The Third Virial Coefficient in Polymer Solutions

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Introduction

By means of grand partition functions, Mc Millan and Mayer[1] derived a rigorous series expansion for the osmotic pressure in terms of concentration. The first applications of their theory to polymer solutions were made by Zimm[2], who expressed the osmotic pressure Π as:

$$\Pi/c=RT[(1/M)+A_2c+A_3c^2+\cdots\cdots], \qquad (1)$$

where c is the concentration of polymer in mass per unit volume of solution. M is the molecular weight of the polymer and the A_n, so called virial coefficients, are constants at constant temperature. Since most measurements are made in fairly dilute solutions, the third and higher coefficients ordinarily need not be considered. To increase the accuracy of the extrapolation procedure, however, it would be desirable to make clearer the expression for the third virial coefficient. From the calculations of Bawn and Wajid[2], moreover, it can be seen that molecular weight dependency of A_2 depends strongly on the kind of expression that is used for the Π vs. c relation. An expression for A_2 had been given by Grimly[4], who deduced approximately in a limited interval of molecular weights,

$$A_2=CM^{-\varepsilon}, \qquad (2)$$

where C and ε are constants depending on the molecular dimensions and the excluded volume of the representative chain element in that interval. In polystyrene-toluene system[3], the value 0.15 is found for ε from a quadratic equation (cf. Eq. (I)), whereas a value of 0.33 is found when the relation of Flory and Krigbaum[5] is used for the third virial coefficient.

Flory and Krigbaum[5] have assumed, as an approximation, that A_2 bears the same re-

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[1] W.G. McMillan and J.W. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

[2] B.H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

[3] C.E.H. Bawn and M.A. Wajid, *J. Polymer Sci.*, **12**, 109 (1954).

[4] T.B. Grimly, *Proc. Roy. Soc. London*, **A212**, 339 (1952).

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

lation to A_3 as in the case of hard sphere molecules, and have written

$$A_3=\frac{5}{8}A_2^2M. \tag{3}$$

This "hard sphere approximation" doubtless makes the third term too great, and actually gives more than ten times greater values for A_3 than those calculated by Bawn's graphical method[6] in the system cited above. Recently, Krigbaum and Flory themselves[7] have concluded from new osmotic measurements on polyisobutyrene in cyclohexane and polystyrene in toluene that this hard sphere treatment gives a greater value for A_3 than the data warrant.

At first sight, the above discrepancy of the A_3 value appears to be eliminated by Stockmayer and Casassa[8]. With the aid of approximate models for the intermolecular potential energy, they have obtained the third virial coefficient as a function of the second coefficient and Flory's parameter α, which is obtainable from intrinsic viscosity. According to them,

$$\Gamma_3/\Gamma_2^2=A_3/A_2^2M=0.257\ \mathrm{A},$$
$$(\Gamma_2=A_2M,\ \Gamma_3=A_3M) \tag{4}$$

where A can be calculated by a graphical method as a function of α only. Close inspection of this ratio $\Gamma_3/\Gamma_2{}^2$ obtained from experiments, however, reveals that their treatment must be in direct contradiction to the experimental results especially on the dependency of the ratio upon molecular weight of the polymer.

TABLE I

THE VIRIAL COEFFICIENTS OF POLYSTYRENE SOLUTION IN TOLUENE AND IN METHYL ETHYL KETONE[3]

$\overline{M}_n\times10^{-4}$	$A_2\times10^4$ (graphic) g.$^{-2}$ cc.	$A_2\times10^4$ (F.F.B. method)	$A_3\times10^3$ (graphic) g.$^{-3}$ cc.	$(\Gamma_3/\Gamma_2^2)_{\mathrm{exp.}}$ (graphic)	$(\Gamma_3/\Gamma_2^2)_{\mathrm{stock.}}$	α_0[13]
Toluene solution at 25°C.						
158	2.89	1.83	1.86	0.0141	0.315	1.51_6
87	3.01	2.13	1.70	0.0216	0.284	1.43_3
32	3.28	3.19	1.58	0.0472	0.248	1.31_9
28.8	3.09	3.03	1.42	0.0516	0.247	1.31_2
24.8	3.32	3.31	1.54	0.0563	0.240	1.29_6
16.2	3.36	3.86	1.70	0.0930	0.215	1.25_7
9.40	3.89	4.47	1.55	0.1090	0.188	1.22_1
7.20	4.35	4.58	1.78	0.1307	0.165	1.21_0
Methyl ethyl ketone at 25°C						
32	0.75	1.22	0.60	0.333	0.105	1.11_1
16.2	0.87	1.30	0.60	0.489	0.100	1.09_9

