and increase $\langle r^2\rangle_0$ because of an almost straight backbone contour for these conformations. Hence, the experimentally observed positive temperature coefficient of D_∞ finds support in the calculations, even though the predicted magnitude is appreciably lower than the observed value.

In view of the now well-established knowledge of the conformational potential energy of PTBVK, observations of dynamical properties would also be of obvious interest. Measurements of dielectric and nuclear magnetic relaxation on solutions of this polymer are in progress and will be reported later. Spin relaxation in solutions of nitroxide-labeled poly(methyl vinyl ketone) has already been described by Bullock, Cameron, and Smith.[21]

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Crossover from the Θ to the Excluded Volume Single Chain Statistics: New Experimental Evidences and a Modified Blob Model

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ABSTRACT: A fortuitous situation created by unexpected results in the study of the poly(acrylamide)-water system in a large range of well-characterized fractions has developed into the proposal of a modified blob model which should be valid for any polymer-solvent system in the range of N/N_c from 0 to 100. Here, as in the simple blob theory, N_c is the chemical distance below which the pair correlation function is supposed to be Gaussian. The experimental results force us, however, to replace the simple jump from Gaussian to excluded volume statistics by a more progressive crossover. Numerical fitting of the whole set of results including the molecular weight dependence of the static and dynamic dimensions as well as the single chain scattering function is consistent for a rather broad crossover up to N/N_c = 15.

The consideration of polymer chains as critical objects[1] has greatly revised our picture of polymer solutions. In the dilute regime, the scaling laws coincide with the asymptotic results of Flory's mean-field two-parameter theory, $\alpha^5 - \alpha^3 \propto z$, where z is proportional to $M^{1/2}$ and to the reduced temperature $\tau = (T - \Theta)/\Theta$.[2,3] The description of a single chain as a succession of Gaussian blobs, each made of N_c segments, with excluded volume interaction between the blobs,[4] introduces, however, some differences at small values of z. A theory based on a very simple model with an abrupt change in the pair correlation function for two segments i and j at $|i - j| = N_c$ constitutes a first approach to the problem of the crossover from the Gaussian scaling law at $N < N_c$ to the excluded volume scaling law at $N \gg N_c$ and has been shown[5] to give a consistent explanation of the difference in the exponents of apparent scaling laws obtained for static and dynamic quantities, when measured in a range of values of N/N_c that is not high enough. This is the case for both the q dependence[6] ($q = 4\pi/\lambda \sin \Theta/2$) and M dependence of the diffusion coefficient as measured by quasielastic light scattering.[7] The blob picture is further substantiated by the observation of a spatial crossover in the static neutron scattering law, $S(q)$, which changes from an excluded volume behavior $[S(q) \propto q^{-5/3}]$ to a Gaussian behavior $[S(q) \propto q^{-2}]$ at $q^* \sim R_c^{-1}$, where R_c is the radius of gyration of a blob.[8]

There are however very few experimental studies with sufficient data at small values of α for a very conclusive comparison of the predictions of the blob and the Flory theories. Such a comparison has nevertheless been published recently by Ackasu and Han[9] and seems to be consistent with the blob hypothesis.

In the course of a systematic study of fractions of poly(acrylamide) (PAM) in water,[10] over a large range of molecular weight, we have obtained new unexpected results concerning the exponent in the apparent scaling law for the molecular weight dependence of the radius of gyration R_G. Further investigation, including dynamic measurements, has led us to interpret them in terms of a modified blob theory,[12] which takes into account a progressive

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crossover from Gaussian to excluded volume statistics around $N = N_c$. It is the purpose of this paper to report the details of this interpretation, which lead to an estimate of the width of this crossover region. Assuming the model to be general, we then discuss some consequences which would be valid for any polymer-solvent system not too far from the Θ point.

Poly(acrylamide)-Water System

We recall here the experimental results which have been published elsewhere.[10,11,13] We insist on the careful characterization of well-defined fractions of unhydrolyzed PAM. Our results have been cross-checked in such a way that the unexpected molecular weight dependences cannot be due to a progressive change in polydispersity, chain branching, internal cross-linking or residual degree of hydrolysis with increasing degree of polymerization. On the other hand, the static and dynamic experiments have been performed in a slightly different range of molecular weights. Despite the fact that they cover the region of crossover from Θ (tricritical) to excluded volume (critical) behavior, the experimental results have been submitted to a linear log-log analysis, leading with a satisfactory statistical reliability to an apparent scaling law, the exponent of which is discussed first.

Light-scattering measurements of the radius of gyration R_G have led to

$$R_G = 0.0749M^{0.64\pm0.01};\ 5 \times 10^5 < M_w < 8 \times 10^6 \quad (1)$$

with an unexpected exponent exceeding 0.60.

Direct handling of the molecular-weight dependence of zero-gradient intrinsic viscosities $[\eta]$ and sedimentation and translational diffusion coefficients (S and D) gives

$$[\eta] = (9.3 \times 10^{-3})M^{0.75\pm0.01} \quad (2)$$

$$S = (1.07 \times 10^{-15})M^{0.48\pm0.01};\ 10^5 < M_w < 8 \times 10^6 \quad (3)$$

$$D = (1.24 \times 10^{-4})M^{-0.53\pm0.01} \quad (4)$$

Using the simple assumptions $D \propto R_D^{-1}$, $S \propto MR_D^{-1}$, and $[\eta] \propto R_G^2R_DM^{-1}$, where R_D is the hydrodynamic radius, one can eliminate R_D and get the power law for R_G from an analysis of the products $[\eta]S$ and $[\eta]DM$, combining not the apparent scaling laws (eq 2, 3, and 4) which represent ill-defined averages over the crossover region, but the individual values of $|\eta|$, S, and D obtained on each fraction (eq 11). We have thus confirmed that

$$R_G \propto M^{0.64\pm0.01} \propto M^{\bar{\nu}_G}$$

while from eq 4

$$R_D \propto M^{0.53\pm0.02} \propto M^{\bar{\nu}_D}$$

The reliability of an exponent $\bar{\nu}_G > 0.60$ in the R_G power law is further cross checked from an analysis of the whole angular dependence of the light scattered by a fraction of very high molecular weight. In that case, the excluded volume exponent $\bar{\nu}_G$ can be calculated from the $q^{1/\bar{\nu}_G}$ asymptotical dependence of the scattering function $S(q)$ or of the usual reduced function more familiar to light-scattering experimentalists, $P(\Theta) = S(q)/S(0)$. We have again found $\bar{\nu}_G = 0.64$.

