strain criterion is by itself not sufficient to specify the conditions for nonlinear behavior. In addition, the inverse rate of deformation $(d\gamma(t)/dt)^{-1}$ must also be large compared with some material response time, such as $\eta_0 R_0$. For these samples studied here, for example, it is necessary for $\eta_0 R_0 \kappa$ to be less than 0.01 to ensure linear viscoelastic behavior. For stresses which lead to larger steady state rate of shear κ, the creep behavior will become nonlinear when $\gamma(t) > \gamma^*$. The molecular origin of this behavior is presently a matter for speculation. Following Graessley's[16] analysis of η_κ, we assume that linear viscoelastic behavior will obtain so long as the κ is much less than the reciprocal of a time constant associated with the diffusion processes tending to maintain the molecular distribution characteristic of the quiescent state and that for larger κ the entanglement density is affected with increasing κ. Thus, for large K, approximately equal to $\kappa > (100\eta_0 R_0)^{-1}$ for solutions studied here, nonlinear creep behavior develops when the molecular distribution is perturbed so far from the quiescent state that it cannot return to that state in the time available as limited by the deformation rate. This condition, which is given by the critical strain γ^*, may be related to the deformation required to achieve a given separation of the molecular centers of gravity.

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Diffusion of Polystyrene in Binary Solvents Near the Theta State

Samran Lacharojana[1] **and David Caroline***

School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd LL57 2UW, U.K.

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ABSTRACT: The diffusion coefficient D of polystyrene near the unperturbed state has been measured by photon-correlation spectroscopy in mixtures of carbon tetrachloride and methanol as a function of polymer molecular weight M (33 000 to 10^6) and concentration c (up to 10 mg/mL) for three solvent compositions with CCl_4 volume fractions $\phi = 0.815$, 0.8025, and 0.790. The hydrodynamic radius a varies as M^b where b decreases from 0.524 through 0.503 to 0.469 (±0.005) as ϕ changes from 0.815 through 0.8025 to 0.790. Thus the intermediate composition represents the "diffusion theta state" with a varying as $M^{1/2}$. The slope of the D–c plots also indicates that A_2 is closest to zero for $\phi = 0.8025$. All three plots of log a against log M are linear and intersect at $M = 80\,000$, so that for $M < 80\,000$, a is greater for the subtheta molecule ($\phi = 0.790$) than the supertheta ($\phi = 0.815$). These results are at variance with the work of Dondos and Benoit who found that A_2 was zero at $\phi = 0.815$ and $[\eta]$ varied as $M^{1/2}$ for $\phi = 0.790$. They also observed nonlinear Stockmayer–Fixman plots which they attributed to a molecular-weight dependence of the preferential adsorption.

In recent years a number of investigations of the equilibrium and dynamic properties of polystyrene molecules in mixed solvents have been carried out using light-scattering and viscometry techniques.[2,3] From such measurements information has been obtained on the second virial coefficient A_2 of the solution, the radius of gyration of the polymer molecule, and the preferential adsorption λ' shown by the polymer for one component of the mixed solvent; λ' is the volume occupied by the excess molecules of the good solvent surrounding a polymer molecule divided by the mass of the polymer molecule. In particular, for systems exhibiting relatively large values of λ', the results of a light-scattering investigation by Dondos and Benoit[2] led them to propose that λ' is a function of polymer molecular weight M through a term depending on polymer segment density: $\lambda' = \lambda'_\infty + A/M^{1/2}$, where A is a constant and λ'_∞ is the limiting value of λ' at large M.

