Velocity Sedimentation in the Semidilute Concentration Range of Polymers Dissolved in Good Solvents

Geneviève Pouyet and Jean Dayantis*

C.N.R.S., Centre de Recherches sur les Macromolécules, 67083 Strasbourg Cedex, France.

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ABSTRACT: The concentration dependence of the sedimentation velocity was observed for two polymers in the semidilute concentration regime. Three polystyrene fractions in the molecular weight range 3.2–9.6 × 10^5 were observed in bromobenzene and one PMMA sample of molecular weight 1.3 × 10^6 was observed in benzene. The results show that the sedimentation velocity s becomes independent of molecular weight when the chains entangle and that s scales with concentration c ($s \simeq c^{-\alpha}$). The observed scaling exponent $\alpha = 0.82$ is somewhat larger than that expected on the basis of the de Gennes model of sedimentation of entangled flexible polymers.

In the past few years considerable progress has been made in the study of semidilute polymer solutions, both from the theoretical and experimental viewpoints.[1-4] des Cloizeaux in particular predicted that for good solvents in the semidilute (see below for the definition) range of concentration the osmotic pressure should vary as the $^9/_4$ power of the concentration c.[1] This prediction is apparently verified by experiment.[5] The present paper is concerned with the experimental verification of a prediction made by de Gennes[6] regarding the sedimentation behavior of semidilute solutions of polymers in good solvents.

The semidilute range of concentration is defined as that for which the concentration c lies between two concentrations c^* and c^{**}:

$$c^* < c < c^{**}$$

The critical concentration c^* is approximately the chain overlap concentration:[2,3]

$$c^* \sim M/R^3 \tag{1}$$

where M is the molecular weight of the polymer and R its radius of gyration. More generally, in a space of dimensionality d where the excluded volume exponent is ν, we should have

$$c^* \sim N^{1-\nu d} \tag{2}$$

where N is the number of repeat units in the polymer.

Since in good solvents $R \sim M^{0.6}$ (Flory law), c^* varies with molecular weight as $\bar{M}^{0.8}$. For example, for polystyrene in benzene $c^* \sim 1\%$ for $M = 1 \times 10^6$ and about 7% for $M = 1 \times 10^5$. As we shall not be concerned here with concentrated solutions, we shall not discuss the somewhat subtle distinction between semidilute and concentrated solutions. Now, the de Gennes' prediction[6c,d] is that in good solvents and the semidilute range the sedimentation coefficient s should be independent of molecular weight and vary as the −0.50 power of concentration. For the reader not familiar with scaling procedures, it may be useful to give a short and simplified outline of how the above result may be derived.

Consider a polymer dissolved in a good solvent, the concentration being greater than the critical concentration c^* where molecules begin to overlap. In this solution, the continium formed by the entangled macromolecules can be divided into spheres or "blobs" of radius equal to the screening length ζ.[6,7] This sceening length[17] is generally a function of the concentration c of the solute. The c dependence of ζ may be determined as follows:

If a single chain is considered in the semidilute solution its mean square radius of gyration is given by

$$\langle R^2 \rangle = \frac{N}{g}\zeta^2 = a\zeta^2 \tag{3}$$

where N is the number of repeat units in the chain and g the mean number of repeat units inside each blob. Equation 3 arises from the fact that beyond the sceening length ζ the statistical units (i.e., the blobs) are assumed to be uncorrelated,[17] therefore, the $a = N/g$ blobs should obey Gaussian statistics. On the other hand, segments in the interior of a blob are not sceened and therefore obey excluded volume statistics, so that we can write

$$\zeta^2 \sim g^{2\nu}b^2 \tag{4}$$

and

$$\langle R^2 \rangle \sim Ng^{2\nu-1}b^2 \tag{5}$$

where ν is the excluded volume exponent and b the length of the repeat unit. The assumption is now made[3] that the number of repeat units g inside a blob is a power function of the concentration c:

$$g \sim c^x \tag{6}$$

The physical justification of this assumption lies in the analogy which has been established between chain statistics and the correlation length in a ferromagnet near critical conditions.[1,2,8] A detailed account of this analogy is outside the scope of the present paper and the reader is referred to the original publications. Entering eq 6 into eq 5 we obtain

$$\langle R^2 \rangle \sim Nc^{(2\nu-1)x} \tag{5$'$}$$

At the particular concentration c^*, using eq 2 we obtain

$$\langle R^2 \rangle \sim N^{(1-\nu d)(2\nu-1)x+1} \tag{5$''$}$$

Now, at this particular concentration c^* chain statistics should obey eq 5″ but at the same time the usual excluded volume relationship (crossover point between two regimes):

