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(38) The cluster has been calculated according to the $AB_2$ model (see Figure 3b), where A can react with B only. Then $P_w$ is given[5,40] as $P_w = 1 - \alpha^2[(1-p)^2 + p^2]/(1-\alpha)^2$, where $p$ is the branching probability and $\bar{n}_{ic} = 1/p$. Evidently the highest branching probability is 0.5 and yields $\bar{n}_{ic} = 2$.
(39) Note: There are three types of internal chain length: $\bar{n}_{ic}$ = a chain connecting two branching points in a cluster; $\bar{n}_{i2}$ = chain length connecting two clusters; $\bar{n}_{is}$ = length of a side chain, emerging from one cluster, carrying on the average $\bar{n}$ clusters.
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# Notes

## On the Excluded Volume Perturbation

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It is a significant contribution that Muthukumar and Nickel recently evaluated the fourth to sixth coefficients, for the first time, in the excluded volume perturbation expansion of $\langle R^2 \rangle$ (the mean-square end-to-end distance) in three dimensions:[1]

$$\alpha_R^2 \equiv \langle R^2 \rangle / \langle R^2 \rangle_0 = 1 + \sum_{i=1}^{\infty} C_i z^i \qquad (1)$$

Here, $\alpha_R^2$ is the square expansion factor defined by the ratio $\langle R^2 \rangle / \langle R^2 \rangle_0$, the subscript 0 refers to the unperturbed state, $C_i$ is the numerical coefficient, and $z$ stands for the (conventional) excluded volume variable.[2] The values of $C_1$ to $C_6$ obtained by them are reproduced in the second column of Table I.[3] Eighteen years ago, Yamakawa and Tanaka calculated the third coefficient as 6.459,[4] while Muthukumar and Nickel now give 6.296... to $C_3$.[5] They claim that the result of Yamakawa and Tanaka is in error but do not even mention a few, more important points in their paper.

The first point concerns the divergence of the series, eq 1, clearly suggested by their numerical figures for $C_i$'s. Fixman[2] and Yamakawa[6] stated, without proof, that the series very slowly converges, but that does not seem to be true. Serious doubt about the convergence has already been cast by several authors.[7-11] The recent results of Muthukumar and Nickel support the latter view on the (conventional) perturbation expansion.

**Table I**
**Numerical Comparison of the Perturbation Coefficients in Eq 1**

| $C_i$ | Muthukumar–Nickel[1] | eq 2[a] |
|---|---|---|
| $C_1$ | $^4/_3$ | 1.333 |
| $C_2$ | −2.075 385 396 | −2.075 |
| $C_3$ | 6.296 879 676 | 6.459 |
| $C_4$ | −25.057 250 72 | −25.13 |
| $C_5$ | 116.134 785 | 109.5 |
| $C_6$ | −594.716 63 | −511.2 |

[a] Coefficients were obtained by expanding eq 2 into a series.

The second point is that the approximate value −25.3 for $C_4$ given by Gordon et al.[8] is in good agreement with −25.057.... The third point concerns the comparison between the results of Muthukumar and Nickel and the coefficients obtained by expanding the following closed-form expression for $\alpha_R^2$:

$$\alpha_R^2 = 0.5716 + 0.4284(1 + 6.225z)^{1/2} \qquad (2)$$

This expression has been published in a form with three significant figures by Yamakawa and Tanaka[4] and Suzuki.[12] Equation 2 is known to be valid at least up to third-order perturbation theory.[12] The first six coefficients obtained by expanding eq 2 are listed in the third column of Table I. From this table, one can see good agreements between the two series of numerical figures. Even for the sixth coefficient, the value from eq 2 differs only by 14% from that of Muthukumar and Nickel. Thus, a simple closed-form expression, eq 2, finds theoretical support from their higher order perturbation calculation. Other expressions also can be assessed by similar comparison.[13]

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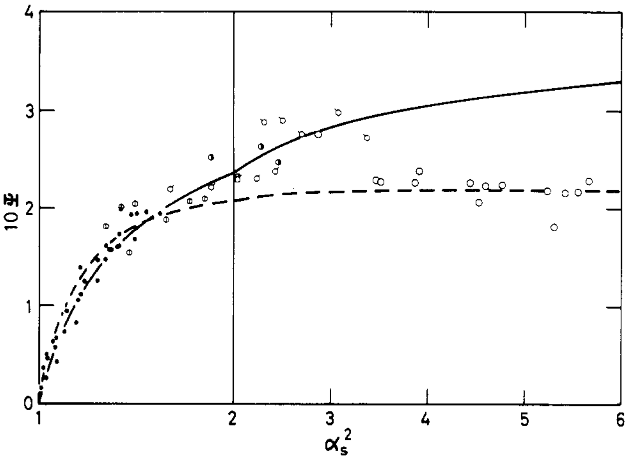

