

Light-Scattering Evidence of a "Critical" Concentration for Polymer Coil Shrinking in Dilute Solution

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SYNOPSIS

The variation of polymer chain dimension with concentration in both dilute and extremely dilute solutions was monitored by measuring the diffusivity of narrowly distributed polystyrene standards in toluene at room temperature through a carefully designed dynamic light scattering experiment. As polystyrene concentration decreases, the measured translational diffusion coefficient levels off after a certain concentration, i.e., in terms of experimental results, there exists a "critical" concentration for polystyrene coil shrinking in dilute toluene solution. The existence of this critical concentration has been predicted by introducing the concept of screening length into the statistical thermodynamic calculation. In this paper, we report, for the first time, its laser light-scattering evidence. © 1994 John Wiley & Sons, Inc.

Keywords: polymer coil shrinking • dynamic light scattering • polymer coil conformation in extremely dilute concentration

INTRODUCTION

The variation of polymer chain dimension with concentration in polymer solution is an important problem both in theory and in practice. Various studies of statistical thermodynamics of polymer solution indicate that the solvated polymer chain in good solvent should shrink monotonically with the increase of concentration,¹⁻⁵ which means that the solvated polymer coil should shrink (contract) theoretically no matter how diluted the solution is. Recently, the scaling theory⁶ predicted the variation of polymer coil dimension with concentration around the so-called overlap concentration C^* at which the physical contact among the polymer coils starts. However, C^* is defined in a slightly different way as $M/(N_A R_g^3)$, or as $3M/(4\pi N_A R_g^3)$, or as $M/[N_A (2R_g)^3]$, by different investigators,⁷⁻⁹ where M , N_A , and R_g are the molecular weight of polymer coil, Avogadro's number, and the radius of gyration, respectively. Numerous experimental methods, which include laser light scattering,^{10,11} have been used to verify the shrinking of polymer coil in dilute, semi-dilute, and concentrated solutions.

After adopting the concept of the screening length into his statistical thermodynamic calculation, Lohse¹² stated that the shrinking of polymer coil in solution starts only as the concentration reaches a certain value, i.e., there exists a critical concentration for polymer coil shrinking in dilute solution. In spite of the concept being well predicted by the mean field theory, its experimental evidence is very limited by the following two facts: First, it has been overlooked in the past. In dilute regime, it is a common practice to linearly extrapolate those measured parameters that are related to polymer coil dimension, such as the translational diffusion coefficient to zero concentration. It has been assumed that the concentration dependence of those measured parameters in extremely dilute regime would be the same as in the dilute regime. Second, it is very difficult to verify experimentally whether a measured parameter is a continuous function of polymer concentration even in the extremely dilute solution. Therefore, the concentration dependence of those parameters in extremely dilute regime are remained as a challenge problem.

In the past, the eximer fluorescence spectroscopic studies of polystyrene solution revealed that the chain segments of the polymer coil starts to feel the repulsive force between the segments of neighboring

polymer coils in solution only when the concentration reaches a critical concentration C_s ,¹³ i.e., the polymer coil started to shrink when the concentration was higher than C_s . The experimental C_s estimated from the concentration dependence of the eximer fluorescent intensities was much lower than C^* . In addition, a delicate reexamination of the variation of the retention volume as a function of concentration in size-exclusion chromatography (SEC) also showed that there exists a critical concentration for polymer coil shrinking in dilute solution.¹⁴ Recently, by following a carefully designed dynamic light scattering (DLS) procedure, we measured the concentration dependence of the translational diffusion coefficient in both dilute and extremely dilute regimes for narrowly distributed polystyrene standards in toluene at 25°C. In this paper, we will report the first light-scattering evidence of a "critical" concentration for polystyrene coil shrinking in dilute solution, which marks the level off of the diffusivity in the extremely dilute regime.

