same general statistical character of a real chain, *viz.*, a chain which exhibits correlation of its bond vectors.

Consider a three-dimensional random flight chain composed of N statistically independent link vectors $(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ each having the same length b. Each vector makes an angle θ with the z axis; θ is always less than or equal to some arbitrary ϵ where $0 \leq \epsilon \leq \pi$. No restrictions are imposed on the remaining angle variable ϕ. The appropriate distribution function $\tau_j(\mathbf{r}_j)$ for random link vector $\mathbf{r}_j$ is

$$\tau_j(\mathbf{r}_j) = C\delta(|\mathbf{r}_j| - |\mathbf{b}|)H(\epsilon - \theta) \tag{1}$$

where (*1*) $\mathbf{b}$ is an arbitrary vector of fixed length, $|\mathbf{b}| \equiv b$; (*2*) $H(\epsilon - \theta)$ is a unit step function defined by

$$H(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \tag{2}$$

---

(1) Taken in part from the Ph.D. Thesis of Isaac C. Sanchez University of Delaware, 1969.

(2) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943); also in "Selected Papers on Noise and Stochastic Processes," N. Wax, Ed., Dover Publications, New York, N. Y., 1954.

(3) (a) Y. Tagami, *Macromolecules*, **2**, 8 (1969); (b) P. A. Sharp and V. A. Bloomfield, *J. Chem. Phys.*, **49**, 4564 (1968).

(4) D. McIntyre, J. Mazur, and A. M. Wims, *ibid.*, **49**, 2887 (1968).

(5) J. E. Hearst and R. A. Harris, *ibid.*, **46**, 398 (1967).

(6) G. Ver Strate and C. von Frankenberg, *J. Polym. Sci., Part A-2*, **5**, 1313 (1967).

(7) A. Peterlin, "Electromagnetic Scattering," H. Kerker, Ed., The Macmillan Co., New York, N. Y., 1963, pp 357–375, and references therein.