One system of interest which they investigated was polystyrene in mixtures of carbon tetrachloride (solvent) and methanol (precipitant) at 25 °C for volume fractions of carbon tetrachloride ϕ around 0.8. They found that λ' was large for this system, with $\lambda'_\infty = 0.49$ cm^3 g^{-1} and $A = 35$ cm^3 g$^{-1/2}$ for $\phi = 0.79$, and $\lambda'_\infty = 0.43$ cm^3 g^{-1} and $A = 30$ cm^3 g$^{-1/2}$ for $\phi = 0.815$. Furthermore, A_2 was zero when $\phi = 0.815$ whereas the intrinsic viscosity $[\eta]$ varied as $M^{1/2}$ for $\phi = 0.79$. For a single solvent these two conditions are associated with the Flory theta state and coincide at the theta temperature. The failure of these conditions to coincide at a particular mixture composition for the given temperature was explained by Dondos and Benoit in terms of the preferential adsorption which causes the composition of the solvent within the molecule to be different from that outside. As a result the intramolecular and intermolecular segment interactions will be different. The variation of $[\eta]$ as $M^{1/2}$, which implies an unperturbed molecular state, will occur at a different solvent composition to the condition $A_2 = 0$, which corresponds to a zero excluded volume term between molecules. Thus they concluded it was not possible to define a true theta state for a mixed solvent

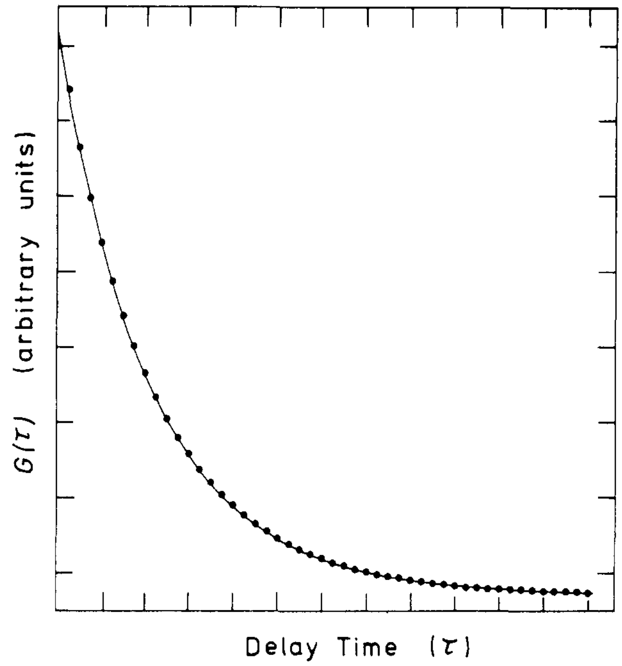

Figure 1. A typical correlation function showing the function $A \exp(-\Gamma\tau) + C$ fitted to the experimental points.

showing high solvation effects. The discontinuity in slope which they observed in the Stockmayer–Fixman plots was also attributed to the rapid increase in λ' as the value of M falls below about 200 000.

We have measured the translational diffusion coefficient D of polystyrene in this mixed solvent with a reproducibility of 1% using photon-correlation spectroscopy. The measurements were made at 25 °C for polymer molecular weights between 33 000 and 10^6 as a function of polymer concentration in three solvent mixtures with $\phi = 0.815$, 0.8025, and 0.790.

This investigation was carried out to complement previous work discussed above and to see whether the anomalous effects observed there have counterparts in the diffusion behavior. In particular we wished to examine how D_0 (D at infinite dilution) varies with M and ϕ, to enquire whether D_0 varies as $M^{1/2}$ at the same composition where $[\eta]$ varies at $M^{1/2}$, and also to see if there is any discontinuity of slope in the log D_0 against log M plots.

Experimental Section

Samples. Polystyrene samples with weight-average molecular weights $\overline{M}_w$ in the range 33 000 to 670 000 were obtained commercially from the Pressure Chemical Co.; the sample with $\overline{M}_w = 10^6$ was kindly given by Professor J. M. G. Cowie of the University of Stirling. The samples had narrow molecular-weight distributions with polydispersity factors $\overline{M}_w/\overline{M}_n$ (the weight-average to number-average molecular weight) shown in Table I.

The value of $\overline{M}_w$ (200 000) quoted for batch No. 1c would appear to be too high. The diffusion coefficient at infinite dilution D_0 has been determined for this sample in many different solutions in work in this laboratory, and in all cases a linear variation of log D_0 with log $\overline{M}_w$ is obtained *if* $\overline{M}_w$ *is taken to be 180 000. This was the value adopted in this work*.