THEORETICAL BACKGROUND

By using the mean field theory for an incompressible polymer solution on a lattice,¹² Lohse has described the concentration dependence of chain dimensions from concentrated solution to extremely dilute solution. The central concept is that of a screening length x_s . The results of this model were developed in terms of the concentration dependence of the polymer chain dimension. The detail of the model can be found in ref. 12. For the convenience of the discussion in this paper, we only outline the basic principle of the Lohse's model in the following:

It is well known that even for a monodisperse polymer sample in solution there exists a tremendous number of polymer chain configurations. At each moment, for those polymer chains whose configurations are larger than x_s , they experience a complete screening due to overlap with neighboring chains and so have the statistics of ideal chains. On the other hand, for those chains whose configurations are smaller than x_s , they experience no overlap and thus have the statistics of isolated chains. A real situation can be represented by a mixture of the fully screened chains and completely isolated chains. The degree of mixture is a function of polymer concentration (ϕ), the size of the polymer chain (s), and the polymer chain length (l).

Quantitatively, in order to describe this mixture, the local segment density ($\bar{\phi}$) as a crucial parameter

has been introduced in this mean field model. In the analysis, the ratio of a given chain segments ($\sim l$) to its pervaded fraction of the volume ($\sim s^3$) is defined as the self-density of a chain (ϕ_s), i.e., $\phi_s \sim l/s^3$. For ideal chains, $\phi_s \equiv \phi_o \sim l/s_o^3$, where s is replaced by the mean-square radius of gyration ($s_o = \langle s^2 \rangle_o^{1/2}$) and the subscript "o" denotes the ideal chains. It should be noted that ϕ_o is a characteristic quantity of a given polymer and independent on the solvent. Since $\langle s^2 \rangle_o \sim l$, $\phi_o \sim l^{-1/2}$. Further, by using the definition of a reduced radius of gyration, $x = s/s_o$, we have $\phi_s = \phi_o/x^3$, where the low limit of x is $\phi_o^{1/3}$, which indicates that every site in the lattice has been filled. At this low limit, every part of its volume is filled with its own segments, i.e., $\bar{\phi} = \phi_s = 1$.

As ϕ (equivalently say s) increases, the volume occupied by a given polymer chain will be intruded on by the segments from other chains and the system becomes more homogeneous. Finally, the local segment density ($\bar{\phi}$) will approach the global density (ϕ). Therefore, $1 \leq \bar{\phi} \leq \phi$. It should also be noted that, on the one hand, $\bar{\phi} \geq \phi_s$ for all ϕ and s since the number of segments inside the volume occupied by a given chain must be at least l , and on the other hand, $\bar{\phi} \geq \phi$ for all ϕ and s since segment density is higher near the center of the chain. Therefore, we can assume that near the point of $\phi_s = \phi$ at $x = x_s \equiv (\phi_o/\phi)^{1/3}$, the change from $\bar{\phi} \approx \phi_s$ to $\bar{\phi} \approx \phi$ will take place, where x_s is defined as a screening length, because the intramolecular excluded volume interactions from a given chain are screened by the presence of segments from other chains when $x > x_s$, and there is no screening when $x < x_s$. The nearly same result can also be obtained by using a more precise cell model.¹⁵ Thus, even for a given monodisperse polymer sample in a good solvent, the size distribution [$P(s)$] will be a function of ϕ or x .

Figure 1 shows a schematic presentation of $P(s)$ at four different cases. Figure 1a shows an ideal distribution, $P_o(s)$, with its center located at s_o .¹⁶ Figure 1b shows $P_i(s)$, a size distribution for an isolated chain.¹⁷ The center of $P_i(s)$ is located at $\alpha_o s_o$, where α_o is the expansion factor of the isolated chain. Since the polymer chain has a fixed length (l), there should exist a maximum value of s , i.e., s_{\max} , in $P_i(s)$. When $s > s_{\max}$, $P_i(s) = 0$. In a dilute solution, based on the concept of the screening length, we can define a very similar parameter: a screening size s_s . For those polymer chains whose size is larger than s_s , they will be screened and behave like the ideal chain. On the other hand, for those chains whose size is smaller than s_s , they will act as the isolated chains without any screening, which is shown in Figure 1c,