Lately, the R_G vs. M relation has been obtained in a Θ solvent made of water and methanol in a 59/41 volume ratio:

$$R_{G_\Theta} = 0.39M^{0.5}\ \text{Å} \quad (5)$$

A simultaneous log-log plot of relations 1 and 5 (Figure 1) reveals that they intersect at a rather high molecular weight ($M^+ \sim 1.8 \times 10^5$; $N \sim 850$). For comparison, we have drawn the corresponding experimental power laws for polystyrene in cyclohexane at the Θ point and in a good solvent (benzene)[14] which cross at a much smaller value of the degree of polymerization ($N \sim 60$). The values of the expansion ratio $\alpha_G = R_G/R_{G_\Theta}$ (Figure 2) remain small even at the highest molecular weight. This indicates that water is a rather poor solvent, as is also shown by the values of the second virial coefficient.[10] However, (i) the molecular weight dependence of α cannot be represented by any Flory type expression $\alpha^5 - \alpha^3 \propto M^{1/2}$ as shown in Figure 2, where the above expression has been fitted so that the asymptotic expansions of the two theories coincide, and (ii) even if the simple blob theory can improve the situation (since it predicts essentially a sigmoidal shape for the variation of α with M and explains qualitatively the difference between $\bar{\nu}_G$ and $\bar{\nu}_D$), it cannot explain a value of $\bar{\nu}_G > 0.60$.

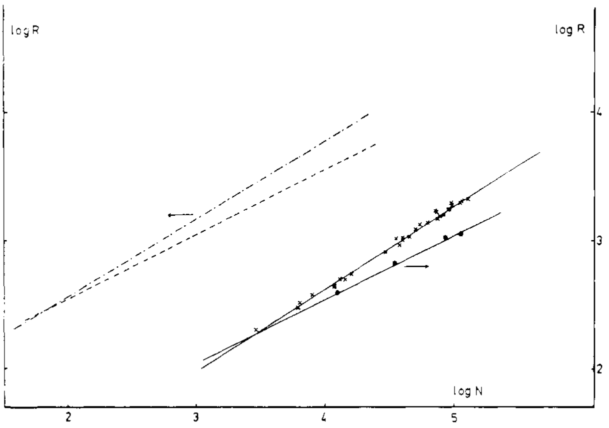

Figure 1. log-log plot of the radius of gyration R_G in a good solvent and a Θ solvent: (×) poly(acrylamide) in water; (O) poly(acrylamide) in a Θ solvent (methanol/water); (—) straight lines corresponding to relations 1 and 5; (···) polystyrene in benzene, $R_G = 0.145M^{0.6}$ (ref 14); and (---) polystyrene in cyclohexane at the Θ point (34 °C), $R_{G_\Theta} = 0.347M^{0.5}$ (ref 14).

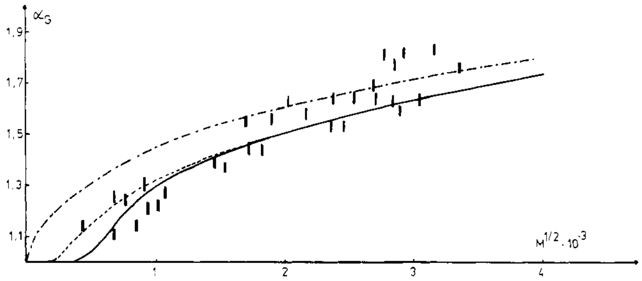

Figure 2. Variation of the expansion factor of α_G vs. $M^{1/2}$: (■) experimental points for poly(acrylamide) obtained from the measured values of R_G in water and the calculated values of R_{G_Θ} according to relation 5; (···) Flory type expression; (---) simple blob theory;[5] and (—) modified blob theory according to this work.

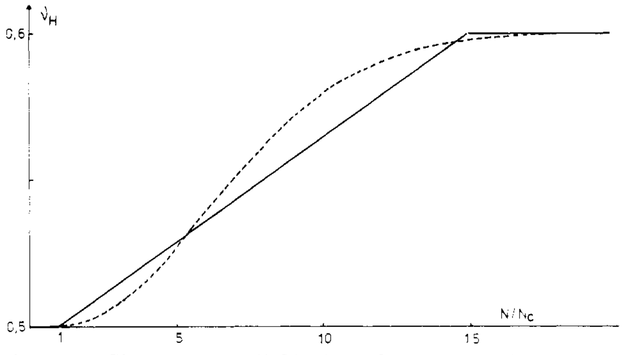

Figure 3. Shape of $\nu_H = f(N/N_c)$ used in our calculation: (---) expression 16a; and (—) expression 16b.