In this paper, the dependency of the parameter α on polymer concentrations will be considered, and it will be pointed out that the source of the above contradiction may be explained, at least qualitatively, by this procedure.

The Dependency of the Ratio Γ_3/Γ_2^2 upon Molecular Weight

For the hard sphere molecular model[5], the ratio Γ_3/Γ_2^2 is 5/8, the value being markedly greater than the experimental, and is independent upon molecular weight of the polymer. If the results of Stockmayer and Casassa[8], the evaluation of the ratio in a more general and elegant manner, were acceptable, the ratio should be greatest at high molecular weight and in good solvents. On the other hand, the experimental results of Bawn et al., which are probably the most reliable osmotic pressure data available for this purpose, show that the ratio Γ_3/Γ_2^2 decreases markedly with increasing molecular weight. This is illustrated in Table I, the ratio being compared with the values of the ratio calculated by Eq. (4) ($(\Gamma_3/\Gamma_2^2)_{\mathrm{stock.}}$). Furthermore, the ratio is greater in bad solvents than in good solvents, in contradiction of the results of the above authors, and its theoretical values are much too great especially in good solvents.

The Dependency of the Parameter α on Polymer Concentrations

In the highly dilute region, where osmotic measurements are most important, the concentration of the segments in solution is not uniform, but is much greater in the

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[6] C.E.H. Bawn, R.F.J. Freeman and A.R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 862 (1950).

[7] W.R. Krigbaum and P.J. Flory, paper read at the meeting of the *Am. Chem. Soc.*, March 25, 1952.

[8] W.H. Stockmayer and E.F. Casassa, *J. Chem. Phys.*, **20**, 1560 (1952).

neighbourhood of the centers of the polymer molecules. Attempts have been made to account for this effect first by Flory and Krigbaum[5] and then others[4]. This is closely related to the (excluded) volume effect, which means the influence of the formation of polymer-polymer contacts between distant segments of a chain molecule (long range interference)[9,10]. Thus, the pair partition function for the Gaussian chains may be written as a function of α, so long as the polymer is homogeneous[5].

Complications arising from non-uniformity in the distribution of segments over the volume, however, must become trivial as the concentration is increased owing to the forced overlapping of polymer molecules. The above theories, therefore, may be applied only to solutions so dilute thot overlapping of the excluded volume is slight. Actually, if the concentration is great enough to be supposed to show intense overlapping of molecules, the earlier theories of polymer solutions[11,12] may be available, although many questions remain unsettled on these theories. At intermediate concentrations neither theory is appropriate.

Here, let us consider the dependency of the parameter α upon the concentration of the polymer and introduce its effect on the partition function of this system. We are going to turn our attention to one polymer molecule and consider the influence of its environment on it. The actual domain pervaded by a polymer chain cannot be defined sharply. Here, the distribution of polymer segments in a polymer chain will be assumed to be Gaussian as usually and may be given by

$$x_j = x(\beta_0'/\pi^{\frac{1}{2}})^3 \exp(-\beta_0'^2 S_j^2) 4\pi S_j^2 \Delta S_j \qquad (5)$$

in the absence of intramolecular interactions, where x_j is the number of segments in the spherical shell of radius S_j from the center of gravity and of thickness ΔS_j, x, the total number of segments in a polymer chain, and

$$\beta_0' = 3/\sqrt{\bar{r}_0^2} = 3/\sqrt{6\bar{s}_0^2}, \qquad (6)$$

where $\bar{r}_0^2$ is the mean-square distance between the ends of the chain, $\bar{s}_0^2$, that between the segments and the center of gravity, both in the absence of intramolecular interactions. It will be assumed that a given set of the segments given by Eq. (5) occupy the spherical shell between αs_j and $\alpha(s_j+\Delta s_j)$ in the equilibrium configuration.