Solutions. The solvent mixtures of carbon tetrachloride and methanol were prepared from Analar grade chemicals, and although they were made up at room temperature, allowance was made for the different volumetric expansions of the constituents to achieve the required composition at 25 °C. Three compositions were used, with volume fractions of carbon tetrachloride $\phi = 0.815$, 0.8025, and 0.790. For each polymer molecular weight and solvent composition, a stock solution was prepared of concentration around 10 mg/mL from which other concentrations were obtained by dilution. To ensure that the polymer dissolved completely, a solution was normally stirred gently for at least 48 h on a magnetic stirrer in a temperature-controlled bath at 30 °C. For the highest molecular weight ($\overline{M}_w = 10^6$) the solutions were generally prepared by gentle shaking to avoid the possibility of breaking the large molecule. However, one or two solutions were prepared by stirring, and no difference was detected in the decay values of the correlation functions.

Table I
Characteristics of Polystyrene Samples Supplied by the Manufacturer

Batch No.	Mol wt (by light scattering)	$\overline{M}_w/\overline{M}_n$
7b	33 000	1.06
4b	111 000	1.06
1c	200 000	1.06
3b	392 000	1.1
13a	670 000	1.1
	1 000 000	1.1

The solutions were clarified to remove dust by either filtering or centrifuging, and the results of these light-scattering measurements show no difference between the samples that were filtered and centrifuged. In the case of filtration, 2000 Å Millipore filters were used, and the process was carried out above 25 °C. In the case of centrifuging, the samples were subjected to 15 000 g for about 2 h at a controlled temperature setting of 28 °C for the whole period.

Throughout the preparation of the samples, great care was taken to ensure the cleanliness of the equipment used, and the solutions were finally transferred to clean optical cells of 1 cm path length.

Photon-Correlation Spectroscopy. This technique is now well established in measuring translational diffusion coefficients, and excellent accounts of the method exist.[4,5]

In this work a Coherent Radiation Model CR-2 argon–ion laser was used at a wavelength of 488 nm with an etalon frequency stabilizer in the optical cavity to ensure single-mode operation. The sample cell was contained in a constant-temperature enclosure which maintained the solution at 25 ± 0.05 °C over normal room-temperature fluctuations. The laser beam was focussed at the center of the cell to a beam diameter of about 100 μm, and the light scattered at a scattering angle $\theta = 90°$ was imaged on the photocathode of an ITT FW130 photomultiplier tube which had been chosen for its low level of after-pulsing and self-correlation. A slit in front of the photocathode effectively defined the scattering volume to be a 100 μm cube. Individual photons were detected and the resulting charge pulses were turned into standard square voltage pulses by a discriminator, amplifier, and pulse shaper before being fed into the correlator. A 48-channel digital photon correlator, manufactured by Malvern Instruments Ltd. (type K7023), was used to compute the clipped autocorrelation function of the scattered intensity.

Correlation Functions. Theory predicts that the correlation functions should be of the form $G(\tau) = A \exp(-\Gamma\tau) + C$, where A and C are constants for a particular set of experimental parameters, and $\Gamma = 2DK^2$ where K is the scattering vector; $K = 2k \sin(\theta/2)$ for an incident wave vector k (in solution). To maximize the efficiency of the data processing, the sample time of the correlator was set so that $\Gamma\tau_{\max}$ was about 4. In practice the data points of the correlation function were first divided by the normalization constant obtained from the correlator, which is the product of the total number of clipped and unclipped counts divided by the number of sample times in a run. The normalized data were computer fitted to a function of the theoretical form with A, Γ, and C as adjustable parameters, and the time-varying part of $G(\tau)$ was always found to be a good single-exponential function except for the low-concentration solutions for $\overline{M}_w = 33\,000$, which are weak scatterers, and where the mutual diffusion of the solvent molecules begins to become apparent for $c < 5$ mg/mL. A representative fit to the data points is shown in Figure 1. The angular dependence of Γ was also checked initially and found to be proportional to $\sin^2(\theta/2)$.