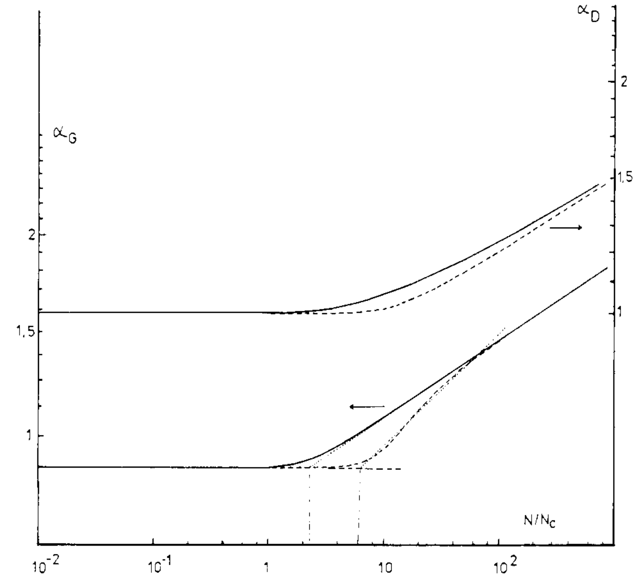

Figure 4. Variation of α_G and α_D vs. N/N_c: (—) simple blob theory; and (- - -) modified blob theory.

We show, in the following section, that the introduction of a more progressive crossover above N_c makes possible values of $\bar{\nu}_G > 0.60$ in an intermediate range of N/N_c and gives a consistent interpretation of all our results, without involving any other peculiarities of the polymer/solvent system, such as has been frequently mentioned for water-soluble polymers.

Blob Theory

The simplest blob theory assumes that the pair correlation function jumps from Gaussian to excluded volume statistics at $N = N_c$. The mean square distance between two segments i and j should then be written

$$\langle r^2_{ij}\rangle = |i-j|b^2 \qquad |i-j| \le N_c$$

$$\langle r^2_{ij}\rangle = N_c\left(\frac{|i-j|}{N_c}\right)^{2\nu} b^2 \qquad |i-j| \ge N_c \tag{6}$$

Introduction of these values in the expression of R_G and R_D

$$R_G^2 = \frac{1}{2N^2}\sum_i\sum_j \langle r^2_{ij}\rangle$$

$$R_D^{-1} = \frac{1}{2N^2}\sum_i\sum_j \left\langle \frac{1}{r_{ij}} \right\rangle \tag{7}$$

and the replacement by integrals leads to

$$R_G^2 = \frac{b^2}{N^2}\left[\int_0^{N_c} p(N-p)\,\mathrm{d}p - \int_0^{N_c} N_c\left(\frac{p}{N_c}\right)^{2\nu}(N-p)\,\mathrm{d}p + \int_0^{N} N_c\left(\frac{p}{N_c}\right)^{2\nu}(N-p)\,\mathrm{d}p \right] \tag{8a}$$

$$R_D^{-1} = \frac{1}{bN^2}\left[\int_0^{N_c} p^{-1/2}(N-p)\,\mathrm{d}p - \int_0^{N_c} N_c^{-1/2}\left(\frac{p}{N_c}\right)^{-\nu}(N-p)\,\mathrm{d}p + \int_0^{N} N_c^{-1/2}\left(\frac{p}{N_c}\right)^{-\nu}(N-p)\,\mathrm{d}p \right] \tag{8b}$$

where the integral from N_c to N has been expressed as the difference of the integrals from 0 to N and from 0 to N_c. The analytical result is

$$R_G^2 = N_c b^2\left[\frac{2\nu-1}{2(2\nu+1)}\left(\frac{N}{N_c}\right)^{-1} - \frac{2\nu-1}{3(2\nu+2)}\left(\frac{N}{N_c}\right)^{-2} + \frac{1}{(2\nu+1)(2\,\nu+2)}\left(\frac{N}{N_c}\right)^{2\nu} \right] \tag{9a}$$

$$R_D = N_c^{1/2} b\left[\frac{2\nu-1}{\nu-1}\left(\frac{N}{N_c}\right)^{-1} + \frac{2\nu-1}{3(2-\nu)}\left(\frac{N}{N_c}\right)^{-2} + \frac{1}{(1-\nu)(2-\nu)}\left(\frac{N}{N_c}\right)^{-\nu} \right]^{-1} \tag{9b}$$

$$\alpha_G = \left[\frac{3(2\nu-1)}{2\nu+1}\left(\frac{N}{N_c}\right)^{-2} - \frac{2(2\nu-1)}{2\nu+2}\left(\frac{N}{N_c}\right)^{-3} + \frac{6}{(2\nu+1)(2\nu+2)}\left(\frac{N}{N_c}\right)^{2\nu-1} \right]^{1/2} \tag{10a}$$

$$\alpha_D = \left[\frac{3(2\nu-1)}{4(\nu-1)}\left(\frac{N}{N_c}\right)^{-1/2} + \frac{(2\nu-1)}{4(2-\nu)}\left(\frac{N}{N_c}\right)^{-3/2} + \frac{3}{4(2-\nu)(1-\nu)}\left(\frac{N}{N_c}\right)^{(1/2)-\nu} \right]^{-1} \tag{10b}$$

One can define apparent indices as

$$\nu_G = \frac{\partial \ln R_G}{\partial \ln N} \text{ and } \nu_D = \frac{\partial \ln R_D}{\partial \ln N} \tag{11}$$

$$\nu_G = \frac{1}{2}\left[\frac{1-2\nu}{2(\nu+1)}\left(\frac{N}{N_c}\right)^{-1} - \frac{2(2\nu-1)}{3(2\nu+2)}\left(\frac{N}{N_c}\right)^{-2} + \frac{2\nu}{(2\nu+1)(2\nu+2)}\left(\frac{N}{N_c}\right)^{2\nu} \right] \Big/ \left[\frac{2\nu-1}{2(\nu+1)}\left(\frac{N}{N_c}\right)^{-1} + \frac{(2\nu-1)}{3(2\nu+2)}\left(\frac{N}{N_c}\right)^{-2} + \frac{1}{(2\nu+1)(2\nu+2)}\left(\frac{N}{N_c}\right)^{2\nu} \right] \tag{12a}$$

$$\nu_D = \left[\frac{1-2\nu}{1-\nu}\left(\frac{N}{N_c}\right)^{-1} + \frac{2(2\nu-1)}{3(2-\nu)}\left(\frac{N}{N_c}\right)^{-2} + \frac{\nu}{(1-\nu)(2-\nu)}\left(\frac{N}{N_c}\right)^{-\nu} \right] \Big/ \left[\frac{1-2\nu}{1-\nu}\left(\frac{N}{N_c}\right)^{-1} + \frac{2\nu-1}{3(2\nu-1)}\left(\frac{N}{N_c}\right)^{-2} + \frac{1}{(1-\nu)(2-\nu)}\left(\frac{N}{N_c}\right)^{-\nu} \right] \tag{12b}$$

The variations of α_G, α_D, ν_G, and ν_D with N/N_c are given in Figures 4 and 5 for $\nu = 0.60$.

