Effect of chain length and molecular architecture on the second virial coefficient of branched polymer molecules

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The effects of chain length and molecular architecture on the second virial coefficient of branched polymer chains has been studied using a perturbation analysis. It is found that the deviation from the infinite chain length asymptote increases as the degree of branching increases for chains having less than about 100 statistical segments. A semi-empirical equation is proposed for higher values of the interaction parameter, *z*.

The second virial coefficient, A_2, of polymer solutions appears in the virial expansion of the osmotic pressure, π, as[1]:

$$\frac{\pi}{c} = RT\left[\frac{1}{M} + A_2 c + A_3 c^2 + \ldots\right] \tag{1}$$

and is important theoretically since it represents the first order deviation from the ideal, van't Hoff behaviour. In equation (1), M is the molecular weight of the polymer, T, the absolute temperature, c, the concentration of the polymer and R, the universal gas constant. Equation (1) forms the basis of the experimental determination of the molecular weight of polymers using dilute solution osmometry.

Zimm[2] suggested that for flexible macromolecules, A_2 depends on two independent factors, the size or length of the molecule and the interaction of short segments of the two chains. Using the McMillan–Mayer theory, Zimm[1–3] obtained the following perturbation solution for A_2 for linear polymers, valid in the limit of large chain length:

$$A_2 = \frac{N_{av} n^2 \beta^*}{2M^2}\left[1 - 2.865z + \ldots\right] \equiv \frac{N_{av} n^2 \beta^*}{2M^2} h_0(z) \tag{2}$$

Equation (2) has been derived using the equivalent chain model[1,4] of the polymer molecule in which the latter is represented as a sequence of $n + 1$ point masses numbered 0 to n, connected by n Kuhn statistical segments. Each statistical segment represents a fixed number of backbone bonds of the physical molecule, this number being so chosen[5] that the components of the end to end vector for any statistical segment are characterized by a Gaussian distribution function. The mean square end to end distance of any statistical segment is l^2. In equation (2), N_{av} is the Avogadro number and β^* is the binary cluster integral defined as:

$$\beta^* = \int_0^\infty 4\pi r^2 \left\{1 - \exp[-V(r)/kT]\right\} \mathrm{d}r \tag{3}$$

where $V(r)$ is the potential energy of interaction between any two of the $n + 1$ point masses of the equivalent chain separated by a distance r and k is the Boltzmann constant. The parameter z in equation (2) is defined as:

$$z = \left(\frac{3}{2\pi l^2}\right)^{3/2} \beta^* n^{1/2} \tag{4}$$

The subscript 0 on $h(z)$ indicates the absence of intramolecular interactions.

Several other theories for the second virial coefficient of linear polymers have also been formulated and have been reviewed by Yamakawa[1]. Very little theoretical work exists, however, for branched polymers. Casassa[6–8] has obtained the perturbation result given by:

$$A_2 = \frac{N_{av} n^2 \beta^*}{2M^2}\left(1 - Cz + \ldots\right) \tag{5}$$

and has obtained an analytical expression for C for uniform star molecules[6] and numerical values of C for uniform normal comb[7] and some more general comb molecules[7,8] (these branched structures are described by Yamakawa[1] and other workers[9–11]). These studies apply only in the limit of high molecular weight.

Significant deviations from the high molecular weight asymptote have been found in earlier studies of the distribution of the radius of gyration[5,9,10,12], the segment density[13,14], the interaction energy associated with a chain[11], the excluded volume effect[5,15,16] and the adsorption of polymers on a surface[17,18]. The same effect was also observed for the second virial coefficient of linear polymers[19]. In this paper, results on the second virial coefficient for uniform star and comb polymers are presented. The method, however, can be used for studying molecules having any generalized molecular architecture.