**Figure 1.** Comparison between theory (solid line, eq 3 and 5; broken line, eq 6 and 7) and experiment: polychloroprene (●) in *trans*-decalin, (⦶) in *n*-butyl acetate, and (◑) in carbon tetrachloride,[16] polyisobutylene (ơ) in *n*-heptane and (ъ) in cyclohexane,[17] and poly(D-$\beta$-hydroxybutyrate) (○) in trifluoroethanol.[18]

Experimentally, the usefulness of eq 2, or more correctly, the corresponding expression for $\langle S^2\rangle$ (the mean-square radius of gyration)

$$\alpha_S^2 = 0.6089 + 0.3911(1 + 6.526z)^{1/2} \tag{3}$$

has repeatedly been demonstrated in plots of $\alpha_s^2$ against $z$,[14,15] by using the experimental data which are considered as reliable. Here, another comparison with experiments will be presented in a different way by plotting $\Psi$ against $\alpha_S^2$. The penetration function, $\Psi$, is defined by

$$\Psi = A_2M^2/4\pi^{3/2}N_A\langle S^2\rangle^{3/2} \tag{4}$$

where $A_2$ is the second virial coefficient, $M$ the molecular weight of a polymer molecule, and $N_A$ the Avogadro number. So $\Psi$ as well as $\alpha_S^2$ may be determined with light scattering data alone. In Figure 1, experimental points calculated from data on polychloroprene,[16] polyisobutylene,[17] and poly(D-$\beta$-hydroxybutyrate)[18] are plotted and compared with the combined theoretical prediction of eq 3 for $\alpha_S^2$ and the following expression for $\Psi$:[19,20]

$$\Psi = [1 - (1 + 3.573z/\alpha_S^3)^{-0.620}]/2.193 \tag{5}$$

Strictly speaking, these equations are not necessarily of the same theoretical nature. Since no higher than the third-order perturbation theory of $A_2$ is available to date, we are satisfied with eq 5, which is only valid up to the quadratic term of $z$. As a whole, one can see reasonable agreement between theory and experiment in a region of $\alpha_S^2$ up to 3. For $\alpha_S^2$ values higher than 3, the agreement becomes poor: $\Psi$ in eq 5 diverges slowly, while the experiments on poly(D-$\beta$-hydroxybutyrate) yield an almost constant value of 0.22 ± 0.01. The disagreement could be a natural result due mainly to the limitation of eq 5.

It must be remarked here that the asymptotic behavior of $\Psi$ has successfully been predicted by Oono with the renormalization theory.[21] His expressions for $\alpha_S^2$ and $\Psi$ are

$$\alpha_S^2 = (1 + Z)^{1/4}[1 - 13Z/96(1 + Z)] \tag{6}$$

and

$$\Psi = \frac{0.452}{\pi^{3/2}}\frac{Z}{1 + Z}\exp\left[\left(\frac{13}{48} + \frac{4\ln 2 - 1}{8}\right)\frac{Z}{1 + Z} + \frac{1}{2}\right] \tag{7}$$

The new variable $Z$ is the counterpart of $z$ in the conventional two-parameter theory and is defined with the renormalized one instead of the cluster integral itself. At large $\alpha_S^2$'s, $\Psi$ of eq 7 approximately takes the value 0.219, which coincides with the experimental values on highly expanded polymer molecules.[18] The prediction of eq 6 and 7 is also illustrated for comparison by the broken line in Figure 1. However, that$\Psi$ has a crest around $\alpha_S^2 = 3$ can be explained neither by eq 5 nor by eq 7.[22] From this behavior of $\Psi$ as well as the lack of higher order perturbation theory, one sees, when compared with those of $\alpha^2$, that further developments in theory of $A_2$ are still desirable.

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# Kinetic Studies of Polyimine Formation

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Polyimine is the polymer produced by the condensation of a primary diamine and a dialdehyde. This polymer, having a CH=N backbone, is very attractive as an electrophysical material.[1] However, there have been many difficulties in obtaining high molecular weight polyimines

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