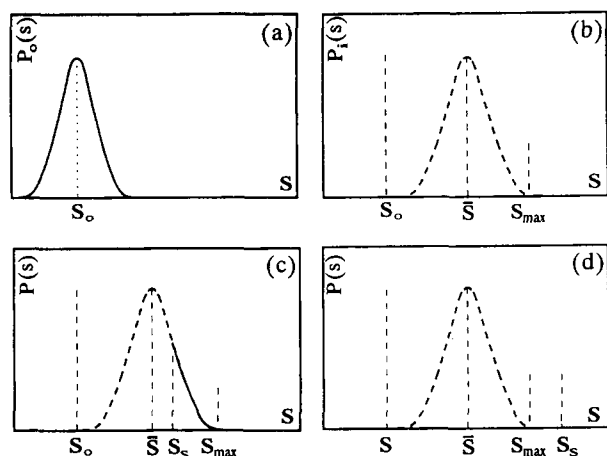


Figure 1. Schematic presentation of the size distribution $[P(s)]$ at four different situations. (a) Ideal distribution, $P_o(s)$; (b) isolated chain distribution, $P_i(s)$; (c) in the dilute solution, $P(s)$, wherein $S_s < S_{max}$; (d) in the extremely dilute solution, $P(s) \approx P_i(s)$, wherein $S_s > S_{max}$.

where the dashed portion behaves as the isolated chain. From the definition of x_s , we know that x_s increases as ϕ decreases, and so does s_s . In practice, we can dilute a given solution, i.e., decrease ϕ , to a certain concentration (ϕ_s) so that s_s (or say x_s) is larger than s_{max} , which means that the size of all polymer chains will be smaller than s_s and they should behave like the isolated chains, i.e., $P(s) \approx P_i(s)$. After ϕ reaches ϕ_s , any further dilution will not change the behavior of the chains. Therefore, it is natural to consider ϕ_s (in normal notation we often use C_s) as a critical concentration for polymer coil shrinking in dilute solution. The solution with $C < C_s$ is called the extremely dilute solution in order to distinguish it from the dilute solution in which

the size of a certain number of polymer chains are larger than s_s .

At this point, it should be stated that the polydispersity and the movement of polymer chains has not been considered in the above discussion. Both of them will increase s_{max} , so that C_s predicted for a given monodisperse polymer sample with the immobile chains will have to be lower in order to assure that the solution is in the extremely dilute regime.

EXPERIMENTAL

Solution Preparation

The light scattering measurements were performed with polystyrene standards in toluene at 25°C. Six narrowly distributed polystyrene samples from Polymer Standard Services, Dow Chemical, and Nanjing University were used. Both the nominal from SEC and measured (from static light scattering) weight-average molecular weight (M_w) and polydispersity (M_w/M_n) are listed in Table I. The $\pm 5\%$ error in the measured M_w includes the errors from the standard Rayleigh ratio (R^0) of toluene at 25°C and 90°, from the measured light intensity, from the specific refractive index increment (dn/dc), and from the solution preparation. The overall agreement between the nominal and measured M_w is within the experimental uncertainty. All light scattering solutions were prepared by successively diluting a stock solution with an exactly known concentration. In the extremely dilute regime, it is very essential to prepare an "absolute" clean solution with the removal of all dust particles in the solution, otherwise the scattered light intensities even from one or two dust particles will dominate the measured signal. We took the following precau-

Table I. Summary of M_w , M_w/M_n , D_o° , k_d , and $f\langle R_g^2 \rangle_z$ of Six Narrowly Distributed Polystyrene Standards in Toluene at 25°C^a

M_w (10^5 g/mol)		M_w/M_n	D_o° (10^{-8} cm ² /s)	k_d (mL/g)	$f\langle R_g^2 \rangle_z$ (10^{-12} cm ²)
Nominal	Measured				
40.0	41.1	1.09	5.61	910	16.0
17.4	18.3	1.07	9.01	430	6.53
9.84	11.2	1.07	11.4	210	4.08
5.82	5.78	1.06	17.5	130	1.72
2.67	2.59	1.08	28.1	54	0.84
1.68	1.65	1.02	36.7	35	0.49

^a The relative errors are in the following: M_w (measured): $\pm 5\%$; M_w/M_n : $\pm 5\%$; D_o° : $\pm 1\%$; k_d : $\pm 3\%$; $f\langle R_g^2 \rangle_z$: $\pm 8\%$.

tions in our solution preparation: (1) prepare a dust-free toluene with a 0.02 μm ANOTOP (Merck) filter; (2) clean all needles, syringes, and even volume flasks with the dust-free toluene; (3) prepare a stock solution in a dust-free volume flask with the dust-free solvent; and (4) dilute the stock solution with the dust-free solvent to desired concentration. In this way, the only dust particles in the final solution were from the polystyrene standards. Before the light-scattering measurement, the final solution was cleaned once more with a 0.22 μm Millipore filter until the scattered intensity fluctuation at 15° is less than $\pm 3\%$ during the whole measurement time. In the extremely dilute regime, the further dilution was done by directly adding dust-free solvent into a specially designed light scattering cell. The top of the cell was equipped with an open-and-close switch together with a needle, a 0.02 μm filter, and a syringe that contains the precleaned solvent.