$$\langle R^2 \rangle \sim N^{2\nu} \tag{7}$$

Equating the exponents in eq 5″ and 7 one finds

$$x = (1 - \nu d)^{-1} \tag{8}$$

From eq 8 using eq 4 and 6 one immediately finds

$$\zeta^2 \sim c^{2\nu/(1-\nu d)} \tag{9}$$

In good solvents $\nu = {}^3/_5$, so that, taking $d = 3$, we find from eq 8 and 9

$$x = -{}^5/_4 \tag{8$'$}$$

$$\zeta^2 \sim c^{-3/2} \tag{9$'$}$$

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This c dependence of ξ has been observed by neutron scattering experiments.[2]

At this point we may introduce the sedimentation coefficient s as proportional to a mass M over a friction f:(9)

$$s \sim M/f \qquad (10)$$

If we assume that in the semidilute range the sedimenting unit to be considered is the blob (instead of the individual molecules in the dilute range), then $M = c\xi^3$; if this blob is impenetrable to solvent molecules, then the friction f is proportional (Stokes' law) to ξ, so that

$$s \sim c\xi^2 \sim c^{-1/2} \qquad (11)$$

Relation 11 is the de Gennes expression[6] for the sedimentation coefficient of polymers dissolved in good solvents and considered in the semidilute range of concentration ($c > c^*$). It expresses in particular the fact that for $c > c^*$ the sedimentation coefficient should be independent of the molecular weight of the dissolved polymer.

An equivalent derivation may be given for polymers dissolved in Θ solvents. In this case the de Gennes prediction is

$$s \sim c^{-1} \qquad (12)$$

The experimental work reported here involves testing eq 11. In particular we wish to establish: (a) the independence of s and M in the semidilute range; (b) the relevance of a power relationship between s and c,

$$s \sim c^{-\alpha} \qquad (13)$$

and (c) if point b is fulfilled, the numerical agreement between predicted and experimentally determined values of α.

Point a is a necessary but not sufficient condition for the blob picture to hold. It is a necessary condition because it was shown theoretically[1] and experimentally established[2] that the screening length ξ is independent of the molecular weight M. If then, following the de Gennes approach, blobs of radius ξ sediment independently, the sedimentation coefficient s should be independent of M. But the condition is not sufficient, because other physical pictures may also lead to M being independent of s. In fact, this is a well-established experimental fact,(10a–d) so that our results, as far as this point is concerned, are to be considered as one more test of a well-known result.

We may point out that if we assume that in the semidilute range the osmotic pressure "sees" blobs, instead of molecules in the dilute range, we should have, at least as a first approximation

$$\pi/c \sim T/c\xi^3 \qquad (14a)$$

or

$$\pi \sim \xi^{-3} \sim c^{+2.25} \qquad (14b)$$

This is the des Cloizeaux relationship,[1] first derived by this author using heavy theoretical procedures. Thus, in a static experiment, the blob image seems to be a relevant one.

Materials and Methods

Three fractions of anionically polymerized polystyrenes (PS) have been used. The characteristics of these fractions, as determined by gel permeation chromatography (GPC), were as shown in Chart I. Solutions in bromobenzene of the above fractions at concentrations (g mL^{-1}) up to 7% were made and centrifuged in a Beckman Model E analytical ultracentrifuge. We used Prolabo reagent grade bromobenzene without further purification. Bromobenzene was chosen as solvent because it is a good solvent for polystyrene[11] and because the index increment of polystyrene is rather small in this solvent, i.e., 0.042.[12] If a 3 mm cell is used, it is possible to centrifuge polystyrene solutions at 56 100 rpm and concentrations of up to 7% without the appearance of a black strip in the schlieren optics pattern (which shows that light rays are deviated outside the scope of the focusing lens). However, for the highest molecular weight used (M_w = 9.6 × 10^5) and at the highest concentration ($c \sim$ 70 mg/mL), a black strip did appear which would not disappear with time at 56 100 rpm. Therefore, the result for the sedimentation coefficient for this particular solution is given in Table I in parentheses.