It is seen that the model can account for $\nu_G > \nu_D$ and $\alpha_G > \alpha_D$. The point where the asymptotic term in α_G

$$\alpha_G = \left[\frac{6}{(2\nu+1)(2\nu+2)}\left(\frac{N}{N_c}\right)^{2\nu-1} \right]^{1/2} \tag{13}$$

becomes equal to 1 is related to N_c by $N^+ = 2.26N_c$.

The model cannot however explain an apparent scaling law with $\bar{\nu}_G > \nu$, since ν_G is always $\le\nu$. But we can show that a simple modification, which takes into account the progressive crossover from Gaussian to excluded volume statistics around N_c, makes such a fact possible. The following argument makes it qualitatively easy to understand.

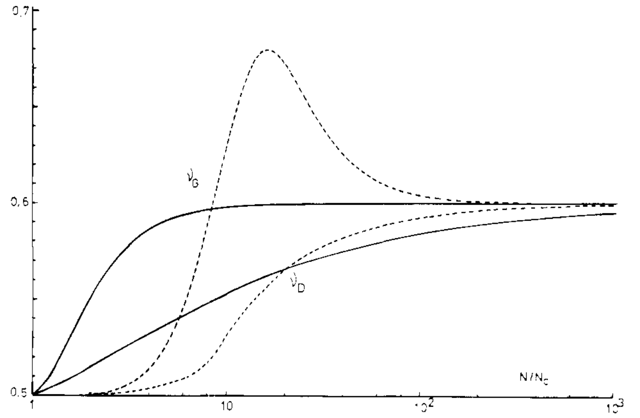

Figure 5. Variation of the effective indices ν_G and ν_D vs. N/N_c: (—) simple blob theory; and (---) modified blob theory.

We retain N_c as the chemical distance at which the departure from Gaussian statistics starts and we introduce a variable exponent ν_h such that

$$\langle r^2_{ij}\rangle = N_c\left(\frac{|i-j|}{N_c}\right)^{2\nu_h} b^2$$

with

$$\begin{aligned} &\nu_h = 0.50 \qquad |i-j| \leq N_c \\ &0.50 \leq \nu_h \leq \nu \qquad N_c \leq |i-j| \leq N_1 \\ &\nu_h = \nu \qquad |i-j| \geq N_1 \end{aligned} \tag{14}$$

The replacement of a simple jump of ν_h from 0.50 to ν at $N = N_c$ by a more progressive change between N_c and N_1 does not change the asymptotic behavior of R_G or R_D. This is easily seen, since the integration can now be split as shown below for R_G:

$$\begin{aligned} R_G{}^2 = \frac{b^2}{2N^2}\Bigg[&\int_0^{N_c} N(N-p)\,\mathrm{d}p + \\ &\int_{N_c}^{N_1} N_c\left(\frac{p}{N_c}\right)^{2\nu_h}(N-p)\,\mathrm{d}p - \\ &\int_0^{N_1} N_c\left(\frac{p}{N_c}\right)^{2\nu}(N-p)\,\mathrm{d}p + \\ &\int_0^{N} N_c\left(\frac{p}{N_c}\right)^{2\nu}(N-p)\,\mathrm{d}p\Bigg] \end{aligned} \tag{15}$$

Whatever the variation of ν_h below N_1, the asymptotic behavior is dominated by the same last integral as in eq 8a.

What will differ, however, is the approach to the asymptotic region. One can suspect that if ν_h varies sufficiently slowly, i.e., if the interval N_c to N_1 is sufficiently broad, R_G will depart very slowly from its Θ behavior so that the actual variation of R_G with M *will approach its asymptotic behavior from below*. This implies that the effective index ν_G can take values $>\nu$.

Detailed calculations are obviously requested to confirm this point of view numerically and to choose a shape for ν_h which fits our experimental results. This means correct averages for $\bar{\nu}_G$ and $\bar{\nu}_D$ over the actual range of molecular weights must be obtained first. But since we have based part of our conclusions on the $q^{-1/\bar{\nu}_G}$ dependence of the scattering function $S(q)$, which is strictly valid for homogeneous statistics with $\langle r^2_{ij}\rangle \propto |i-j|^{2\nu_G}$, it is of importance to calculate numerically $S(q)$ and to check that, for statistics such as those defined in relation 14, there is still a correspondence between the apparent power laws for R_G ($R_G \propto M^{\bar{\nu}_G}$) in a given range of molecular weight and for $S(q) \sim q^{1/\bar{\nu}_G}$ in the corresponding range of $q \sim 1/R_G$.