The values found for A ranged up to 0.2 and for C were around 1.0005 rather than the theoretical value of unity. Considerable attention has been given to this "misnormalization" although it is very small. The value of the misnormalization δ ($= C - 1$)) varied from run to run on the same sample, and this suggests that it may be due to minute traces of dust in the solution. On this basis the normalized data were fitted to the function $1 + \{\alpha \exp(-\gamma\tau) + \beta\}^2$ with α, γ, and β as adjustable parameters. This would be the form if there were sufficient dust particles in the scattering volume for the light scattered by them to be Gaussian and if their diffusion coefficients were much smaller

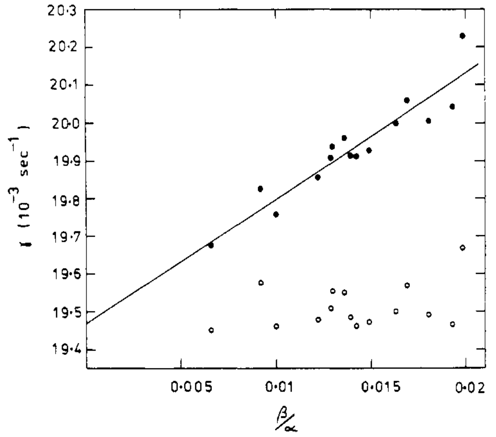

Figure 2. Values of γ (●) as a function of β/α for different runs on the same sample; corresponding values of $\Gamma/2$ are also shown (○).

than that of the polymer molecules. The coefficients α and β are proportional to the scattered intensities from the polymer and dust, which beat together. Force fitting this function to many sets of data from the same sample gave values for γ which increased linearly with β/α as shown in Figure 2. Such an effect would result from the absence of the cross term $2\alpha\beta\exp(-\gamma\tau)$ in $G(\tau)$.

Indeed, the simpler three-parameter fit $A\exp(-\Gamma\tau) + C$ applied to the same sets of data gave values of Γ which agreed within 1% from run to run and showed no dependence on the misnormalization δ; the values of $\Gamma/2$ are also plotted on Figure 2 below the values of γ corresponding to the same data sets. Furthermore, the extrapolation of the linear relation between γ and β/α of the previous analysis intersects the γ axis at the value of $\Gamma/2$ of the simpler analysis. For this reason the simpler fitting procedure was adopted in this work.

Pusey[6] has considered in detail the effect of the character of the dust on the correlation function, and shown that intermittent dust particles in the scattering volume have the effect of adding a constant term to $G(\tau)$ and a cross-term which, for a given mean intensity of dust-scattered light, becomes smaller relative to the constant term as the number of dust particles in the scattering volume is decreased and their size increased. This may be the explanation for the observed misnormalization, though dust particles were not visible in the beam.

The small misnormalization term precluded the use of the method of moments or cumulants in the data analysis to allow for polydispersity effects. However, Brown, Pusey, and Dietz[7] have shown that for the narrow fractions of polystyrene used in this work, particularly the low $\overline{M}_w$ samples, the time-dependent part of the correlation function is adequately described by a single exponential.

Results and Discussion

For each polymer molecular weight, the variation of D with polymer concentration c is shown for the three solvent compositions in Figure 3.

The polystyrene of $\overline{M}_w = 10^6$ could only be dissolved easily in the $\phi = 0.815$ mixture, and the concentrations used were much lower than those typically employed for the other molecular weights because of the small quantities available. However, since the scattered intensity is proportional to $\overline{M}_w$ as well as c, the intensity was adequate to obtain reliable values for D.

In contrast, much higher concentrations were used for the solutions of polystyrene of $\overline{M}_w = 33\,000$ since they are much weaker scatterers. Furthermore, as mentioned earlier, the amplitude of the Rayleigh scattering due to the mutual diffusion of the mixed solvent becomes comparable with that of the translational diffusion of the polymer at low concentrations, and since the decay rates associated with these two processes are also comparable the correlation function is no longer a single exponential. In practice, concentrations of 5 mg/mL and above had to be used to obtain a good single exponential.