The total free energy of dilution is

$$\Delta F_{\text{dil.}} = \sum_j \Delta F_j. \qquad (7)$$

In an entirely analogous manner to Flory's treatment of intrinsic viscosities[13],

$$\partial \Delta F_{\text{dil.}}/\partial(\alpha^3) = (1/N)\sum(\mu_{1j}-\mu_{10})\{\partial n_{1j}/\partial(\alpha^3)\}, \qquad (8)$$

where μ_{1j} and μ_{10} are the chemical potentials of solvent in the shell j and of pure solvent, respectively, and n_{1j}, the number of solvent molecules in the shell j (N: Avogadro's number). The terms in the right hand side of Eq. (8) may be written, to a satisfactory approximation, as follows:

$$\mu_{1j}-\mu_{10} = RT(\kappa_1-\varphi_1)v_{2j}^2, \qquad (9)$$

where κ_1 and φ_1 are the parameters representative of heat and entropy terms respectively, and

$$v_{2j} = xV(\beta_0'/\alpha\pi^{1/2})^3 \exp(-\beta_0'^2 S_j^2) \qquad (10)$$

(V is the volume of a segment). And

$$\partial n_{1j}/\partial(\alpha^3) \cong 4\pi S_j^2 \Delta S_j N/V_1, \qquad (11)$$

where V_1 is the molar volume of the solvent. Substituting Eqs. (10) in (9), and (9) and (11) in (8), replacing the summation by an integral and integrating over S_j from 0 to ∞, there is obtained

$$\partial \Delta F_{\text{dil.}}/\partial(\alpha^3) = kTK^*(\kappa_1-\varphi_1)/\alpha^6, \qquad (12)$$

$$K^* = \{27/2\pi^{3/2}\}(\bar{v}^2/NV_1)(M/\bar{r}_2^0)^{3/2}M^{1/2}, \qquad (13)$$

($\bar{v}$ is the specific volume of the polymer).

The configurational entropy $\Delta S_{\text{el.}}$ of the chain may be evaluated according to the method employed in the theory of rubber elasticity as follows[14]:

$$\Delta S_{\text{el.}}/k \doteqdot 3\ln\alpha - 3(\alpha^2-1)/2. \qquad (14)$$

Hence, if the total free energy in the "domain" pervaded by a polymer chain may be written ΔF, the following relationship may be derived from Eqs. (12) and (14):

$$\begin{aligned}\partial \Delta F/\partial(\alpha^3) &= \partial \Delta F_{\text{dil.}}/\partial(\alpha^3) - \partial(T\Delta S_{\text{el.}})/\partial(\alpha^3)\\ &= kT[K^*(\kappa_1-\varphi_1)/\alpha^6 + (1/\alpha) - (1/\alpha^3)].\end{aligned} \qquad (15)$$

Now, it may be assumed that each molecule is distributed within an effective volume of sphere of radius $\alpha\sqrt{\bar{r}_0^2}$. Then,

$$(4/3)\pi\alpha^3(\bar{r}_0^2)^{3/2} = xV + (n_1V_1/N), \qquad (16)$$

where n_1 is the number of the solvent molecules in this sphere[15]. Therefore, from Eqs. (15) and (16) the partial molal free energy of the solvent in this effective volume may be given by

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9) B.H. Tompa, *Trans. Faraday Soc.*, **48**, 363 (1952).

10) A. Münster, *Mackromol. Chem.*, **2**, 227 (1948).

11) For instance, P.J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).

12) M.L. Huggins, *Ann. N.Y. Acad. Sci.*, **44**, 431 (1943).

13) P.J. Flory and T.G. Fox Jr., *J. Am. Chem. Soc.*, **73**, 1904; 1915 (1951).