Table I

N/N_c	simple blob theory α_G	simple blob theory α_D	modified blob theory α_G	modified blob theory α_D
1	1	1	1	1
2	1.015	1.003	1.000	1.000
3	1.043	0.010	1.001	1.000
4	1.067	1.017	1.004	1.000
5	1.089	1.025	1.008	1.002
6	1.107	1.032	1.015	1.003
7	1.124	1.039	1.024	1.005
8	1.138	1.045	1.034	1.007
9	1.151	1.051	1.047	1.010
10	1.163	1.056	1.059	1.017
20	1.252	1.013	1.200	1.053
30	1.301	1.132	1.274	1.084
40	1.338	1.155	1.322	1.109
50	1.368	1.174	1.357	1.130
60	1.393	1.191	1.385	1.148
70	1.414	1.205	1.408	1.164
80	1.432	1.217	1.428	1.178
90	1.449	1.229	1.446	1.190
100	1.464	1.239	1.462	1.202
200	1.569	1.313	1.568	1.282
300	1.633	1.360	1.633	1.333
400	1.681	1.395	1.681	1.370
500	1.719	1.423	1.719	1.400
600	1.750	1.447	1.750	1.425
700	1.777	1.467	1.777	1.446
800	1.801	1.486	1.801	1.465
900	1.823	1.502	1.823	1.482
1000	1.842	1.517	1.842	1.497

Detailed Model and Numerical Fitting

A. Molecular Weight Dependence of R_G and R_D. There is no theoretical expression available for ν_h. Direct renormalization along the chain as given by Gabay[15] provides a crossover function which does not take into account the competition between a tricritical and a critical fixed point, i.e., the basis for the blob theory. It has also been suggested that the blob theory could be modified in such a way that the values of α at small N/N_c fit the predictions of perturbation theories.[9] But in that case the effective index ν_G is always smaller than or equal to ν.

Therefore ν_h has been given the two following arbitrary shapes for $N > N_c$:

$$\nu_h = 0.60 - 0.1\exp\left[-\left(c\left(\frac{p}{N_c}\right) - 1\right)^2\right] \tag{16a}$$

$$\begin{aligned} &\nu_h = 0.5 + 0.1\frac{p - N_c}{N_c(k-1)} \qquad N_c < p \leq kN_c \\ &\nu_h = 0.60 \qquad p \geq kN_c \end{aligned} \tag{16b}$$

Calculations of R_G and R_D have been performed with different values of c and k by numerical integration of eq 15 (and the corresponding expression for R_D) on a minicomputer with a connected plotter. The fit to the experimental data implies a correct mean slope in the log–log plot of R_G and R_D over more than 1 decade of N/N_c. Two satisfactory sets of parameters $c = 0.02$ and $k = 15$ have been found corresponding in both cases to an interval of crossover between $N/N_c = 1$ and $N/N_c \sim 15$ (Figure 3). Using these values, we have calculated the effective indices ν_G and ν_D, with the use of relation 11 (Figure 4), as well as α_G and α_D (Figure 5 and Table I). On Figure 4, one should note the maximum value $\nu_G = 0.68$ at $N/N_c \sim 15$ which makes possible an average value $\bar{\nu}_G = 0.64$ for N/N_c between 10 and 100. On Figure 5, it should be noted that the curve log α_G vs. log N/N_c can be closely approximated by three linear segments $\alpha_G = 1$ for $N/N_c < 6$; $\alpha_G \propto$

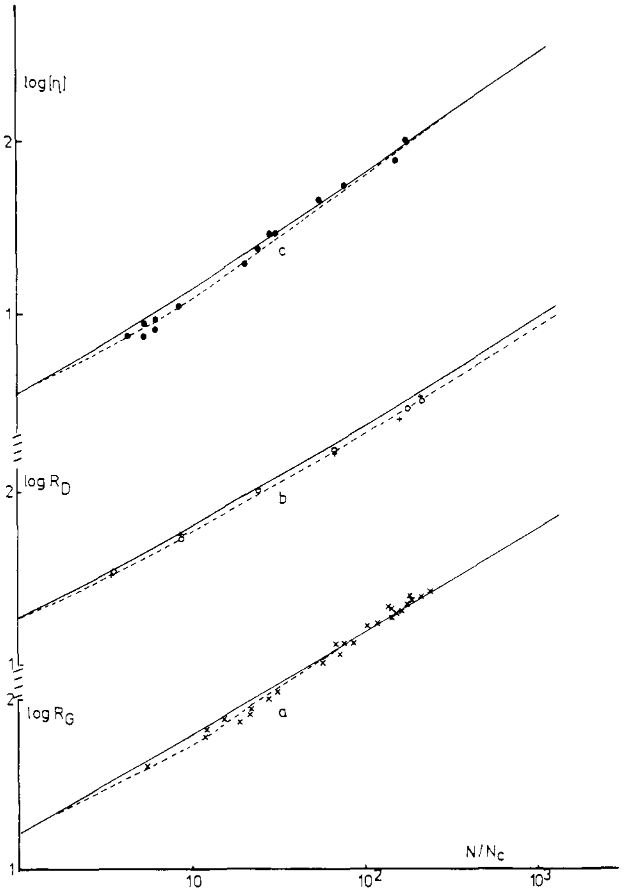

Figure 6. log-log plots of R_G, R_D, and $[\eta]$ and comparison with the experimental results for poly(acrylamide) in water. Values of R_D are calculated from either diffusion coefficients (+) or sedimentation coefficients (O): (—) simple blob theory; and (- - -) modified blob theory.

$(N/N_c)^{0.14}$ for $6 < N/N_c < 50$; and $\alpha_G \propto (N/N_c)^{0.10}$ for $N/N_c > 50$.

Therefore, we can deduce from the intersection M^+ of the curves in Figure 1 a value of M_c for the poly(acrylamide)-water system $M_c = M^+/6 = 3 \times 10^4$ and the corresponding radius of gyration $R_c = 57$ Å. N_c is known to be related to the reduced temperature τ by $N_c \propto k_1\tau^{-2}$. Akcasu and Han[9] have proposed $k_1 = 4$. Our value of N_c (500 at 21 °C) therefore involves $\tau^{-1} \sim 11$ and a Θ temperature of ca. -3 °C.

Knowing M_c, we can now calculate the value of N/N_c for each sample and place the experimental values of log R_G and log R_D on the calculated curves (Figure 6a,b). The agreement is extremely good, as is the molecular weight dependence of the viscosity, compared to the calculated values of the product $R_G{}^2R_DM^{-1}$ (Figure 6c).

Finally, the comparison between calculated and experimental values of α_G can be seen in Figure 2. It seems that, despite some scattering in the experimental points, the modified blob theory gives the best account of the experimental results.