In all cases D is seen to vary linearly with c: $D = D_0(1 + k_Dc)$. Each experimental point represents the average of about 15 separate determinations of D for a particular solution, with a standard deviation which was typically less than 1%. A least-squares-fit procedure was employed to obtain values of D_0 and k_D for each system, and the uncertainties in these values were determined from an error analysis of the data points. The uncertainty in D_0 was found to be between 0.5 and 1% from this analysis.

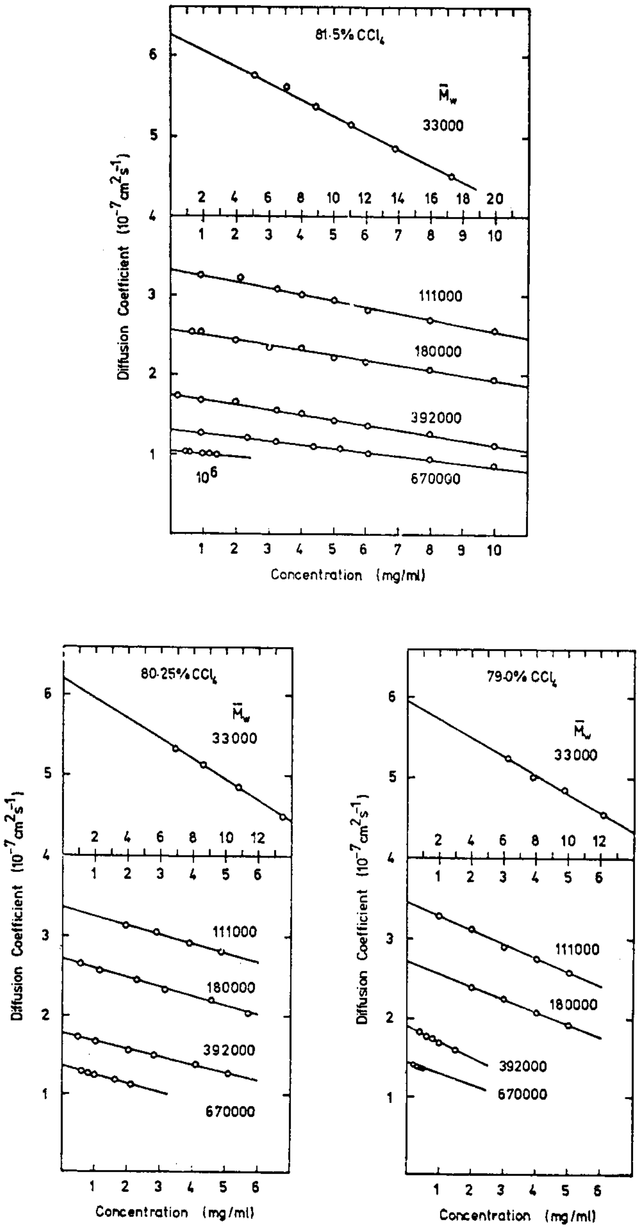

Figure 3. The concentration dependence of the diffusion coefficient of polystyrene in mixtures of carbon tetrachloride and methanol for three solvent compositions with CCl$_4$ volume fractions ϕ = 0.815, 0.8025, and 0.790.

The variation of log D_0 with log $\overline{M}_w$ is shown in Figure 4 for the three solvent compositions. Each plot is seen to be linear with a negative slope which falls from 0.524 through 0.503 to 0.469 as ϕ changes from 0.815 through 0.8025 to 0.790. Again, an analysis of the points gives an uncertainty in slope of 1% in each case. Thus no discontinuity in slope is observed as might have been expected on the basis of the viscometry study of Dondos and Benoit. Furthermore, there is a smooth variation in slope as ϕ changes. We shall call the composition $\phi = 0.8025$ the "diffusion theta state", since the slope is very close to -0.5; thus the composition $\phi = 0.815$ represents a "super-