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

15) T. Kawai, This Bulletin, **24**, 69 (1951).

$$\Delta\overline{F}_1=\{\partial\Delta F/\partial(\alpha^3)\}\{\partial(\alpha^3)/\partial n_1\}$$
$$=RTB[K^*(\kappa_1-\varphi_1)/\alpha^6+(1/\alpha)-(1/\alpha^3)], \quad (17)$$

where $B=(V_1/N)/(4/3)\pi(\bar{r}_2^0)^{3/2}=C_\mathrm{B}x^{-3/2}$. (18)

Next, that of the solvent in the environment region of this sphere (designated by prime) may be written as

$$\Delta\overline{F}_1'=-RT[(1/x)v_2+a_2v_2^2+a_3v_2^3+\cdots\cdots], \quad (19)$$

where v_2 is the volume fraction of the polymer in the whole region of the system.

Thus, the α vs. v_2 relation will be introduced from the condition of the equilibrium between the inside and outside of the above effective volume;

$$\Delta\overline{F}_1=\Delta\overline{F}_1'.$$

In Eq. (19) the activity of the solvent in the environment region is replaced to the mean value in the whole region. This approximation may be permitted as far as we deal with the equilibrium between one polymer chain and its environment in the vast region involving other molecules. Furthermore, the virial coefficients, a_2, a_3 and others in Eq. (19), should be a function of α. As is shown later, however, this complication can be avoided to a satisfactory approximation, since this "reflection of α" appears only in the higher terms in v_2[16].

At infinite dilution, we may write $\alpha=\alpha_0$, and from Eq. (17),

$$K^*(\kappa_1-\varphi_1)/\alpha_0^6+(1/\alpha_0)-(1/\alpha_0^3)=0. \quad (20)$$

Replacing α by $\alpha_0+\Delta\alpha$, and expanding the terms in the right hand side of Eq. (17) in the series of $\Delta\alpha$,

$$\Delta\overline{F}_1=RTB[(5\Delta\alpha/\alpha_0^2)-(3\Delta\alpha/\alpha_0^4)$$
$$-\{20(\Delta\alpha)^2/\alpha_0^3\}+\{15(\Delta\alpha)^2/\alpha_0^5\}+\cdots\cdots], \quad (21)$$

where the condition of Eq. (20) has been applied and then, K^* in Eq. (17) has been able to be eliminated. Since $\Delta\alpha$ is supposed to be sufficiently smaller than α_0[17], this series expansion would converge, and furthermore, it is possible to show that the terms beyond the first two in the right hand side of Eq. (21) may be neglected to a first approximation[18].

Combining Eq. (19) with (21) from the above equilibrium condition,

$$B\{(5/\alpha_0^2)-(3/\alpha_0^4)\}\Delta\alpha\doteqdot-[(1/x)v_2+a_2v_2^2+\cdots\cdots]. \quad (22)$$

So long as the third coefficient is concerned, Eq. (22) may be written

$$\Delta\alpha\doteqdot-(\alpha_0^2/5Bx)v_2[1+(3/5\alpha_0^2)+(3/5\alpha_0^2)^2+\cdots\cdots]. \quad (23)$$

The third Virial Coefficient

The partition function, Z for a solution of the homogeneous polymer may be deduced by considering the volume available to each successive polymer molecule added to the solution;

$$\ln Z=N^*\ln v-\binom{N^*}{2}\mu_2/v-(N^*/6)\mu_3/v^2+\cdots\cdots, \quad (24)$$

where v is the total volume of the solution, N^*, the total number of polymer molecules, and μ_2 and μ_3 are the excluded volumes for the pair and triplet of the molecules, respectively. For a sufficiently dilute solution to justify neglect of the influence of the other molecules, Flory and Krigbaum[5] evaluated the excluded volume μ_2 for the pair as

$$\mu_2=2Jm^2F(X), \quad (25)$$

where

$$J=(\varphi_1-\kappa_1)\bar{v}^2/V_1, \quad (26)$$

$$X=4C_\mathrm{M}(\varphi_1-\kappa_1)M^{1/2}/\alpha^3, \quad (27)$$

$$C_\mathrm{M}=(27/2^{5/2}\pi^{3/2}N)(\bar{v}^2/V_1)(M/\bar{r}_0^2)^{3/2}=K^*/2M^{1/2}, \quad (28)$$

$$F(X)=1-X/2\ 2^{3/2}+X^2/3!\,3^{3/3}-\cdots\cdots, \quad (29)$$

and m is the weight of a polymer molecule. Since Flory et al. had employed α as a parameter (although they assumed for α to be independent on the polymer concentration), and their calculation itself should be independent upon the effect of the concentration on α, it may be permitted approximately[19] that the results of Eqs. (25)∼(29) are available for the parameter α dependent on the polymer concentration.