B. Angular Dependence of the Scattered Intensity. The calculation of the scattering factor $P(\Theta)$ has been undertaken in a way similar to that used by Loucheux et al.[16] and Farnoux et al.[8] $S(q)$ is the Fourier transform of the pair correlation function $w(r_{ij})$, i.e., its moment generating function expressed as a polynomial expansion of the successive moments. Its log can also be expressed as a series of cumulants,[17]

$$\log S(q) \propto \sum_{k=1}^{\infty} \frac{K_k}{k!}(iq)^k$$

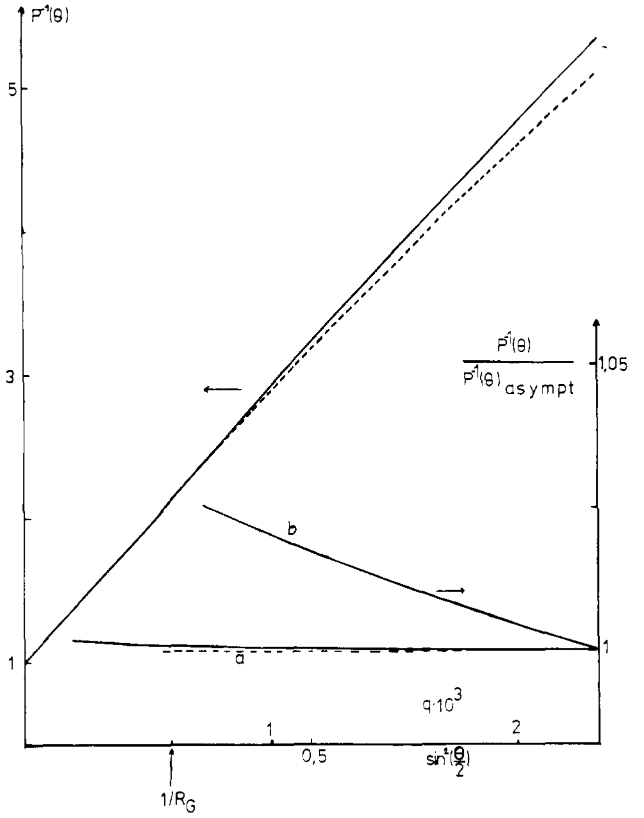

Figure 7. $P^{-1}(\Theta)$ as a function of $\sin^2(\Theta/2)$ or q^2 [(—) simple blob theory; (- - -) modified theory]. The ratio of the numerically computed value to that derived from the analytical asymptotic expression by using an effective $\bar{\nu}$: (a) $\bar{\nu} = 0.655$; and (b) $\bar{\nu} = 0.60$.

where the kth cumulant can be represented as a function of the moments $\langle r^j \rangle$ with $j \leq k$. Retaining only the first cumulant gives

$$P(\Theta) = \frac{1}{N^2}\sum_i\sum_j \exp\left[-\frac{q^2\langle r^2{}_{ij}\rangle}{6}\right] = \frac{1}{N}\int_0^N \left(1 - \frac{p}{N}\right) \exp\left[-\frac{q^2\langle r^2{}_p\rangle}{6}\right] \mathrm{d}p \qquad (17)$$

This approximation, which is more correct at larger q, corresponds to the use of the Gaussian function

$$w(r_{ij}) \propto \exp\left[-\frac{3r^2}{2\langle r^2{}_{ij}\rangle}\right] \qquad (18)$$

If $\langle r^2{}_{ij}\rangle \propto |i - j|$ one gets for $P(\Theta)$ the classical Debye result while the result for $\langle r^2{}_{ij}\rangle \propto |i - j|^{2\nu}$ has been given by Loucheux et al.

The asymptotic expansion can be written as

$$P(\Theta) = \left[q^2R_G{}^2\frac{(2 + 2\nu)(1 + 2\nu)}{6}\right]^{-1/2\nu} \times \left[\frac{1}{\nu}\Gamma\left(\frac{1}{2\nu}\right) - \frac{1}{\nu}\Gamma\left(\frac{1}{\nu}\right)\left(q^2R_G{}^2\frac{(2 + 2\nu)(1 + 2\nu)}{6}\right)^{-1/2\nu}\right] \qquad (19)$$

or

$$P^{-1}(\Theta) = \left[R_G{}^2\frac{(2 + 2\nu)(1 + 2\nu)}{6}\right]^{1/2\nu} q^{1/\nu} - \nu\frac{\Gamma(1/\nu)}{[\Gamma(1/2\nu)]^2}$$