Chart I

fraction	$M_w \times 10^{-5}$	M_w/M_n
1	3.2	1.06
2	6.2	1.15
3	9.6	1.12

Table I

	sample 1, $M_w = 3.2 \times 10^5$		sample 2, $M_w = 6.2 \times 10^5$		sample 3, $M_w = 9.6 \times 10^5$	
run	c[a]	s[b]	c[a]	s[b]	c[a]	s[b]
A	0.99_1	1.24	0.99_1	1.78		
B			1.96_4	1.13	1.48	1.43
C	2.98_6	0.82_7	2.91_6	0.80	3.40	0.75
D	4.78_0	0.56_0	4.78	0.56_6	5.27	0.53
E	6.62_9	0.41_6	6.57_2	0.41_6	7.15	(0.39)

[a] g mL^{-1} × 10^2. [b] svedberg.

Photographs of the schlieren pattern were taken every 16 or 32 min as appropriate. The plates were analyzed using a Nikon Model 6C profile projector. The sedimentation coefficient was determined as usual by making a log r vs. t plot (r being the distance from the center of rotation of the peak of the schlieren pattern) and measuring the slope of the resulting straight line. It is known[13] that, especially for polydisperse systems, the sedimentation coefficient should preferably be determined by following the evolution with time of the second moment of the schlieren pattern. However, as our samples were reasonably monodisperse and our speed of rotation high, which resulted in sharp boundaries, we have assumed that using the peaks of the schlieren patterns to measure sedimentation coefficients would introduce only negligible errors.

The concentrations of the solutions were measured as follows: A given amount of polymer was weighed and then 1 mL of bromobenzene added. The volume of the solution was calculated taking for $\bar{v}_2$, the partial specific volume of polystyrene in bromobenzene, the value of 0.924.[11,14] Excess volumes of mixing were thus neglected. The weighed amount of polymer was then divided by the calculated volume of the solution to obtain the concentration in g mL^{-1}. On the other hand, since in our experiments sedimentation was in fact flotation, correction of the concentration for compression of the solution has to be considered. At the bottom of a 1-cm column of bromobenzene the pressure at 56 100 rpm approaches 400 bars. Taking 6.7 × 10^{-11} cm^2 dyn^{-1} for the isothermal compressibility of bromobenzene at atmospheric pressure and 25 °C,[15] one finds that the compression of pure bromobenzene is of the order of 2.5%. However, as shown in Figure 1, we are primarily interested in this work in plotting log s vs. log c, and as all our runs were performed at 56 100 Hz, the pressure at the bottom of the cell was very nearly the same in all our runs. The same remark applies for the compression, since to a good approximation the difference of compressibility of the various solutions may be neglected. Therefore, all concentrations at atmospheric pressure are multiplied during flotation by a nearly constant factor, and this will result in a slight translation to the right of all points in a log–log plot. This has no effect on the slope of the straight line of Figure 1. Therefore, changes of concentration due to compression were not taken into account, since the exact determination of the concentration at the bottom of the cell during each run would be difficult and would yield negligible benefit regarding the reliability of the results.

In addition to the three PS fractions, a syndiotactic poly(methyl methacrylate) sample has also been studied in solution in benzene.

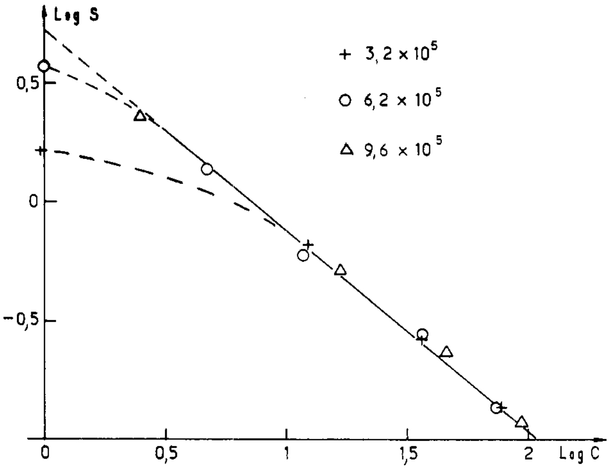

Figure 1. The log s vs. log c plot for three polystyrene fractions. log c^* (c^* being the critical concentration where ideally the semidilute range begins) takes respectively for the fractions of molecular weight 3.2×10^5, 6.2×10^5, and 9.6×10^5 the values 0.88, 0.35, and 0.0. These correspond to c^* values of 2.4%, 1.4%, and 1.0%. It is seen that the two points at the left of the figure are outside the semidilute range. If these are not considered, the plot is a straight line of slope −0.82.