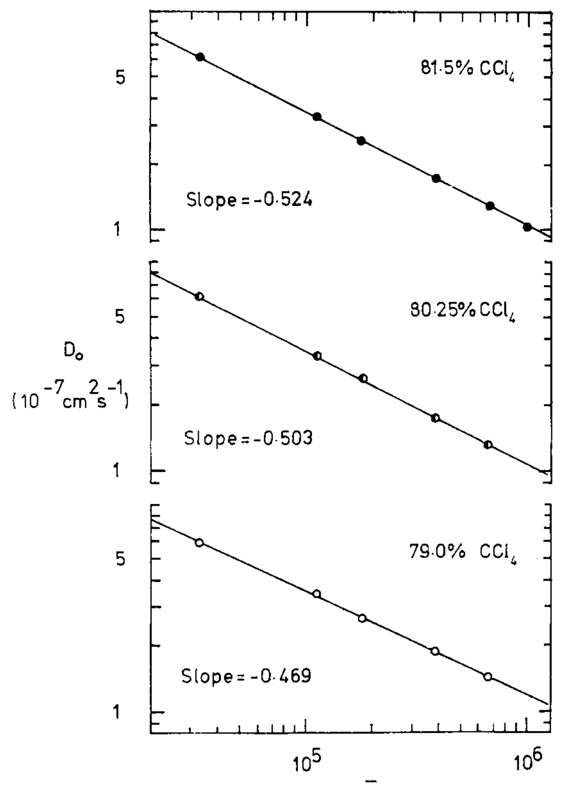

Figure 4. The molecular-weight dependence of the diffusion coefficient at infinite dilution for the three solvent systems investigated.

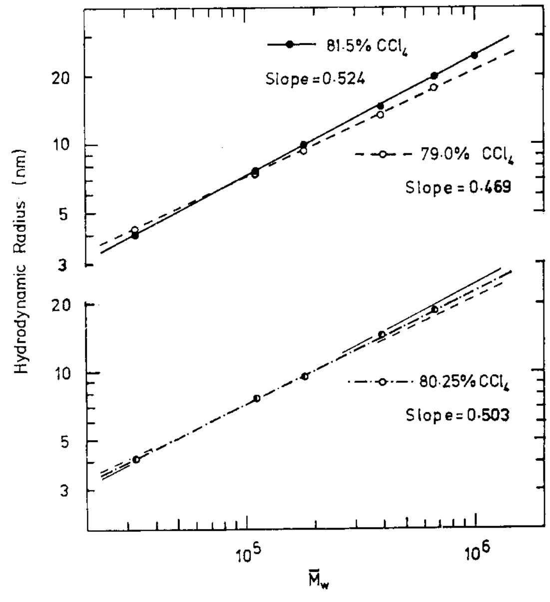

Figure 5. The molecular-weight dependence of the hydrodynamic radius for the three solvent systems investigated.

theta state" and $\phi = 0.790$ a "subtheta state". Altogether these systems seem well-behaved and show no obviously anomalous behavior.

Since D_0 depends directly on the solution viscosity η, it is best to use the hydrodynamic radius a in comparing the frictional properties of the polymer in the different solvent mixtures: $D_0 = kT/f_0$, where f_0 is the friction coefficient at infinite dilution and equals $6\pi\eta a$ for a Stokes sphere of radius a. The variation of log a with log $\bar{M}_w$ is shown in Figure 5 for the three compositions. The lines corresponding to the supertheta and subtheta states are seen to intersect at $\bar{M}_w = 80\ 000$ with the surprising result that for $\bar{M}_w < 80\ 000$ the value of a is larger for the subtheta molecule than the supertheta. The plot for the intermediate composition $\phi = 0.8025$ is seen to lie between the other two and also pass through their common intersection.

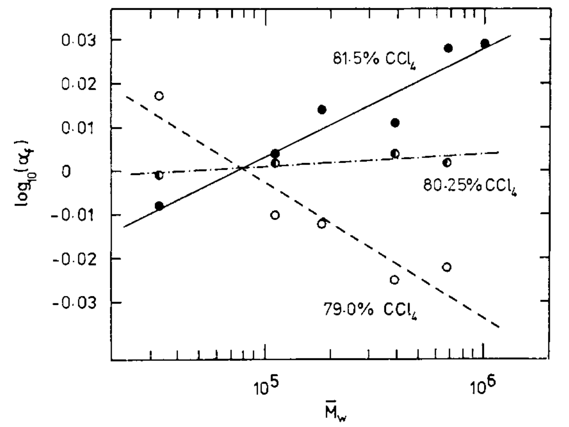

Figure 6. The molecular-weight dependence of the expansion factor α_f for the three solvent systems investigated.