We may now express Eq. (29) in the form of a Taylor series expansion around α_0 from Eq. (27) and the relation, $[X]_{\alpha=\alpha_0}=2(\alpha_0^2-1)$[5];

$$F(X)=[F(X)]_{\alpha=\alpha_0}+[\partial F(X)/\partial\alpha]_{\alpha=\alpha_0}\Delta\alpha+\cdots\cdots, \quad (30)$$

where

$$[\partial F(X)/\partial\alpha]_{\alpha=\alpha_0}=\left[\frac{dF(X)}{dX}\ \frac{\partial X}{\partial\alpha}\right]_{\alpha=\alpha_0}$$
$$=-6\{\alpha_0-(1/\alpha_0)\}F'(\alpha_0) \quad (31)$$

$$\left(F'(\alpha_0)=\left[\frac{dF(X)}{dX}\right]_{\alpha=\alpha_0}\right).$$

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[16] Strictly speaking, the α vs. v_2 relation must be obtained from the condition that the value of α minimizes the total free energy in the system, which were given a function of α and v_2.

[17] The value of α_0 is seldom greater than 1.8 apparently including all practical cases for any polymer-solvent pair so far investigated. However, even at the critical missibility point, $\alpha=1$. Thus, it is reasonable to suppose that α would not be much smaller than α_0.

[18] This series expansion reduces to $2\Delta\alpha-5(\Delta\alpha)^2+\cdots$ when $\alpha_0=1$, and is $(17/16)\Delta\alpha-(65/32)(\Delta\alpha)^2+\cdots$ when $\alpha_0=2$ ($\Delta\alpha$ may be supposed to be in the range, 0∼0.2).

Employing Eqs. (23)~(31), and noting that $v_2=m\bar{v}N^*/v$, Eq. (24) may be written

$$\ln Z=N^*\ln v-(N^*/2)\mu_{20}/v-(N^*/6)\mu_{30}/v^2 -[J(1/Bx)m^3\bar{v}N^{*3}/v^2]f(\alpha_0), \tag{32}$$

where

$$f(\alpha_0)=-[\partial F(x)/\partial\alpha]_{\alpha=\alpha_0}(\alpha_0{}^2/5) [1+(3/5\alpha_0{}^2)+(3/5\alpha_0{}^2)^2+\cdots\cdots], \tag{33}$$

and μ_{20} and μ_{30} are the excluded volumes for the constant value of α_0 as are employed ordinarily (i.e. in the case of $\alpha=\alpha_0$)[5,8]. Since $\Pi=kT\partial\ln Z/\partial v$, the expression of the osmotic pressure is easily obtained from Eq. (32), and comparison of the resultant formula with Eq. (1) yields the third coefficient as follows:

$$A_3=(\bar{v}^3/V_1)[0.257Ax(\varphi_1-\kappa_1)^2\{F(\alpha_0)\}^2 +2(\varphi_1-\kappa_1)(1/Bx)f(\alpha_0)], \tag{34}$$

and

$$\Gamma_3/\Gamma_2^2=0.257A+2f(\alpha_0)/B(\varphi_1-\kappa_1)x^2\{F(\alpha_0)\}^2, \tag{35}$$

where the expression of Flory et al. (Eq. (39) in their paper[5]) for the second coefficient and that of Stockmayer et al. for the third, are assumed to correspond to the above excluded volumes, μ_{20} and μ_{30} respectively ($F(\alpha_0)\equiv[F(x)]_{\alpha=\alpha_0}$).

The above treatment is not a straightfoward evaluation of the virial coefficients, and it seems rather strange that the secont coefficients, is not influenced through the change of the α value with the concentration. As mentioned in reference (19), the molecules should flatten in the direction of their centers and expand in the perpendicular direction. According to Krigbaum's calculation[19], however, the change in the second coefficient was found to be very small even if such an effect was considered.