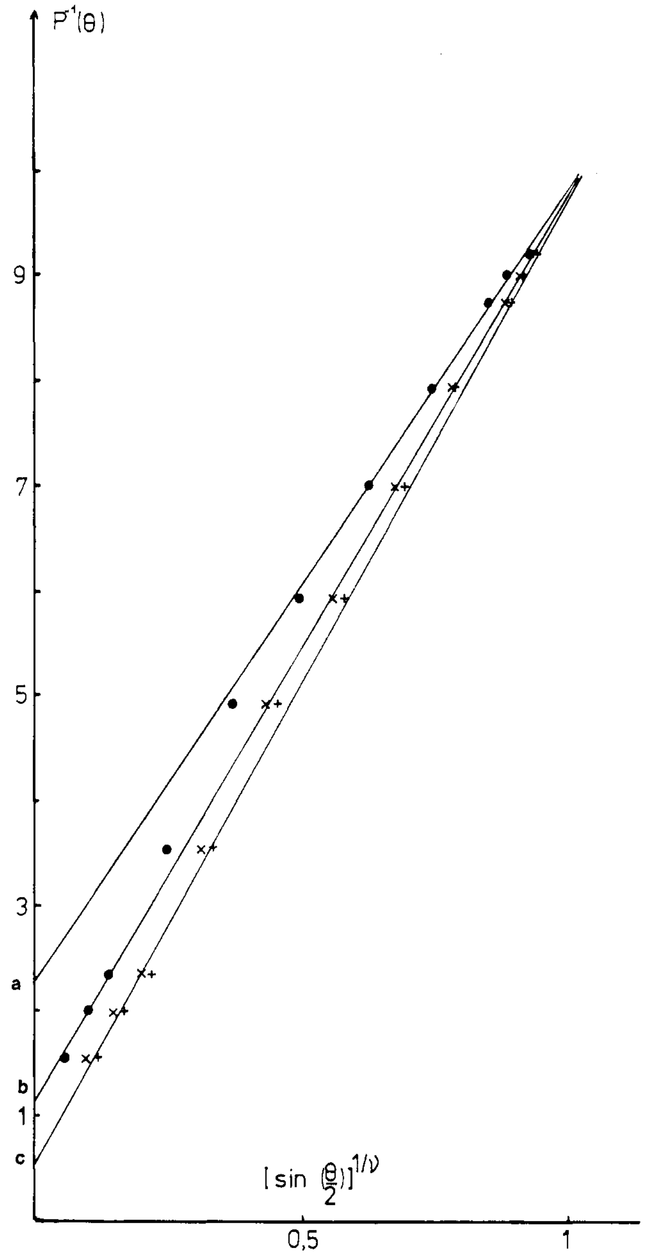

Figure 8. Experimental variation of $P^{-1}(\Theta)$ for a fraction $M = 6.7 \times 10^6$ plotted as a function of $[\sin(\Theta/2)]^{1/\bar{\nu}}$ with $\bar{\nu} = 0.50$ (O), 0.60 (×), and 0.655 (+). The extrapolated values (a), (b), and (c) give polydispersity indices M_w/M_n equal to 4.8, 2.0, and 1.3 to be compared to the GPC value of 1.2.

(where Γ is the gamma function), showing that ν can be derived from the large q behavior of $P^{-1}(\Theta)$.

The case where ν jumps from 0.50 to 0.60 at $N = N_c$ has been treated by Farnoux et al.,[8] who show that there is a crossover from a q^{-2} to a $q^{-1/\nu}$ behavior at $q \sim (N_c b^2/6)^{-1/2}$.

In our case, since ν_h is a continuous function, it is difficult to predict how the exponent $\partial \log P(\Theta)/\partial \log q$ at a given value of q is related to the value of ν_G for $R_G \sim 1/q$.

For that reason, we have carried out a calculation of $P(\Theta)$ for one of our largest fractions ($M = 6.7 \times 10^6$; $R_G = 1690$ Å) by using the previously found values of M_c and R_c. The results are given in Figure 7 together with the values obtained for the simple blob theory. We also show that one can define an average $\bar{\nu} = 0.655$ such that the result of our numerical calculation coincides with the asymptotic expansion for $\nu = \bar{\nu}$ (eq 19) at large angles corresponding to values of $q \sim 1.5 \times 10^{-3}$ Å^{-1}.

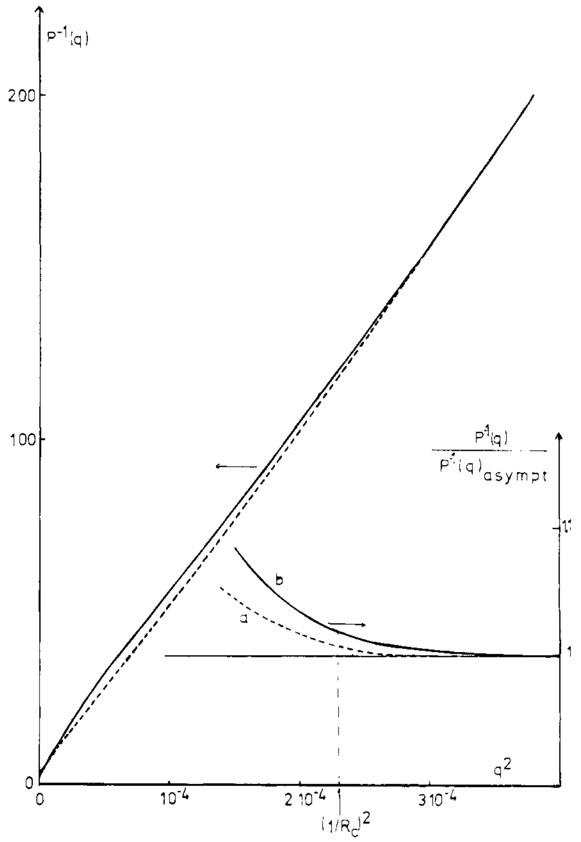

Figure 9. $P^{-1}(q)$ as a function of q^2 for the same fraction as that in Figure 8 in a range of q corresponding to neutron scattering [(—) simple blob theory; (---) modified blob theory]. The ratio, as in Figure 7, is now calculated for $\bar{\nu} = 0.50$.

This value of $\bar{\nu} = 0.655$ is in fair agreement with the value $\bar{\nu}_G = 0.64$ obtained in a range of R_G corresponding to $1/q$. It justifies that use of a power law for $P(\Theta)$ as reported in the section Poly(acrylamide)–Water System and visualized in Figure 8. It also explains why the polydispersity index calculated from the ordinate of the asymptote at $q = 0^{16}$ is in good agreement with the result obtained by GPC.[10]

We have also carried out the calculation of $S(q)/S(0)$ in a much larger range of q (Figure 9). It is seen that the calculated value coincides with the asymptotic expansion with $\nu = 0.5$ for $q > 1.7 \times 10^{-2}$ Å as expected from the value of R_c.