Dynamic Light Scattering

In dynamic light scattering, the measured intensity-intensity time correlation function $G^{(2)}(q, \tau)$ is related to the normalized first-order electric-field correlation function $|g^{(1)}(q, \tau)|$ by the relation^{18,19}

$$[G^{(2)}(q, \tau) - A]/A = \beta |g^{(1)}(q, \tau)|^2 \quad (1)$$

where A is the baseline, τ is the delay time and $q = ((4\pi n)/\lambda_0) \sin(\phi/2)$ with λ_0 , n , and θ being the wavelength of light in vacuum, the refractive index of solvent and the scattering medium and the scattering angle, respectively. The β , whose value is between 0 and 1, is a spatial coherent factor depending only upon the optical configuration, which reflects the maximum ratio of the net signal ($G^{(2)}(q, \tau) - A$) to the baseline A . For a polydisperse system, $g^{(1)}(q, \tau)$ can be related to the line-width Γ by

$$g^{(1)}(q, \tau) = \int_0^\infty G(\Gamma) e^{-\Gamma\tau} d\Gamma \quad (2)$$

where $G(\Gamma)$ is the line-width distribution function. In practice, for extremely dilute solution, the excess scattered light intensity ($I - I_s$) is so weak that we have to consider the intensity scattered by the solvent and β in eq. (1) will be replaced by an apparent intercept $\beta^* \{ [(I - I_s)/I]^2 \beta \}$, with I and I_s being the light intensities scattered by solution and solvent, respectively. In some of our measurements, $[(I - I_s)/I]^2$ were as low as ~ 0.07 . Therefore, it is essential to have an optical setup with a higher β value, otherwise a precise measurement would not

be possible because β^* will approach 0 in the extremely dilute solution, i.e., the signal-to-noise ratio will be rather poor. Further, Γ can be related to the diffusion coefficient (D) by

$$\Gamma/q^2 = D = D^0(1 + f \langle R_g^2 \rangle_z q^2) \quad (3)$$

where f is a dimensionless number in the range of 0.10–0.33. Many factors, such as the chain structure, polydispersity, and solvent quality, might affect the value of f .⁷ In the dilute solution, D^0 is normally expressed as a linear function of C by

$$D^0 = D_0^0(1 + k_d C) \quad (4)$$

where superscripts “0” and subscript “0” indicate that $q = 0$ and $C = 0$, respectively. The k_d is the second virial coefficient of translational diffusion, which includes both the thermodynamic and hydrodynamic contributions.³ It is of interest to find what k_d will be if the solution is in the extremely dilute regime.

All light scattering results reported in this paper were obtained by using an ALV-5000 light scattering spectrometer with an argon-ion laser (Coherent INNOVA 90, operated at 488 nm and 400 mW) as light source. By placing a polarizer in front of the detector, we measured only the vertically polarized scattered light. In our present setup, the value of β is about 0.85, which is rather high for a spectrometer that is capable of doing both static and dynamic laser light scattering experiments. All experiments were done at $25.0 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

The line-width distribution $[G(\Gamma)]$ were obtained by using a Laplace inversion program (CONTIN).¹⁴ The average values of the line width ($\bar{\Gamma}$) and the distribution width ($\mu_2/\bar{\Gamma}^2$) were obtained by using both the CONTIN and Cumulants¹⁵ programs, which are built in the ALV-5000 time correlator, where $\bar{\Gamma} = \int G(\Gamma)\Gamma d\Gamma$ and $\mu_2 = \int G(\Gamma)(\Gamma - \langle \Gamma \rangle)^2 d\Gamma$. Since the samples were so narrowly distributed, both methods yield essentially the same values of $\bar{\Gamma}$ and $\mu_2/\bar{\Gamma}^2$. By using $\Gamma/q^2 = D$, the line-width distribution $[G(\Gamma)]$ can be easily converted in the translational diffusion coefficient distribution $[G(D)]$.