Comparison with Experiments

Until the above theoretical treatment is applied to the experimental results, it would be well to bear in mind that the values of the third virial coefficient must be calculated from osmotic data with close attention. Fox, Flory and Bueche[20] proposed an approximate method for extrapolation of the experiments. Since they adopted Eq. (3) giving greater values for the third coefficient, the resultant values of $(\Pi/c)_0$ (Π/c at infinite dilution) and A_2 are probably somewhat incorrect. Moreover, the values of the third coefficient thus obtained might fall into an error of great consequence, owing to the fact that the third term $A_3\ C^2$ in Eq. (I) ordinarily contributes little to the value of Π/c. Thus, it seems to be reasonable to adopt the empirical method of Bawn[6] for the calculation of A_3 rather than the above method of Flory et al. (designated F. F. B. method in Table I). In Bawn's method, however, appreciable variations of the A_2 and A_3 values were observed with the concentration range to which the method was applied; In the polystyrene-toluene system[6], the values of RTA_2 and RTA_3 were 7.0×10^7 (cm^4/g.) and 4.3×10^9 (cm^7/g.^{2}), respectively, for the concentration range up to 1.0 g./100 cc., whereas the values were $RTA_2=10\times10^7$, $RTA_3=1.6\times10^9$ for the concentrations from 1.0 to 2.5 g./100 cc..

Here, from the osmotic data of Flory[21] on a number of polyisobutylene in cyclohexane, the method of least squares was used for 4~5 concentrations in the most dilute region with the requirement that Eq. (I) holds its validity in the closed form terminated after the term in C^2. The values of Γ_2 and Γ_3 thus obtained are given in Table II, where the values for the fractions B(0–3) and C(4–9) are those calculated by Stockmayer and Casassa by the same method[8]. It is obvious that the ratio Γ_3/Γ_2^2 decreases considerably

TABLE II

THE VIRIAL COEFFICIENTS OF POLYISOBUTYRENE SOLUTIONS IN CYCLOHEXANE[21]

Polymer fraction	$\overline{M}_n\times10^{-4}$	$(\Pi/c)^{2*}$	Γ^{2*}	Γ^{2*}	$(\Gamma_3/\Gamma_2^2)_{exp.}$	$(\Gamma_3/\Gamma_2^2)_{stock.}$	α_0[24]
B(0—3)	77	0.33	4.20	2.17	0.12	0.31	1.51
C(4—9)	25.6	0.99	1.51	0.58	0.25	0.27	1.39
B(9—13)	7.82	3.24	0.54_7	0.11_1	0.37	0.14	1.18
A(14—25)	2.92	8.67	(0.21_3)	(0.31_2)	(6.92)	0.11	1.12

* Π: g./cm^2, C: g./100 cc.

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[19] Strictly speaking, a mean potential of average force between the pair of molecules is affected otherwise than in the above treatment. For instance, the spherically symmetrical character of the molecules may be no longer preserved owing to the presence of the other molecules. Krigbaum investigated this theoretically using the cloud model, although the work has not been published (Reprint from Proceedings of the International Conference of Theoretical Physics, Kyoto, Sept. 1953). In my opinion, however, it may be prohibitively difficult to evaluate straightfowardly the partition function in consideration of these effects.

[20] T.G. Fox, Jr., P.J. Flory and A.M. Bueche, *J. Am. Chem. Soc.* ,73, 285 (1951).

[21] P.J. Flory, *J. Am. Chem. Soc.*, 65, 372 (1943).

with the increasing molecular weight, just as in the case of polystyrene in toluene cited in Table I. This tendency, however, cannot be explained quantitatively by the above treatment.