GENERALIZED FORMULATION FOR THE SECOND VIRIAL COEFFICIENT

Zimm[2] adapted the McMillan–Mayer theory to obtain A_2 for polymer solutions:

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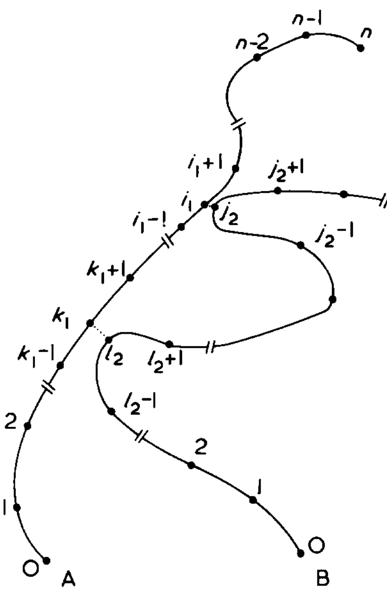

Figure 1 Two polymer chains, 1 and 2, having contact between the i_1th and j_2th masses and between the k_1th–l_2th masses. A, chain 1, B, chain 2

$$A_2 = -\frac{N_{\text{av}}}{2V_1M^2}\int\cdots\int F_1(1)F_1(2)\times$$

$$\left\{\prod_{i_1=0}^{n}\prod_{j_2=0}^{n}(1+\chi_{i_1,j_2})-1\right\}\text{d}(1)\text{d}(2) \tag{6}$$

where

$$\chi_{i_1,j_2} = -\beta^*\delta(B_{i_1,j_2}) \tag{7}$$

In this equation, V_1 is the volume of the solution, $F_1(1)$ and $F_1(2)$ are the single molecule distribution functions for any two polymer molecules 1 and 2, $\underline{\underline{R}}_{i_1,j_2}$ is the vector between the i_1th point mass of the first molecule and the j_2th mass of the second molecule (subscripts 1 and 2 on i and j refer to molecules 1 and 2, respectively) and d(1,2) represents the differential over all the coordinates of molecules 1 and 2. The integration is performed over all of these coordinates. Equations (6) and (7) may be simplified[19] by using the Wang–Uhlenbeck[1,20,21] theorem to give finally:

$$A_1 = \frac{N_{\text{av}}(n+1)^2\beta^*}{2M^2}\left[1-\frac{z}{2n^{1/2}(n+1)^2}\times\right.$$

$$\left.\sum_{i_1=0}^{n}\sum_{j_2=0}^{n}\sum_{k_1=0}^{n}\sum_{\substack{l_2=0\\ \sim(i_1=k_1).(j_2=l_2)}}^{n}\frac{1}{c^{3/2}_{i_1,j_2,k_1,l_2}}+\ldots\right] \tag{8}$$

The notation $\sim(i_1 = k_1)$. $(j_2 = l_2)$ on the quadruple summation indicates that there are no terms corresponding to $i_1 = k_1$ and $j_2 = l_2 \cdot c_{i_1,j_2,k_1,l_2}$ is the total number of statistical segments in the loop shown in *Figure 1* where two molecules 1 and 2, having $n + 1$ point masses each, numbered 0 to n, are shown with masses i_1 and j_2 in contact (broken lines) and k_1 and l_2 in contact. For linear chains:

$$c_{i_1,j_2,k_1,l_2} = |i_1-k_1| + |j_2-l_2| \tag{9}$$

For any branched chain, $|i_1 - k_1|$ and $|j_2' - l_2|$ are the shortest distances, in terms of the number of statistical segments, encountered while going from masses i_1 to k_1, and j_2 to l_2, respectively. Since chains 1 and 2 have identical molecular architectures, c_{i_1,j_2,k_1,l_2} can be written as a sum of two elements of an $(n + 1) \times (n + 1)$ symmetric matrix $\underline{\underline{\xi}}$:

$$c_{i_1,j_2,k_1,l_2} = \xi_{k,i} + \xi_{l,j} \tag{10}$$

where $\xi_{p,q}$ (p, q going from 0 to n) represents the *smallest number* of statistical segments lying between point masses p and q on a polymer chain and is always positive. For a linear chain, $\xi_{p,q}$ is $|q - p|$. For branched chains having any molecular architecture, $\underline{\underline{\xi}}$ may be easily generated[22].