Figure 2 shows typical translational diffusion coefficient distributions $[G(D)]$ at four different concentrations ranging from the dilute to extremely dilute regime for polystyrene ($M_w = 2.59 \times 10^5$ g/

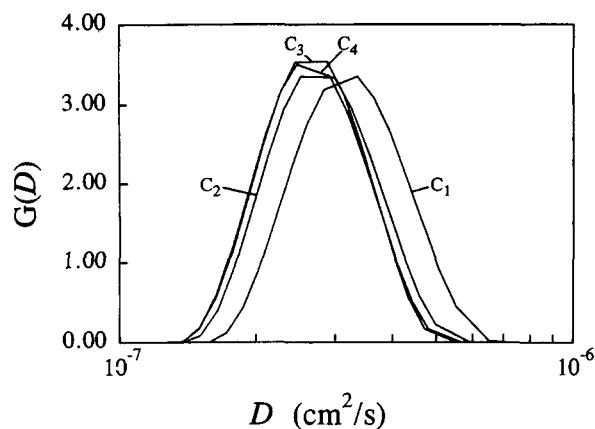


Figure 2. Translational diffusion coefficient distributions [$G(D)$] at four different concentrations ranging from the dilute to extremely dilute regime for polystyrene ($M_w = 2.59 \times 10^5$ g/mol) in toluene at $T = 25^\circ\text{C}$ and $\theta = 15^\circ$, where the values of C_1 , C_2 , C_3 and C_4 are listed in Table II.

mol) in toluene at $T = 25^\circ\text{C}$ and $\theta = 15^\circ$. The calculated \bar{D} and $\mu_2/\bar{\Gamma}^2$ of the distributions are listed in Table II, which shows that both \bar{D} and $\mu_2/\bar{\Gamma}^2$ decrease as the concentration decrease in the dilute solution. The relatively small values of $\mu_2/\bar{\Gamma}^2$ show that $G(D)$ s in Figure 2 are narrowly distributed. However, we should not be very serious about the exact values of $\mu_2/\bar{\Gamma}^2$ and its variation with C since there is a large uncertainty associated with them.

Figure 3 shows typical plots of \bar{D} vs q^2 for six narrowly distributed polystyrene standards in toluene at 25°C in the extremely dilute regime, i.e., $C < C_s$. The lines represent the least-square fitting. On the base of eq. (3), both \bar{D}^0 and $f\langle R_g^2 \rangle_z$ can be obtained from the intercept and slope of the fitting. The values of \bar{D}^0 and $f\langle R_g^2 \rangle_z$ are summarized in Table I. By using the known values of $\langle R_g^2 \rangle_z$ from the static laser light scattering, we found that the values of f are in the range of 0.14–0.19, which is in the predicted range for polymer coils in good solvent.

Figure 4 shows typical plot of D^0 vs C for six narrowly distributed polystyrene standards in tol-

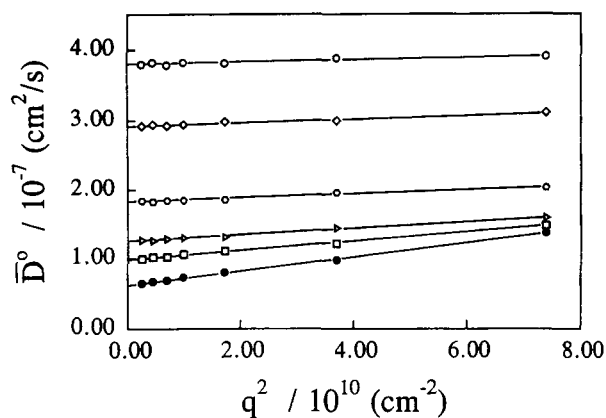


Figure 3. Plots of \bar{D} vs q^2 for six narrowly distributed polystyrene standards in toluene at 25°C in the extremely dilute regime, i.e., $C < C_s$, where \circ represents for $M_w = 4.11 \times 10^6$ g/mol; \diamond , for $M_w = 1.83 \times 10^6$ g/mol; \square , for $M_w = 1.12 \times 10^6$; ∇ , for $M_w = 5.78 \times 10^5$ g/mol; \square , for $M_w = 2.59 \times 10^5$ g/mol; and \bullet , for $M_w = 1.65 \times 10^5$ g/mol. The lines represent the least-square fitting.