Considering the dependency of the ratio Γ_3/Γ_2^2 upon the molecular weight, Eq. (35) may be written as:

$$\Gamma_3/\Gamma_2^2 \doteq 0.257A+\{12/[5C_{\mathrm{B}}(\varphi_1-\kappa_1)x^{1/2}\{F(\alpha_0)\}^2]\}$$
$$\times\{-F'(\alpha_0)\}\{(\alpha_0{}^3-\alpha_0)+(3/5)(\alpha_0-1/\alpha_0)+\cdots\cdots\} \tag{36}$$

(see Eqs. (18), (31), and (33)), which, employing the relation $\alpha_0{}^5-\alpha_0{}^3=2C_{\mathrm{M}}(\varphi_1-\kappa_1)M^{1/2}$ [13], may be converted to

$$\Gamma_3/\Gamma_2^2=0.257\,A+C^*\{-F'(\alpha_0)\}\{(1/\alpha_0{}^2)$$
$$+(3/5)(1/\alpha_0{}^4)+\cdots\cdots\}/\{F(\alpha_0)\}^2$$
$$[C^*=(24/5)(C_{\mathrm{M}}/C_{\mathrm{B}})(M/x)^{1/2}]. \tag{37}$$

Experimentally, the dependency of $F(\alpha_0)$ and α_0 on the molecular weight can be determined from Eq. (2) and from the intrinsic viscosity$\sim$molecular weight relationship, respectively (α_0 is given by the relation $\alpha_0{}^3=[\eta]/KM^{1/2}$ [13]). The value of $\{-F'(\alpha_0)\}$ does not vary sensitively with the molecular weight of the polymer, although it decreases to some degree with the increasing molecular weight[22].

Employing the relationships $A_2 \propto M^{-0.10}$ [21,23] and $[\eta]=K_m M^{0.64}$ [21] for the polyisobutyrene-cyclohexane system, there, is obtained

$$\Gamma_3/\Gamma_2^2=0.257\,A+[C_1{}^{**}M^{0.1}+C_2{}^{**}+C_3{}^{**}M^{-0.1}$$
$$+C_4{}^{**}M^{-0.2}+\cdots\cdots]\{-F'(\alpha_0)\}, \tag{38}$$

where

$$C_2{}^{**}/C_1{}^{**}=C_3{}^{**}/C_2{}^{**}=C_4{}^{**}/C_3{}^{**}$$
$$=(3/5)(1/\alpha_0{}^2)=(3/5)(K/K_m)^{2/3}.$$

Since $K=1.08\times10^{-3}$ (at 24°C)[24] and $K_m=3.60\times10^{-4}$ [21] in this case, it may be no wonder that the ratio Γ_3/Γ_2^2 might decrease with the increasing molecular weight, even though not remarkably, if the term $0.257\,A$ in Eq. (38) is sufficiently small. However, such marked decrement with the molecular weight as is shown in Table I and II, cannot be interpreted by the above estimation of the ratio.

This discrepancy may be partly due to the uncertainty in the determination of the A_2 and A_3 values from experiments. As mentioned already, the smaller Γ_3/Γ_2^2 value was obtained when the higher concentration range was utilized in an empirical evaluation of the A_2 and A_3 values by the Bawn's method[6]. Also in the case where the method of least squares is used, considerable errors may be possible owing to the similer effect. Actually, a plot of the quantity, $[(\Pi/c)/(\Pi/c)_0-1]/c$ against c shows the considerable scatter of the experimental data especially for the frac- (A 14—25) (although this graph is not given here). Thus, the determination of the ratio Γ_3/Γ_2^2 allows some scope for judgement as to what the true value is; the Γ_3/Γ_2^2 values quoted in Tables I and II should therefore not be taken too literally, and the values of the ratio and also its dependency upon the molecular weight thus obtained may be supposed to be too great due to the effect mentioned above.

The inconsistency of Eq. (4) may, however, be evident since the ratio must increase considerably with the increasing molecular weight if Eq. (4) were approvable. If the result of Eq. (35) holds its validity, the ratio Γ_3/Γ_2^2 should be greater than $0.257\,A$, that expected from the theory of Stockmayer et al. (designated by $(\Gamma_3/\Gamma_2^2)_{\mathrm{stock.}}$ in Tables I and II). The fact that $(\Gamma_3/\Gamma_2^2)_{\mathrm{stock.}}<(\Gamma_3/\Gamma_2^2)_{\mathrm{exp.}}$, especially in the case of higher molecular weights, would mean the overestimation of this ratio by them. It has been pointed out by various authors[24,25,26], that, strictly speaking, current theories fail to account for abnormally low values of the entropy of dilution in actual polymer solutions. Possible reasons for this failure may exist in neglecting the orientation effect i.e. the effect of anisotropy in the force fields arround the molecules, and in not taking into account the influence of the geometrical character of the solvent in relation to that of the polymer segment; at any rate, the entropy of dilution, accordingly the ratio Γ_3/Γ_2^2 should become smaller, due to the above effects[27]. Thus, an apparent agreement of $(\Gamma_3/\Gamma_2^2)_{\mathrm{stock.}}$ with the experimental values for a particular molecular weight, does not always mean the consistency of the theory of Stockmayer et