RESULTS AND DISCUSSION

Using equations (8) and (10), and the fact that several terms in the quadruple summation are identical, we can obtain a simplified equation for A_2:

$$A_2 = \frac{N_{\text{av}}(n+1)^2\beta^*}{2M^2}\times$$

$$\left[1-\frac{z}{2n^{1/2}(n+1)^2}\sum_{p=0}^{n}\sum_{\substack{q=0\\ \sim(p=0\cdot q=0)}}^{n}\frac{n_pn_q}{(p+q)^{3/2}}\right]$$

$$\equiv\frac{N_{\text{av}}(n+1)^2\beta^*}{2M^2}\left[1-C_nz\right] \tag{11}$$

where n_p is the number of times any number p (p = 0, 1, 2, . . . n) occurs in $\underline{\underline{\xi}}$ and $\sim(p = 0.\ q = 0)$ means that the term when *both* p and q are zero is excluded from the summation.

Results for C_n/C_∞ as a function of n are shown in *Figure 2* for several uniform star and uniform normal comb chains, along with the earlier results for linear chains[19]. Values of C_∞ for the corresponding chains were obtained from Yamakawa[1]. It is observed that the deviation from the asymptote increases as the chain becomes more highly branched for values of n below about 100. However, the value of C_n/C_∞ is found to be independent of branching above n about 100. This is most interesting since no equivalent phenomenon was observed in earlier studies of the effect of molecular archi-

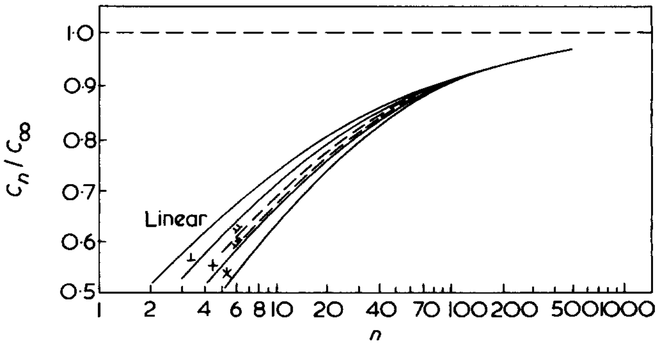

Figure 2 C_n/C_∞ vs. n for linear and some branched chains

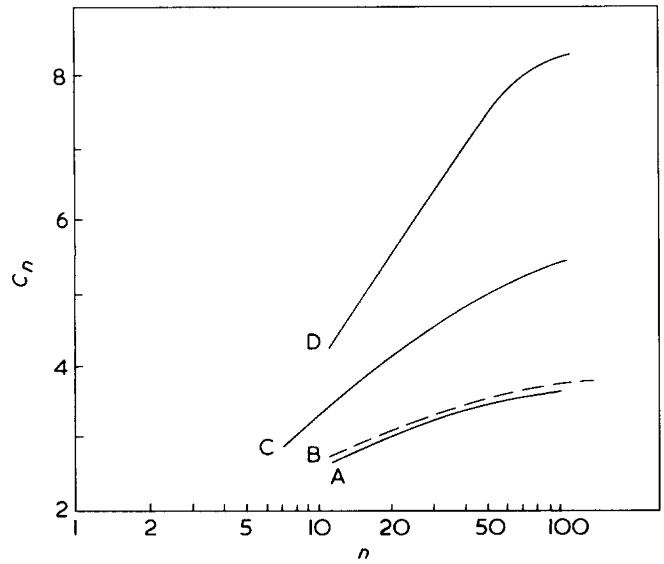

Figure 3 C_n vs. n for some uniform star, uniform normal comb and tree-branched chains. A, 5-branched comb; B, tree; C, 7-branched star; D, 11-branched star

Table 1 C_∞, k and x in equation (12) for some branched chains

Type	C_∞ (ref 1)	k	x
3-branch uniform star	3.279	1.02317	0.5146
4-branch uniform star	3.873	1.3924	0.576
5-branch uniform star	4.586	2.2132	0.67
2-branch uniform comb	3.536	1.1880	0.544
3-branch uniform comb	3.753	1.562	0.599

tecture on the distribution of the radius of gyration[9,10] and segment density distribution[14].