Table II

c, g mL^{-1} × 10^2	1.02	2.02	4.83	6.72	8.40
s, svedberg	3.44	2.05	1.02	0.75	0.62

This sample was very polydisperse ($M_w = 1.3 \times 10^6$; $M_w/M_n \sim 7$), and was used without being fractionated. Concentrations were determined as previously, using the value 0.817 for the partial specific volume of syndiotactic PMMA in benzene. This is the mean of three values for atactic PMMA given in the Polymer Handbook.[16] Small deviations from the above value would not introduce significant error in our calculations.

All runs were performed at 25 °C.

Results

The results for the polystyrene samples are summarized in Table I.

From the results in Table I the plot of Figure 1 was drawn. It is seen that to a good approximation the sedimentation coefficient is independent of molecular weight in the semidilute range of concentration (the two points at the left of the figure are not in the semidilute range). This is in accord with the blob theory. On the other hand, the log–log plot of this figure yields the following values for the exponent α in eq 13 for samples 1, 2, and 3, respectively: 0.86, 0.81, 0.81. The mean value for the three samples is 0.82.

The results for the syndiotactic PMMA sample in benzene are given in Table II.

Although the PMMA sample was very polydisperse, the results for the PS fractions, showing, in the semidilute range, independence of the sedimentation coefficient with polymer molecular weight, encouraged us to calculate the exponent α in eq 13 for PMMA in benzene. It is found that $\alpha = 0.82 \pm 0.03$.

Discussion

Sedimentation in the semidilute range has been described in the past as equivalent to the flow of the solvent through a porous plug. This equivalence was first recognized by Signer and Egli[10b] and Fessler and Ogston[10c] and subsequently used by Mijnlieff and Jaspers.[10d] In this porous plug picture, the solvent is forced through disordered "channels" as the polymer network sediments. It seems that the main difference between this picture and that of de Gennes is that in the latter the "channels" form in an orderly fashion around the spherical blobs of radius ξ, the interior of the blob being impenetrable to the solvent. The possible physical pictures for the sedimentation of a polymer network are therefore: (a) solvent forced through disordered channels in a porous-plug-like material; (b) solvent flowing around "hard" spheres of radius equal to the sceening length ξ; and (c) the intermediate situation, where the solvent mainly flows around the blobs but is also allowed to some extent to penetrate the blobs. (If this penetration of the blobs is too important we are led back to case a.) Our experimental results cannot distinguish between cases a and c, but seem to exclude case b. Our value for α, i.e., 0.82, is too far from the expected theoretical value of 0.50 in case b to be due to experimental errors. Furthermore, even if the excluded volume exponent ν is recalculated using the Mark–Houwink viscosity coefficient for polystyrene in bromobenzene[11] (instead of taking the theoretical value of $^3/_5$), the theoretical value for α is somewhat increased but still remains below 0.60. The difference between 0.60 and 0.82 cannot be ascribed, as already pointed out, to experimental errors.

We consider the fact that the two systems investigated, polystyrene–bromobenzene and poly(methyl methacrylate)–benzene, give the same value, 0.82, for α to be fortuitous. Other systems would probably yield different values for α. Therefore, further experimental investigations are needed, both to increase the number of systems and the concentration range investigated.

The findings of the present paper may be summarized as follows: (a) A power relationship exists between the sedimentation coefficient s and the concentration c in the semidilute range of concentration. Such a power relationship is readily explained using scaling procedures, whereas this does not seem to be the case using previous procedures. (b) For polymers dissolved in good solvents, the exponent for the power law does not fit the theoretically predicted value.

Summary

Three polystyrene fractions of respective molecular weights 3.2×10^5, 6.2×10^5, and 9.6×10^5 and a polydisperse syndiotactic poly(methyl methacrylate) sample of molecular weighth 1.3×10^6 have been centrifuged in a Beckman analytical ultracentrifuge. The solvent for the polystyrene fractions was bromobenzene and that for the poly(methyl methacrylate) sample benzene. The concentration range studied was the semidilute range, which begins where molecules start to overlap. From the results a log s (s = sedimentation coefficient) vs. log c (c = concentration) plot was drawn which showed: (a) that the plot is a straight line, so that, to a good approximation, s is a power function of c; and (b) that in the equation $s \sim c^{-\alpha}$, $\alpha = 0.82 \pm 0.03$. The first of these conclusions supports the de Gennes use of "blobs" (or correlation lengths) to deal with the sedimentation of flexible macromolecules in the semidilute range of concentration. The observed value of α, however, is not in accord with the expected theoretical value of 0.50 for polymers dissolved in good solvents.