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[22] This function $\{-F'(\alpha_0)\}$ is expressed approximately by $\{-F'(\alpha_0)\}=0.195-0.146\log_{10}\{[x]_{\alpha=\alpha_0}\}$, where $[x]_{\alpha=\alpha_0}=2(\alpha^2{}_0-1)=\dfrac{2KC_{\mathrm{M}}(\varphi_1-\kappa_1)M^{1-\beta}}{K_m}([\eta]=K_mM^{\beta})$.

[23] This relation has been obtained from the A_2-values in Table II.

[24] T.G. Fox, Jr. and P.J. Flory, *J. Am. Chem. Soc.*, **73**, 1909 (1951).

[25] H. Tompa, Discussion in reference 3); *J. Chem. Phys.*, **21**, 250 (1953).

[26] M.J. Schick, P. Doty and B.H. Zimm, *J. Am. Chem. Soc.*, **72**, 530 (1950).

[27] The expression of the second coefficient is not changed because the above complicated effects upon it are involved in the parameter φ_1 in the treatment of reference 5).

al. with experiments[8].

Furthermore, the ratio is greater in methyl ethyl ketone (a bad solvent) than in toluene (a good solvent) for polystyrene as is shown in Table I. This is consistent with what is predicted from our theory (see Eq. (37), where α_0 is larger in a good solvent than in a bad solvent[28]), in direct contradiction of Stockmayer and Casassa's theory. It would be instructive to point out that the theories based on lattice models[11,12,29] imply the similar tendency on this ratio; the Γ_3/Γ_2^2 value is predicted to be greatest in poor solvents or at low molecular weights, although these theories involve some unsatisfactory approximations[24,25]. Our treatmet may be considered to be an intermediate one between the treatments developed in consideration of the volume effect[4,5] and the earlier theories in which the effect was not taken in to account[11,12,29]. So far as the third coefficient is concerned, the volume effect theory would have to be modified appreciably as is mentioned above.

In order to obtain confirmatory evidence on the quantitative interpretation for the third coefficient, there exist many difficulties to be resolved both experimentally and theoretically, and it seems, first of all, to be preferable to obtain additional data available for this purpose.

Finally, it may be remarked that a possibility may be predicted from our theory as to the existence of an inflexion point in the Π vs. C curve. If the treatment of Stockmayer et al. were assumed to afford a legitimate representation of the third coefficient except the correction term arising from μ_2 in Eq. (24), by empolying the parameter α dependent on the polymer concentration, instead of α_0, it does not seem to be unlikely that the effect of this concentration dependency of α would make the fourth coefficient negative, since the ratio $(\Gamma_3/\Gamma_2^2)_{\text{stock.}}$ decreased with decreasing α. Actually, experiments[8,26,30] over a wide concentration range indicate a negative deviation at high concentrations from the curve fitting the data well at lower values by employing Eq. (I) with the omission of the terms beyond the third. Also theoretically the existence of this inflexion point was pointed out by Rushbrooke et al.[31] from another point of view.

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[28] Although $F(\alpha_0)$ in Eq. (37) is smaller for the larger value of α_0, its change with α_0 is very small ($F(\alpha_0)=1\sim0.8$ in the usual range of α_0), and moreover, $\{-F'(\alpha_0)\}$ is smaller for the larger α_0.

[29] A.R. Miller, "Theory of Solutions of High Polymers", Oxford University Press, London (1948).

[30] G.V. Browing and J.D. Ferry, *J. Chem. Phys.*, 17, 1107 (1949).

[31] G.S. Rushbrooke, H.I. Scoins and A.J. Wakefield, *Trans. Faraday Soc., Discussion*, 15, 57 (1953).