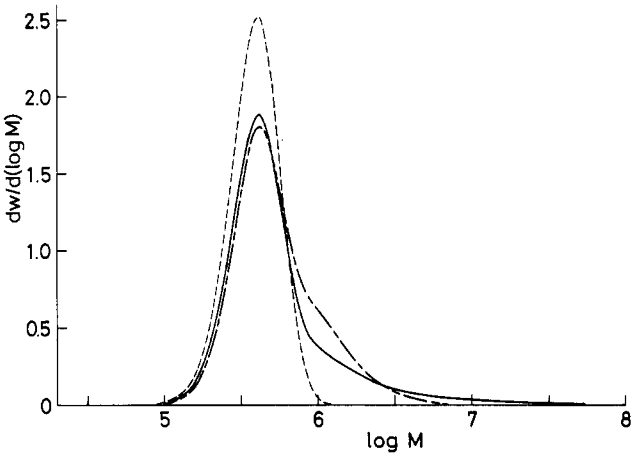

Figure 6. Comparison of the molecular weight distributions obtained from the computer simulation of the random (dash-dot curve) and nonrandom cross-linking (solid curve) for the initial Schultz–Zimm distribution (broken curve).

rapidly than the random cross-linking in certain localized regions of the polymer at the expense of cross-linking in the other regions, forming considerably highly- and only slightly-cross-linked polymers at the same time, even at relatively low total doses. The highly-cross-linked polymers, although small in the weight fractions, will increase the M_z/M_w ratio more highly than those in the random cross-linking. These characteristics in the computer simulation of the nonrandom cross-linking are in fact observed for fast-neutron irradiated polystyrene both in the molecular weight distribution (Figure 5) and in the plot of M_z/M_w vs. $u\chi$ (Figure 4a). It is concluded, therefore, that the actual cross-linking of polystyrene does not take place at random for fast-neutron irradiation, and the nonrandom cross-linking is caused by the microscopic inhomogeneity of energy deposition.

Acknowledgment. The authors wish to express their appreciation to Dr. Seiichi Tagawa and the operating staff of the fast-neutron research reactor YAYOI for their cooperation in carrying out the irradiations.

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Crossover Effects on the Sedimentation Velocity Scaling Laws in Semidilute Solutions of Polymers

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Received October 2, 1979

ABSTRACT: Measurements of the sedimentation constants in the semidilute regime have been performed in an extended range of concentration, made experimentally available by the use of high molecular weight polystyrene in bromobenzene, a good solvent with a small refraction index increment. The blob hypothesis is confirmed in the sense that the concentration dependence of S is independent of M, but the exponent in the apparent scaling law is shown to be concentration dependent. This can be rationalized considering the size of the blob compared to the radius of gyration of a chain of N_c segments, N_c being the number characteristic of the polymer solvent system, above which the pair correlation function changes from Gaussian to excluded-volume statistics.

The treatment of polymer solutions as critical systems has considerably renewed our picture of polymer solutions.[1,2] The Daoud–Jannink diagram[3] clearly describes the domains corresponding to different scaling laws for the monomer–monomer pair correlation function in the concentration–temperature plane. For a polymer with a given degree of polymerization N, the crossover from one domain to the other is a function of two characteristic quantities.[4,5]

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(a) N_c is the chemical length required for the development of excluded volume effects in the pair correlation function. In the simplest hypothesis, the mean distance r_{ij} between monomers $|i-j|$ is given by

$$\langle r^2_{ij}\rangle = |i-j|a^2 \qquad |i-j| < N_c \tag{1a}$$

$$\langle r^2_{ij}\rangle = N_c\left(\frac{|i-j|}{N_c}\right)^{2\nu} a^2 \qquad |i-j| > N_c \tag{1b}$$

a being the statistical segment length and ν the excluded-volume exponent ($\nu \sim 0.60$). N_c is a function of the reduced temperature $\tau = (T-\Theta)/\Theta$

$$N_c \sim k_1\tau^{-2} \tag{2}$$

where k_1 is a numerical factor of order unity. The radius of gyration R_G of the chain of length N_c and molecular weight M_c will be called R_c. A chain with $N \gg N_c$ can be viewed as being made of a succession of Gaussian subunits of size R_c with excluded volume interaction.