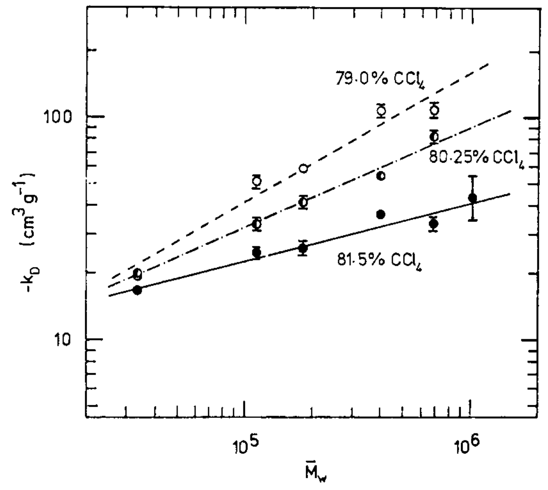

Figure 7. The molecular-weight dependence of the diffusion concentration coefficient k_D for the three solvent systems investigated.

These results can also be expressed in terms of the expansion factor (α_f) for the friction radius: $a = \alpha_f a_\theta$, where a_θ is the value of a under theta conditions. Values of α_f have been obtained by dividing the points in Figure 5 by the line passing through the intersection with slope of 0.5. In Figure 6 log α_f is plotted against log $\bar{M}_w$ for the three solvent systems and is seen to change sign at $\bar{M}_w = 80\ 000$.

It is not possible to explain these results in terms of the various two-parameter theories[8] based on the quantities nl^2 and $n^2\beta$ where n is the number of segments of the polymer chain, each of length l, and β is the binary cluster integral for a pair of segments. The first parameter nl^2 is the mean-square end-to-end distance of the unperturbed chain $\langle R^2 \rangle_0$, and the second is twice the total excluded volume between segments. In these theories the expansion coefficients are expressed in terms of the excluded volume parameter $z = (\frac{3}{2}\pi\langle R^2 \rangle)^{3/2} n^2 \beta$. For example, the Kurata–Yamakawa theory[9] gives $\alpha_f = 1 + 0.416z - \ldots$, which would imply that z changes sign at $\bar{M}_w = 80\ 000$ in opposite senses for the supertheta and subtheta states. It can only be assumed that the basis of the two-parameter theories ceases to hold in the systems investigated, although they are very close to the theta state. Perhaps the form of the segment distribution, which will be changing markedly as the solvent composition is varied near the theta state, plays a more dominant role than the radius of gyration in determining the friction properties. As the molecule passes into the subtheta state, it will form a tighter coil, and the increased segment density and preferential adsorption at low molecular weights may result in the solvent being trapped in the molecule and being dragged along with it. This change in the draining property of the molecule may increase its hydrodynamic size.

The values of k_D, the slopes of the D–c plots normalized against D_0, can be used to indicate the theta-state composition for the mixed solvent. Thermodynamic arguments[8] relate k_D to k_f, the concentration coefficient for the friction coefficient

$f\,[= f_0(1 + k_f c + \ldots)]$:

$$k_D + k_f = 2A_2M - \bar{v}$$

where $\bar{v}$ is the partial specific volume of the polymer (=0.92 mL g^{-1} for polystyrene). Several theories exist which predict values for k_f. For example, Yamakawa[10] proposes that $k_f = \lambda(x)A_2M + \bar{v}_h$, where $\lambda(x)$ is a function depending on x ($=z/\alpha^3$) and equals 1.345 for $x = 0$, the theta state, and $\bar{v}_h$ is the specific hydrodynamic volume of the polymer, which can be obtained from D_0. Pyun and Fixman[11] have considered two models; the hard-sphere model, where the spheres are inpenetrable, gives a value of $k_f = 7.16\bar{v}_h$, while for the soft-sphere model, where the molecules are interpenetrable, $k_f = 2.23\bar{v}_h$ at the theta state, rising to the hard-sphere value as z increases.