The effect of molecular architecture on C_n is more vividly illustrated in *Figure 3* where C_n is plotted as a function of n for a 5-branch uniform normal comb, a 7- and 11-branch uniform star and an 11-branch tree molecule studied earlier[9]. Curves A, B and D show the behaviour of C_n when eleven sub-units of equal length are connected together in various ways. Significantly high values of C_n and lower A_2 are observed when these sub-units are all connected in a compact manner as in the 11-branch star than when they are connected more sparsely as in a uniform tree or comb.

The following *empirical* equation was found earlier[19] to represent C_n fairly well over the range of n above ~10:

$$C_n = C_\infty\left(1 - \frac{k}{n^x}\right) \tag{12}$$

Table 1 lists the values of C_∞, k and x for some uniform star and uniform normal comb chains.

Equation (12) is a perturbation result valid for small values of the parameter z, characterizing the polymer–solvent interaction (and molecular weight). A semi-empirical equation for A_2, valid for higher values of z may be written by assuming A_2 to be given by an equation of the same form as the Flory–Krigbaum–Orofino[1,23,24] theory and matching the series expansion for the latter with the perturbation result. This leads to:

$$A_2 = \frac{N_{av}(n+1)^2\beta^*}{2M^2}\left[\frac{1}{2C_n z}\ln(1+2C_n z)\right] \tag{13}$$

Such a procedure has been used before[1,5,19,25] both in the excluded volume problem and A_2, and has been found to give better agreement with experimental results on the excluded volume effect. Equation (13) can be rewritten in terms of n as:

$$A_2 = \frac{N_{av}(n+1)^2\beta^*}{2M^2}\left[\frac{1}{2C_nKn^{1/2}}\ln(1+2C_nKn^{1/2})\right] \tag{14}$$

where K relates z to $n^{1/2}$ and accounts both for the solvent–polymer interaction terms as well as the relationship between M and n. For the θ solvent K is zero and it increases as the solvent is improved, to a value generally below 10 (though theoretically, it can go to infinity). Since $N_{av}(n+1)^2\beta^*/(2M^2)$ is independent of molecular weight, equation (14) suggests that a log–log plot of:

$$\frac{\ln(1+2KC_n n^{1/2})}{2KC_n n^{1/2}}\quad\{= 2M^2A_2/[N_{av}(n+1)^2\beta^*]\}$$

vs. n will be identical to a log–log plot of A_2 vs. M, except for horizontal and vertical shifts, for a polymer–solvent system at a fixed temperature. *Figure 4* shows these plots for linear as well as several uniform star chains for some values of K. It is observed that the deviation from linear chain plots increases as the degree of branching increases and also as the solvent becomes thermodynamically improved. This is intuitively expected and represents the fact that when two polymer molecules are close together, repulsive forces between polymer segments predominate whereas when the molecules are further apart, polymer–solvent interactions are predominant.