(b) The critical or overlap concentration C^* is

$$C^* = M/(k_2R^3{}_GN_A) \tag{3}$$

where k_2 is a numerical factor of order unity and N_A is Avogadro's number. Experimental manifestations of coil overlap might depend on the observed phenomenon. For $C > C^*$ there exists a molecular weight independent screening length

$$\xi = R_G\left(\frac{C}{C^*}\right)^{\nu/(1-3\nu)} = R_G\left(\frac{C}{C^*}\right)^{-0.75} \tag{4}$$

above which the overall behavior is Gaussian. The semidilute solution can be viewed as a succession of noninteracting "blobs" of dimension ξ and of molecular weight

$$M(\xi) = C\xi^3 \sim C^{1/(1-3\nu)} \tag{5}$$

This static picture has been substantiated by small-angle neutron-scattering experiments.[4,5] From these experiments, values of k_1 and k_2 of the order respectively of 4[6] and 6[4,5,14] seem quite reasonable.

The extension of this model to dynamic experiments has been the object of much concern.

In the dilute regime, it has been shown[7,8] that for not sufficiently large values of N/N_c the difference of contributions of the short-chain statistics (see relation 1) to the summations can well explain the difference in the apparent molecular weight scaling laws for the mean square static radius of gyration R_G

$$\langle R^2{}_G\rangle = \frac{1}{2N^2}\sum_i\sum_j\langle r^2{}_{ij}\rangle \tag{6}$$

obtained from neutron- and light-scattering experiments and the hydrodynamic radius R_D

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

obtained from autodiffusion or sedimentation measurements.[9-11] Explicit expressions for the apparent indices

$$\nu_G = \frac{\mathrm{d}\log R_G}{\mathrm{d}\log N} \text{ and } \nu_D = \frac{\mathrm{d}\log R_D}{\mathrm{d}\log N} \tag{8}$$

have been calculated[7] for the simple statistic of relation 1. While both tend asymptotically to ν, ν_G becomes nearly equal to ν at $N/N_c \sim 5$ while ν_D is significantly lower than ν up to $N/N_c \sim 100$. It is however very difficult, from experiments in a restricted range M_1–M_2 of molecular weight, to identify in a log–log plot of R_G or R_D vs. M the progressive change in slope, and the results can very often be successfully interpreted by a linear least-squares analysis. The exponent, in this "apparent scaling law", should correspond to the apparent index at an intermediate molecular weight where the tangent to the true curve is parallel to the chord joining the two extreme points at M_1 and M_2 and could therefore be dependent on them.

In the semidilute regime, it has been postulated[12] that ξ should represent the mean distance between entanglements and that the collective diffusion coefficient D and the sedimentation coefficient s should be molecular weight independent. Their scaling laws with concentration are obtained from the assumption that a "blob" behaves like a "molecule" of size ξ and molecular weight $M(\xi)$. It is therefore expected that when ξ is not much larger than R_c, the short distance statistics should also lead to different concentration scaling laws for the static dimension ξ and its hydrodynamic counterpart $\xi_D \sim D^{-1}$. One expects

$$\xi_D \sim \left(\frac{N(\xi)}{N_c}\right)^{\nu_D} R_c \sim (C\xi^3)^{\nu_D} \sim C^{\nu_D/(1-3\nu_G)} \tag{9}$$

to be compared to relation 4. Concentration scaling laws of the form

$$D = C^{-\beta} \tag{10}$$

have indeed been found for polystyrene in benzene in the semidilute regime[13,14] with $\beta = +0.67$. The same remark as above can be made on the influence of the range of concentration under study on the value of β. Moreover, as pointed out by one referee, it is not at all definite that a relation which involves a combination of exponents and is strictly correct at each molecular weight or concentration will still hold for apparent indices obtained while forcing the individual experiments to an apparent scaling law. It is however interesting to note that the value $\beta = 0.67$ is in fair agreement with that calculated using the published values of $\nu_D = 0.55 \pm 0.02$ and $\nu_G = 0.60$ for the same system: $\beta = 0.69 \pm 0.03$.