In this work, A_2M is unknown, but should be zero at the theta state. Hence under this condition

$$\begin{aligned} k_D{}^\theta &= -\bar{v}_h - \bar{v} && \text{(ref 10)} \\ &= -7.16\bar{v}_h - \bar{v} && \text{(hard sphere; ref 11)} \\ &= -2.23\bar{v}_h - \bar{v} && \text{(soft sphere; ref 11)} \end{aligned}$$

Thus $k_D{}^\theta$ should vary as $\bar{v}_h$ since $\bar{v}_h \gg \bar{v}$, and thus as $M^{1/2}$.

We have plotted log ($-k_D$) against log $\overline{M}_w$ for the three solvent mixtures in Figure 7, and the composition $\phi = 0.8025$ gives a slope 0.45 which is closest to 0.5 of the three slopes. This adds support to the strong evidence from the variation of log D_0 with log $\overline{M}_w$, which suggests that this value of ϕ represents the theta composition. For this composition, the line fitted to the points in Figure 7 would point to a value of about 7 for the coefficient of $\bar{v}_h$ in the expression for $k_D{}^\theta$, and thus favors the hard-sphere model of Pyun and Fixman. However, this result can only be taken as an indication.

In conclusion, we would emphasize that the results of these diffusion measurements of high precision do not reflect the effects observed in the viscometry measurements of Dondos and Benoit on the same system, which they attributed to the preferential adsorption. Indeed, our measurements would indicate a well-defined diffusion theta composition at $\phi = 0.8025$. However, the z-parameter theory is inadequate to explain the curious behavior of the hydrodynamic radius with polymer molecular weight and solvent composition.

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Hydrodynamic Properties and Unperturbed Dimensions of Poly(γ-hydroxy-L-proline) in Aqueous Solution

Donald S. Clark and Wayne L. Mattice*

Department of Biochemistry, Louisiana State University,
Baton Rouge, Louisiana 70803. *Received October 8, 1976*

ABSTRACT: Intrinsic viscosities and sedimentation coefficients have been measured as a function of molecular weight for poly(γ-hydroxy-L-proline) in water. The molecular weight range covered is 9 000–35 000. High molecular weight poly(γ-hydroxy-L-proline) in water has the hydrodynamic behavior of a random coil immersed in a good solvent, as judged by d ln $[\eta]$/d ln M, d ln s_0/d ln M, dβ/dM, and the size of β [$= Ns_0[\eta]^{1/3}\eta M^{-2/3}(1 - \bar{v}\rho)^{-1}$]. The characteristic ratio, $(\langle r^2\rangle_0/n_p l_p{}^2)_\infty$, is found to be 15.9 ± 1.6, which is not significantly different from the result of 13.7 ± 0.9 obtained for poly(L-proline) by Mattice and Mandelkern under the same conditions. This observation casts doubt on the importance of intrachain hydrogen bonded bridges from the hydroxyl group to a carbonyl oxygen via a water molecule. The characteristic ratios and the effects of calcium chloride on the hydrodynamic properties suggest that poly(L-proline) and poly(γ-hydroxy-L-proline) possess a similar source of flexibility which is often overlooked. Two possibilities for this flexibility are a second energy minimum about the C$^\alpha$–C′ bond and cis-trans isomerization about the peptide bond.

The pyrrolidine ring exerts a profound effect on the conformational properties of poly(L-proline) and poly(γ-hydroxy-L-proline). It confines the dihedral angle ϕ[1] to the vicinity of 120°, and steric interactions between neighboring pyrrolidine rings also impose severe restrictions on the accessible values for ψ. For these reasons the two homopolypeptides share certain conformational properties. The most detailed x-ray diffraction patterns for poly(γ-hydroxy-L-