CONCLUSIONS

The effect of varying the molecular architecture, chain

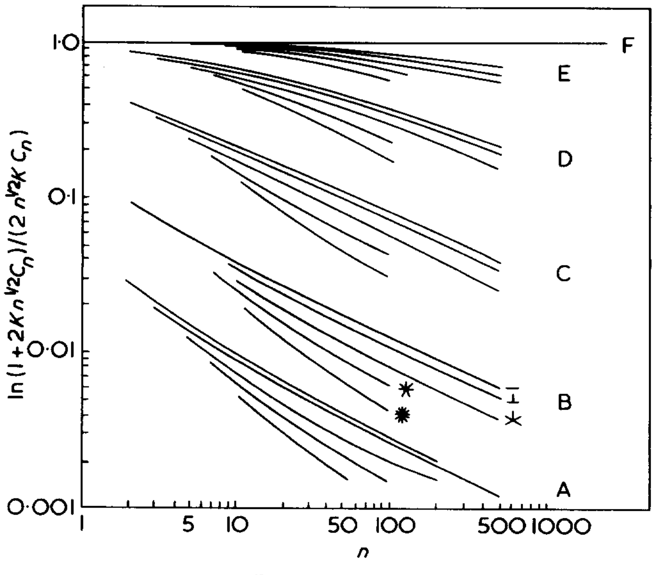

Figure 4 $\ln(1+2KC_n n^{1/2})/(2KC_n n^{1/2})$ vs. n for some values of K. A, K = 50; B, K = 10.0; C, K = 1.0; D, K = 0.1; E, K = 0.01; F, K = 0 (bottom line on each set is for 11-branch uniform star)

length and the solvent–polymer interaction energy on the second virial coefficient has been studied. It has already been reported[19] that the use of C_∞ in place of the more exact coefficient C_n in the semi-empirical equation (11) leads to considerable error in the A_2 vs. M plot for linear chains, especially in good solvents. Larger errors are expected for branched chains in view of the results shown in *Figures 2* and *4*.

REFERENCES

1 Yamakawa, H., 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971
2 Zimm, B. H. *J. Chem. Phys.* 1946, **14**, 164
3 Fixman, M., *PhD Dissertation* MIT, Cambridge, Massachusetts, (1953)
4 Kumar, A. and Gupta, S. K. 'Fundamentals of Polymer Science and Engineering', Tata–McGraw–Hill, New Delhi, India, 1978
5 Gupta, S. K. and Forsman, W. C. *Macromolecules* 1972, **5**, 779
6 Casassa, E. F. *J. Chem. Phys.* 1962, **37**, 2176
7 Casassa, E. F., *J. Chem. Phys.* 1964, **41**, 3213
8 Cassassa, E. F. and Tagami, Y. *J. Polym. Sci. (A-2)* 1968, **6**, 63
9 Gupta, S. K. and Forsman, W. C. *Macromolecules* 1974, **7**, 853
10 Gupta, S. K. and Forsman, W. C. *J. Chem. Phys.* 1976, **65**, 201
11 Goel, R., Kumar, A. and Gupta, S. K. *Polymer* 1977, **18**, 201
12 Hoffman, R. F. and Forsman, W. C. *J. Chem. Phys.* 1969, **50**, 2316
13 Gupta, S. K., Kumar, A. and Forsman, W. C. *Chem. Phys. Lett.* 1976, **39**, 291
14 Goel, R., Kumar, A. and Gupta, S. K. *Chem. Phys. Lett.* 1976, **40**, 45
15 Hoffman, R. F. *PhD Dissertation* University of Pennsylvania (1967)
16 Aronowitz, S. and Eichinger, B. E. *Macromolecules* 1976, **9**, 377
17 Hoffman, R. F. and Forsman, W. C. *J. Polym. Sci., (A-2)* 1970, **8**, 1847
18 Mohan, R., Gupta, S. K. and Kumar, A. *Chem. Phys. Lett.* 1977, **52**, 463
19 Deo, S. R., Kumar, A. and Gupta, S. K. *Chem. Phys. Lett.* 1978, **54**, 332
20 Wang, M. C. and Uhlenbeck, G. E. *Rev. Mod. Phys.* 1945, **17**, 323
21 Fixman, M. *J. Chem. Phys.* 1955, **23**, 1656
22 Deo, S. R. *MTech Dissertation* Indian Institute of Technology, Kanpur, 1977
23 Flory, P. J. and Krigbaum, W. R. *J. Chem. Phys.* 1950, **18**, 1086
24 Orofino, T. A. and Flory, P. J. *J. Chem. Phys.* 1957, **26**, 1067
25 Stockmayer, W. H. *Makromol. Chem.* 1960, **35**, 54