Ultracentrifugation in the semidilute regime constitutes an experimentally simple check of the blob hypothesis since it predicts

$$s \sim \frac{M(\xi)}{f} \propto M(\xi)D \propto C^{(\nu_D-1)/(3\nu-1)} \propto C^{-\beta'} \tag{11}$$

Several papers dealing with s vs. c scaling laws in the semidilute regime have been published recently. Destor and Rondelez[10,11] working with high molecular weight polystyrene in benzene at small C report $\beta' = 0.57$ in very good agreement with the values of ν_D and ν_G obtained in dilute solution (β' calculated with relation 11 = 0.56 ± 0.03). On the other hand, Pouyet and Dayantis[15] working with lower molecular weight samples of PS in bromobenzene (a solvent where the intrinsic viscosity law nearly exactly matches that for benzene)[16] at higher concentrations report $\beta' = 0.82 \pm 0.03$. The same exponent holds for poly(methyl methacrylate) in benzene. For the large number of polymer–good-solvent systems recently studied by Roots and Nyström,[17] 0.7–0.8 appears to be a very common value for β'.

A possible explanation of this discrepancy can be found in the fact that at higher concentrations the size of the blob becomes of the order of R_c, so that the static value of ν in relation 11 should be replaced by its effective value $\nu_G < \nu$ ($0.5 \le \nu_G \le 0.6$). Therefore one should write

$$s \propto C^{(\nu_D-1)/(3\nu_G-1)} \tag{12}$$

with the same limitation as was pointed out for relation 9.

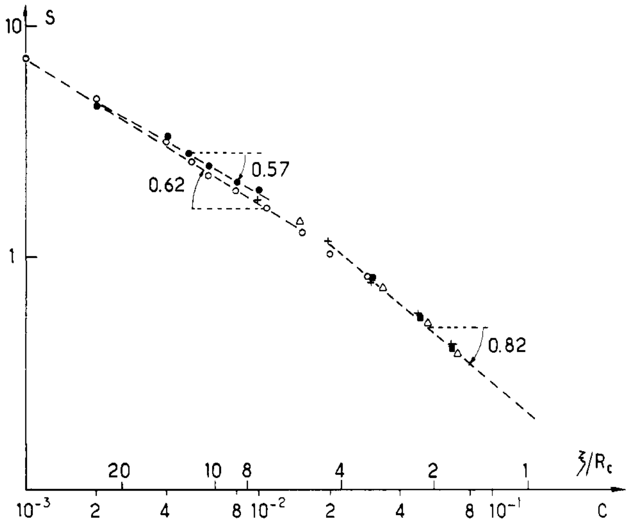

Figure 1. Log s (svedbergs) vs. log c (g/cm^3) for polysterene in the semidilute concentration range: ■ ($M_w = 3.2 \times 10^5$) + ($M_w = 6.2 \times 10^5$), Δ ($M_w = 9.6 \times 10^5$ in bromobenzene) from ref 15 and ○ ($M_w = 1 \times 10^7$ in bromobenzene) and ● ($M_w = 3.8 \times 10^6$ in benzene) this work.

Transposing the dependence of ν_D and ν_G with N/N_c,[7] or more exactly with $R_G/R_c \sim (N/N_c)^{1/\nu}$, to a dependence with ξ/R_c, one expects that, with increasing c (i.e., decreasing ξ) β' should continuously increase from 0.5 ($\xi/R_c \gg 1$, $\nu_D = \nu_G = 0.6$) to 0.625 ($\nu_G = 0.6$, $\nu_D = 0.5$, $\xi/R_c \sim$ 2–3) and up to 1 ($\xi/R_c < 1$, $\nu_D = \nu_G = 0.5$).

It is the purpose of this paper to report new experiments made in a large concentration range to confirm that the differences in the values of β' are indeed related to the concentration range and to check that the corresponding values of ξ/R_c support the above description.

Materials and Methods. Two anionically polymerized samples of polystyrene (PS) have been used, one of $M_w = 10^7$ (Polyscience) and the other of $M_w = 3.8\ 10^6$ (Waters standard sample).

The poly(acrylamide) (PAM) fraction of $M_w = 8.2 \times 10^6$ has been prepared by fractionation of a commercial sample.[18]

The experimental sedimentation procedures were similar to those previously described.[15] All runs were performed at 56100 rpm, the cell being filled with solution up to the same level to ensure equal "solvent quality" at the bottom.

A solvent with a low index of refraction increment ($dn/dc \sim 0.042$ for PS in bromobenzene) permits measurements on a very large concentration range up to $\sim 10^{-1}$ g/cm^3. It is much more limited for PS in benzene or PAM in water.

