content to 22 mol % under a CO_2 pressure of 5 kg·cm^{-2}.[7] Thus, it is interesting to note that the chelating of a porphyrin ligand with aluminum facilitated the attack of the aluminum alkoxide (the living polyether) on carbon dioxide and produced a block copolymer with a similar oxycarbonyl content in its blocked chain under a CO_2 pressure of 8 kg·cm^{-2} (run 1). In this connection, the copolymerization of carbon dioxide (8.1 kg·cm^{-2}) and propylene oxide with (tetraphenylporphinato)aluminum methoxide as catalyst was reported to give a copolymer with an oxycarbonyl content of 40 mol %.[8]

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High Apparent Excluded Volume Exponents: A Comment on the Remarks by Fujita and Norisuye

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Fujita and Norisuye[1] have recently commented on a modified blob model[2] developed in order to explain the exprimental finding of an apparent excluded volume exponent ν_G higher than 0.60 in the crossover region between the Θ regime and the asymptotic excluded volume regime. ν_G is defined as

$$\nu_G(N) = \frac{1}{2}\frac{\partial \ln \langle S^2\rangle}{\partial \ln N} \quad (1)$$

where S is the radius of gyration and N the number of segments.

Their point is that a high value of ν_G implies a similar high value of ν_r, the apparent excluded volume exponent for the mean-square distance $\langle r^2(t)\rangle$ between two segments separated by t units along the chain:

$$\nu_r(t) = \frac{1}{2}\frac{\partial \ln \langle r^2(t)\rangle}{\partial \ln t} \quad (2)$$

This is quite correct since ν_G is a weighted average over ν_r

$$\nu_G = \frac{\int_0^N (1 - t/N)\langle r^2(t)\rangle \nu_r(t)\, dt}{\int_0^N (1 - t/N)\langle r^2(t)\rangle\, dt} \quad (3)$$

This seems at first in contradiction with our starting hypothesis:

$$\langle r^2(t)\rangle \propto t^{2\nu(t)} \quad (4)$$

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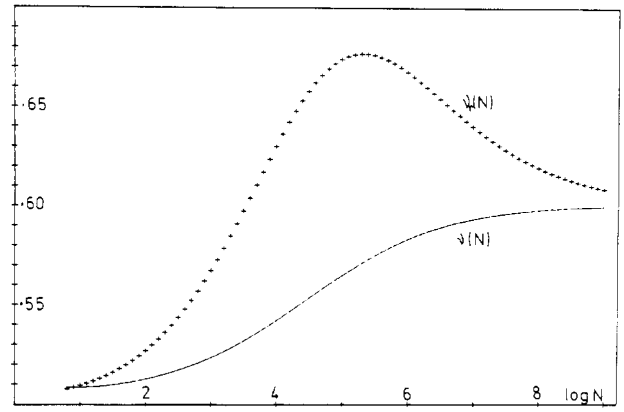

Figure 1. $\nu(N)$ and $\nu_r(N)$ as a function of log N for Ullman's expression of $\nu(t)$ with $\upsilon_e = 0.05$.

with $0.5 \leq \nu(t) \leq 0.6$.

However, $\nu(t)$ should not be confused with $\nu_r(t)$ since from (4) and (2)

$$\nu_r(t) = \nu(t) + \ln t\,\frac{\partial \nu(t)}{\partial \ln t} \quad (5)$$

$\nu_r(t)$ may therefore exceed the limiting value 0.6 of $\nu(t)$ for many choices of the t dependence of $\nu(t)$.

However, Fujita and Norisuye jump to the conclusion that "...according to the theories available to date for linear flexible chains, $\nu_r(N)$ ($=\partial \log \langle R^2\rangle/\partial \log N$) is a monotonically increasing function of N, where $\langle R^2\rangle$ denotes the mean-square end-to-end distance of the entire chain. We believe that this feature holds for $\nu_r(t)$ as well".