The success of our model in the interpretation of the experimental results justifies the consideration of the poly(acrylamide)–water system as an example of a polymer in a rather bad solvent, with a subsequent high value of N_c. The question is now to establish if the predictions of the model can be confirmed for other polymer–solvent systems, in the same range of N/N_c. We have not found published data covering a sufficient number of experiments to be treated conclusively with our model. The data used by Akcasu and Han[9] in their comparison of the Flory type and simple blob theory of the expansion factors α_G and α_D, which seem to favor the blob theory, do not extend sufficiently and with enough precision in the region $\alpha_D < 1.2$, where the differences between the simple blob theory and our model could appear (see Figure 2 and Table I). We have therefore started such a systematic study. We will now nevertheless examine some consequences of the model on the interpretation of the measurements of static and dynamic dimensions not far from the Θ point.

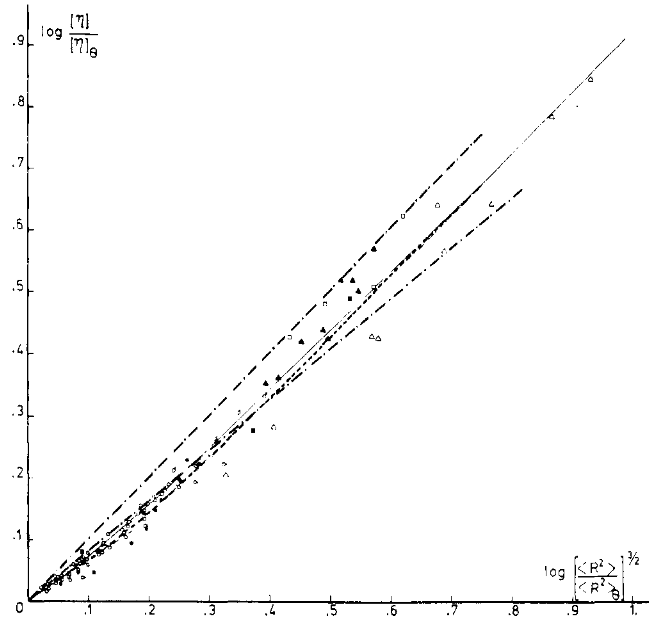

Figure 10. ln α_η^3 as a function of ln α_G^3 for different systems: poly(methylstyrene) in diethyl succinate (○) and in several good solvents (△);[19] polystyrene in cyclohexane (○-), decalin (ơ), and in several good solvents (□);[20,21] polychloroprene in decalin (●) and in several good solvents (■);[22,23] poly(methyl methacrylate) in butyl chloride (ʊ) and in several good solvents (▲);[19] (-····-) the two limiting cases of Flory $\alpha_\eta^3 = \alpha_G^3$ and Yamakawa $\alpha_\eta^3 = \alpha_G^{2.43}$; (---) $\alpha_\eta^3 = \alpha_G^2\alpha_D$, simple blob theory; and (—) $\alpha_\eta^3 = \alpha_G^2\alpha_D$, modified blob theory.

General and Concluding Remarks

Among the general properties of polymer solutions, the understanding of which is quantitatively improved by the blob theory, is the difference between the static and dynamic indices ν_G and ν_D and the corresponding expansion ratios α_G and α_D. In particular the simple blob theory[5] gave a semiquantitative interpretation of the differences between $\alpha_\eta^3 = [\eta]/[\eta]_\Theta = \alpha_G^2\alpha_D$ and α_G^3 collected by Yamakawa.[3] We have replotted the results of the modified blob theory in Figure 10. It slightly improves the statistical reliability in the low α region.

It has often been remarked that the Stockmayer–Fixman extrapolation of R_G $[R_G/M^{1/2} = f(M^{1/2})]$ or $[\eta]$ $[[\eta]/M^{1/2} = f(M^{1/2})]$ to obtain unperturbed dimensions was very often used well beyond its domain of validity according to the Flory theory, i.e., where α can be approximated by $1 + aM^{1/2}$. As was clearly stated by Stockmayer,[18] this originates from the fact that this approximation was justified in a much larger range when α was supposed to be given by an expression of the type $\alpha^3 - \alpha \propto M^{1/2}$ with an asymptotic value of $\nu = 0.66$. It is interesting to remark that the blob theory is much closer to it in the region where experiments are generally performed. We have carried out the actual Stockmayer–Fixman extrapolation of our results (Figure 11). It is clear that one obtains straight lines on a large range of values of α, but that unperturbed dimensions are only obtained if one replaces the extrapolation at $M = 0$ by an extrapolation at $M^+ \sim 6M_c$. This is a logical result if one recalls that α_G can be represented above that value by a power law with $\bar{\nu}_G \sim 0.64$ over 1 decade (Figure 5). For practical purposes, the quality of the solvent is often good enough for M_c to be very small and to justify the extrapolation procedure.

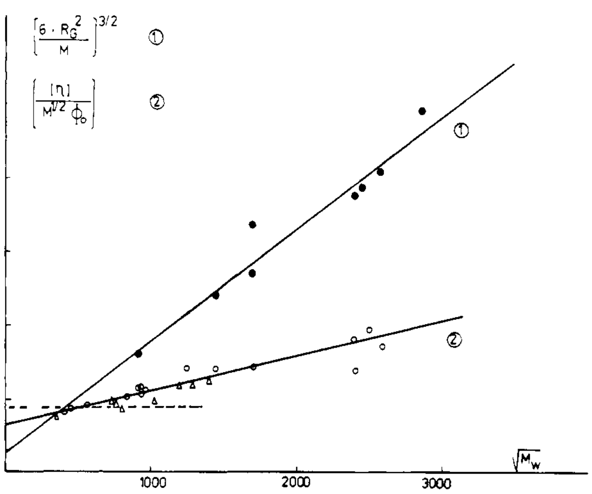

Figure 11. Stockmayer–Fixman plots of R_G and $[\eta]$. The dashed line represents the unperturbed dimensions (relation 5).

We obviously need more systematic studies of both α_G and α_D on other polymeric systems near the Θ temperature to establish the general character of the tricritical to critical crossover, empirically derived from our present experiments (Table I), as a challenge for further theoretical work.

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