Results and Discussion

The results relative to PS in benzene and bromobenzene have been plotted in Figure 1 together with the results of a previous study[15] on lower molecular weight samples in a high concentration range. A change in slope in the log s–log c relation appears clearly on this plot. Although there is probably a continuous curvature, we have fitted the points in the two regions $c < 1\%$ and $c > 2\%$ with straight lines. In the low concentration range, $\beta' = 0.57$ for PS in benzene, in excellent agreement with the result of Destor and Rondelez,[11] and $\beta' = 0.62$ for PS in bromobenzene. Despite this small difference and considering the similarity in intrinsic viscosity, we shall not distinguish between the two solvents. The new points for bromobenzene in the high concentration range confirm the value $\beta' = 0.82 \pm 0.03$ previously reported.

In order to compare with the above predicitions, the c scale has to be transformed into a ξ/R_c scale. This is achieved by the following steps: (a) R_c is calculated from the comparison of the radius of gyration–molecular weight relation in a good and in a Θ solvent. For PS we have $R_G = 0.145M^{0.6}$ in benzene at 20 °C and $R_G = 0.347M^{0.5}$ in cyclohexane at 34 °C.[18] The two values become equal at $M^* = (0.347/0.145)^{10} = 6160$. The relation of M^* to M_c is easily derived from the asymptotic expression of R_G calculated for the statistic given in relation 1.

$$R^2{}_G = \frac{1}{(2\nu + 1)(2\nu + 2)} N_c{}^{1-2\nu} N^{2\nu} a^2 \tag{13}$$

It becomes equal to the Θ value

$$R^2{}_G = \frac{1}{6} N a^2$$

at

$$\frac{N^*}{N_c} = \left[\frac{(2\nu + 1)(2\nu + 2)}{6} \right]^{1/(2\nu-1)} \tag{14}$$

Therefore $M^*/M_c = 2.2$. This is a useful relation to evaluate N_c from published data on a large number of polymer solvent systems.

For polystyrene in benzene $M_c \sim 2800$ and $R_c = 18$ Å.

(b) Taking the radius of gyration of the 1×10^7 sample in benzene or bromobenzene from relation 11, $R_G = 2300$ Å, we calculate ξ from relation 4. Since it implies that $\xi = R_G$ at C^*, it is natural to use in the calculation of C^* a value of $k_2 = 6$ which corresponds approximately to a close packing of spheres. The arbitrariness in this choice stresses however the semiquantitative nature of our comparison. We find that

$$c^* = 2.3 \times 10^{-4}\ \text{g/cm}^3$$

Values of ξ/R_c have then been calculated and reported above the log c scale of Figure 1. To precise orders of magnitudes at $c = 10^{-2}$ g/cm^3, $\xi \sim 135$ Å and $\xi/R_c \sim 7.5$, and at $c = 10^{-1}$ g/cm^3 $\xi = 24$ Å and $\xi/R_c \sim 1.3$. It is clear that for concentrations below 1%, ξ/R_c is in the range where $\nu_G = \nu$ and $\nu_D < \nu$, justifying values of β between 0.5 and 0.625. At higher concentration ξ/R_c is sufficiently small to expect $\nu_D = 0.5$ and $0.5 < \nu_G < 0.6$. $\beta' = 0.82$ would correspond to $\nu_G \sim 0.54$.

An exact calculation of β' as a function of c would require a more exact knowledge of the real crossover around both N_c and C^*. The first one is more easily studied using a poor solvent–polymer system with a large N_c. Consequently large values of β' should already be present at much lower concentrations. This is the case for the poly(acrylamide)–water system for which the log s–log c relation is given in Figure 2.

For that polymer the following radius of gyration–molecular weight relations have been found: $R_G = 0.0749M^{0.64}$ in water–0.1 M NaCl, and $R_G = 0.39M^{0.50}$ in a water–methanol Θ solvent.[17,19]

The connection between the unusual excluded volume exponent 0.64 and the diffuse crossover will be analyzed elsewhere.[21] We just notice here the high value of $M^* = (39/7.49)^{1/0.14} \sim 130.000$. Using for a semiquantitative comparison the relation between M^* and M_c derived for an abrupt crossover, we find $R_c = 95$ Å. Using the value of $R_G = 1990$ Å directly obtained by light scattering for the fraction of $M_w = 8.2 \times 10^6$, we calculate $c \sim 2.9\ 10^{-4}$ g/cm^3. Therefore for $c = 10^{-2}$ g/cm^3, $\xi = 140$ Å and $\xi/R_c \sim 1.5$, and for $c = 10^{-3}$ g/cm^3, $\xi = 790$ Å and $\xi/R_c \sim 8.3$. The data obtained in the range $10^{-2} > c > 10^{-3}$ g/cm^3 correspond to small values of ξ/R_c, and β' is found equal