We do not fully agree with these conclusions. What is firmly established from a theoretical point of view is[3] (i) the first-order perturbation expansion relating the swelling ratios α_r and α_s to the excluded volume parameter $z \propto \beta N^{1/2}$, where β is the excluded volume integral,[4] and (ii) the exact excluded volume exponent ν in the asymptotic excluded volume regime $\alpha \propto N^{\nu-1/2}$.[5]

The original Flory formula $\alpha^5 - \alpha^3 = Cz$ gives a value of $\nu = 0.60$, in good agreement with the more exact result 0.5885. But the value of C and the shape of the function $\alpha(z)$ in the crossover region are not as well founded. The original Flory formula with $C = 2.60$ does not fit the perturbation expansion and it has been proposed[6] to retain its $\alpha^5 - \alpha^3$ form and to readjust C to a value 1.276. But it is quite evident on a log α–log z plot that a change in C (which displaces the position of the asymptote) and/or in the shape of $\alpha(z)$ can produce an inflection which is the sufficient condition for ν_r and $\nu_G > \nu$ in the crossover region.

Our choice of $\nu(t)$ certainly overemphasizes this point since the strict choice of $\alpha = 1$ inside a blob of size N_C imposes a point of discontinuity in the log α–log N relation but evidently does not fit the low-α perturbation expansion. We want to show that other choices of $\nu(t)$ which respect this expansion lead also to values of $\nu_r(t) > \nu$.

Ullman has recently proposed[7] an empirical expression of $\nu(t)$ which satisfies the two limiting behaviors (i) and (ii) for α

$$\nu(t) = 0.6 - \frac{0.1}{1 + P(t,N)}$$

$$P(t,N) = \upsilon_e f(t,N)/\ln t \quad (6)$$

where $\upsilon_e = 5zN^{-1/2}$ is proportional to β and $f(t,N)$ is taken as to fit the low-α perturbation expansion.[3] It therefore depends both on the position of the t segments inside the chain and on the total length N of the chain.

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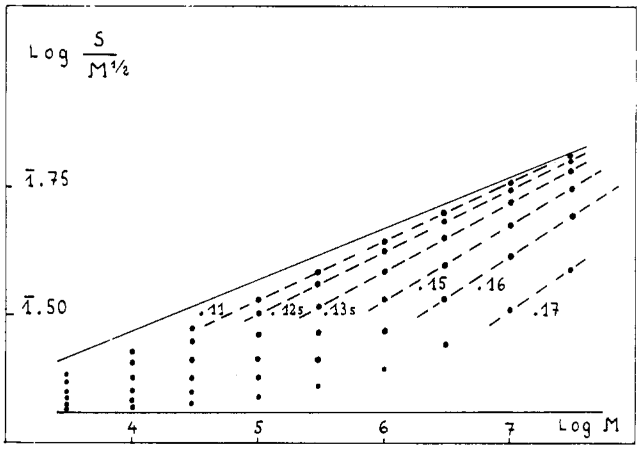

Figure 2. $^1/_2 \log \langle S^2 \rangle / M$ vs. $\log M$ taken from ref 7 for increasing values of v_e (from bottom, 0.02, 0.05, 0.1, 0.2, 0.4, 0.7). Apparent indices in excess of 0.1 for the linear part of the log–log plot are indicated.

This expression of $\nu(t)$ leads indeed to apparent exponents $\nu_r(t)$ and $\nu_G(t)$ in excess of 0.60 in the crossover region. This is easily seen for $\nu_r(t)$ in the simple case where $t = N$ and for $\nu_G(N)$ using the values of $\langle S^2 \rangle$ taken from Table III of Ullman's paper.

Using $f(N) = {}^4/_3 N^{1/2}$ for $t = N$

$$\nu(N) = 0.6 - \frac{0.1}{1 + (4/3)v_e N^{1/2}/\ln N} \qquad (7)$$

Values of $\nu(N)$ and of $\nu_r(N)$ calculated with (7) and (5) are plotted in Figure 1 for $v_e = 0.05$. Values of $^1/_2 \log [\langle S^2 \rangle / M]$ vs. $\log M$ are plotted in Figure 2. This plot is equivalent to $\log \alpha$ vs. $\log N$. It is clearly seen in both cases that apparent exponents in excess of 0.6 are found.

Exact expressions for $\nu(t,N)$ in the crossover region and a definitive answer on the position of the asymptote are presently lacking. It is the role of careful and repeated experimental investigations in the crossover region to bring new evidence which can serve as a basis for further theoretical developments.

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