Note Added in Proof. If the recent results by B. Nyström et al. (*Eur. Polym. J.*, **13**, 683 (1977)) for polystyrene in toluene are plotted the same way, a straight line is obtained in the semidilute concentration range, except for two erratic points on both sides of the straight line. The slope of the straight line is −0.75, so that $\alpha = 0.75$. There are also the results of P. F. Mijnlieff and W. J. M. Jaspers (ref 10d) for poly(α-methylstyrene) (PAMS) in toluene, using a high molecular weight ($M_w = 6.5 \times 10^6$). The temperature is not precisely constant in these experiments, but if a point at 30.2 °C is not taken into account, the seven most concentrated solutions, quite certainly lying in the semidilute concentration range, have been centrifuged at a nearly constant temperature (24.5–25.1 °C). These solutions yield a good straight line of slope −0.64. The conclusion which may be drawn from these results and our own results is that in the semidilute concentration range the sedimentation coefficient s obeys a $c^{-\alpha}$ power law, where the exponent α takes a spectrum of values with presently ill-defined limiting values, but which extends for polymers dissolved in good solvents at least in between 0.64 and 0.82.

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(17) The statistical definition of the sceening (or correlation) length ζ originates in the density–density correlation function. In a Θ solvent ζ is defined from this function as[6d] $\sim \langle c(0)c(r) - c^2 \rangle = C^{\mathrm{te}} \cdot c^2\ (b/r) \exp(-r/\zeta)$, where the corner brackets represent a time average; r is the distance between the two points where the concentration is considered. In a good solvent, the defining relationship is of the same form, but of course ζ is a different function of r. Now, in the blob picture, correlations are assumed zero beyond the screening length ζ. This is a convenient approximation and is indeed introduced as such by de Gennes[6d] in a first qualitative derivation of the collective diffusion coefficient and the permeability (which is closely related to the sedimentation coefficient). However, in the above reference, a more rigorous derivation is given which leads to the same results.

Viscoelastic Properties of a Dilute Polymer Solution at Elevated Pressures and Comparison with Molecular Models

Robert G. Rein, Jr.[1]

High Pressure Laboratory, University of Oklahoma, Norman, Oklahoma 73069.

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ABSTRACT: Measurements at 98.9 °C (210 °F) and pressures to 172 MPa (25 000 psi) with an oscillating quartz crystal apparatus show that the shear storage modulus and dynamic viscosity of a 4 wt % solution of poly(alkyl methacrylate) in a base oil can be predicted at high pressures by using appropriate values of pressure-dependent parameters in the Zimm model for dilute polymer solutions. Measurements on the base oil gave no evidence of viscoelastic behavior at 98.9 °C (210 °F) and pressures to 276 MPa (40 000 psi).

There have been few measurements of the viscoelastic properties of dilute polymer solutions at elevated pressures and there has been little discussion of the applicability of molecular models, such as those by Rouse[2] and Zimm,[3] to calculation of viscoelastic properties at elevated pressures. Measurements that have been made at elevated pressures have included solutions of polyisobutylene,[4] polymethacrylates,[4] and poly(alkyl methacrylate)[5] in base oils at pressures to 104 MPa (15 000 psi). These measurements indicate viscoelastic behavior over the entire pressure range. However, the relative contribution of elasticity to the overall behavior decreased with pressure.[5] It was also suggested that the hydrodynamic interaction between the polymer and the solvent did not change over this pressure range,[4] so no change in interaction would have to be considered in applying molecular models to this pressure range. However, none of the reported data were compared with predictions of molecular models. This paper reports data obtained at pressures to 172 MPa (25 000 psi) for a 4 wt % solution of poly(alkyl methacrylate) and compares the data with the predictions of the Rouse and Zimm models.

The Rouse and Zimm models describe the frequency-dependent behavior of the shear storage modulus, $G'(\omega)$, and the dynamic viscosity, $\eta'(\omega)$, of dilute solutions of polymers with a single molecular weight in a Θ solvent (a poor solvent which causes negligible expansion of the polymer by solvent action). The models differ in the way they treat the frictional interaction between the polymer and solvent. In the Rouse, or free-draining, model the viscous resistance of a hypothetical subdivision of the polymer is unaffected by the presence of other subdivisions. In the Zimm, or nondraining, model viscous resistance is dominated by the presence of the other sub-