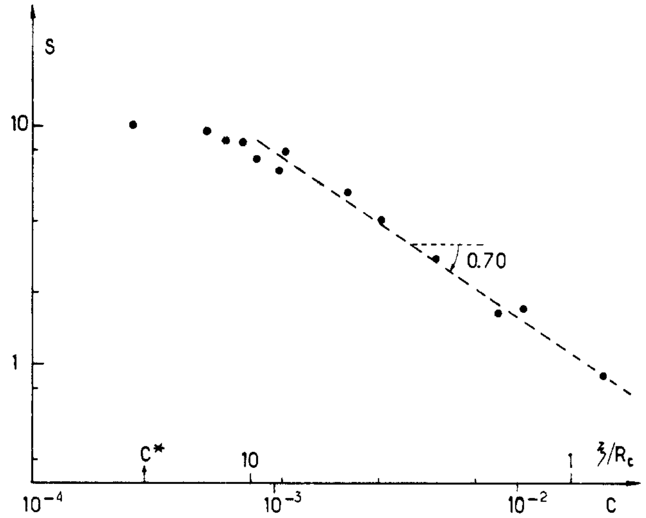

Figure 2. Log s (svedbergs) vs. log c (g/cm^3). For poly(acrylamide) $M_w = 8.2 \times 10^6$ in water–0.1 M NaCl solution in the semidilute concentration range $c > c^*$.

to 0.7 which from relation 10 could correspond to $\nu_D = 0.5$ and $\nu_G = 0.57$.

Conclusion

Forcing the dynamic properties of semidilute solutions into the scaling laws predicted from the blob hypothesis may be in very many cases dangerous. Consistency between the dilute and semidilute results can only be expected if the experiments are performed in similar conditions, i.e., if the range of molecular weights (in the dilute domain) and concentrations (in the semi dilute domain) define equivalent values for the radius of gyration R_G and blob size ξ. Even in good solvents, this generally requires very high molecular weight samples to be used for the study of the semidilute behavior. A more exact consideration of the influence of short distance statistics in the blob hypothesis would be required to describe quantitatively the full concentration dependence.

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Correlation between ^{13}C NMR Chemical Shifts and the Conformation of Polymers. 2. An Improved Method of Calculation

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ABSTRACT: An improved semiempirical method for calculating the ^{13}C NMR chemical shifts of methyl and methylene carbons is presented. The mixture of diastereomers of 2,4,6,8,10,12-hexamethyltridecane (HMTD), ^{13}C enriched on carbon C$_7$, was prepared, and the observed ^{13}C NMR spectrum of HMTD is reported here, together with the assignment of each tetrad resonance of carbon C$_7$. The conformational origin of the stereochemical shifts of polypropylene is qualitatively discussed. It is found that the quantitative agreement between calculated and observed chemical shifts for both the CH$_2$ and CH$_3$ carbons in polypropylene model compounds is improved by taking into account the effect of distortions of the dihedral angles on the γ shielding parameter. The value of γ is found to be considerably smaller for the CH$_2$ carbon than for CH$_3$, suggesting caution in transferring such best-fitting parameters from one carbon to another.

In a previous paper,[1] hereafter referred to as paper 1, a simple statistical treatment was proposed for the calculation of the methyl carbon stereochemical shifts in polypropylene and its model compounds. The method was based on the assumption that the chemical shift of a methyl carbon is determined by the average number of γ gauche and δ syn-axial interactions and on the three-state rotational isomeric model. This method allowed a satisfactory interpretation of the methyl spectrum of 3,5,7,9,11,13,15-heptamethylheptadecane (HMHD); however, in paper 1 we observed that the calculation did not predict wider isotactic bands than syndiotactic bands, as found experimentally, and that the best-fitted γ parameter had a small temperature dependence. We remarked that these facts were likely to be ascribed to the oversimplifications of the three-state model and concluded that the knowledge of the dependence of the γ and δ parameters as functions of the torsional angles was a preliminary requirement in order to fruitfully use more sophisticated statistical models.

Improvements of such semiempirical methods appear necessary for predicting the chemical shifts within (or close to) the limits of current experimental errors. In a recent paper,[2] Tonelli reduced the mentioned defects of our previous calculations[1] by using the Suter–Flory[3] statistical model and disregarding the δ effect; however the overall

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