uene at 25°C . The dashed line was drawn just to guide the eye. In general, Figure 4 clearly shows two regimes of D^0 vs C for every sample, which is divided by C_s . When $C > C_s$, i.e., in the dilute regime, D^0 is a linear function of C as predicted by eq. (4). The results of D^0 and k_d are also summarized in Table I. On the other hand, D^0 levels off after $C > C_s$, where D^0 is nearly a constant if we consider the $\sim \pm 2\%$ experimental uncertainty in this regime due to weak scattered intensity. It might be right to consider that this level-off behavior of D^0 in the extremely dilute regime is an essential feature of polymer solution as predicted by the concept of the screening length. Experimentally, C_s might be addressed as a “critical” concentration for polymer coil shrinking in good solvent in the dilute concentration. For polymers with low M_w , the linear extrapolation of D^0 to $C = 0$ introduces small difference between D^0 and the level-off value, but for polymers with high M_w , the extrapolation could lead to a relative difference of as high as $\sim 8\%$, which has been overlooked in the past.

Table II. Summary of the z -Average Diffusion Coefficient (\bar{D}) and the Relative Width ($\mu_2/\bar{\Gamma}^2$) of $G(D)$ s in Figure 2^a

	C_1	C_2	C_3	C_4
C (g/mL)	5.03×10^{-3}	3.05×10^{-3}	5.41×10^{-4}	2.11×10^{-4}
\bar{D} (cm^2/s)	3.54×10^{-7}	3.05×10^{-7}	2.91×10^{-7}	2.90×10^{-7}
$\mu_2/\bar{\Gamma}^2$	6.40×10^{-2}	6.10×10^{-2}	5.90×10^{-2}	5.50×10^{-2}

^a The relative errors are in the following: \bar{D} : $\pm 1\%$; $\mu_2/\bar{\Gamma}^2$: $\pm 7\%$.

Figure 5 show the variation of C_s as a function of M_w . In general, the higher M_w , the lower C_s will be. Unfortunately, a quantitative formulation of C_s as a function of M_w is lacking at this moment. The values of C_s from the present dynamic light scattering experimental results are close to those from the eximer fluorescence spectrum.¹³ However, the values of C_s from the size exclusion chromatograph are considerably lower than C_s obtained from both DLS and eximer fluorescence spectrum,¹⁴ which has not been fully understood, but can be partially explained by the influence of the flow rate in SEC.¹⁴ In theory, the concept of C_s and its determination will be important to the screening length and thermodynamic modelling of polymer solution. Finally, it should be emphasized once more that in the lattice model the mobility of polymer coils has not been considered. In reality, no matter how dilute a solution will be, polymer coils always have a chance or probability of colliding with each other, so that the screening effect will be introduced at that moment. In the extremely dilute solution, such chance or probability will be so small that the screening effect cannot be detected in terms of the experimental observation. This is why C_s might be termed the "critical" concentration for polymer coil shrinking in good solvent in the dilute solution.

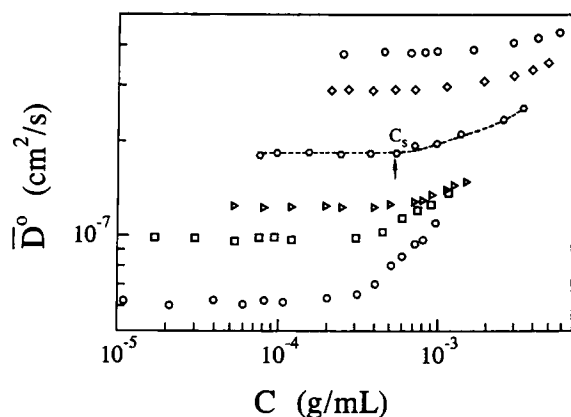


Figure 4. Plot of \bar{D}° vs C for six narrowly distributed polystyrene standards in toluene at 25°C. The dashed line was drawn just to guide the eye. In general, plots of \bar{D}° vs C might be divided by C_s into two regimes, where the symbols represent the same samples as in Figure 4, respectively.

CONCLUSIONS

We have, for the first time, observed the existence of a "critical" concentration (C_s) for polymer coil

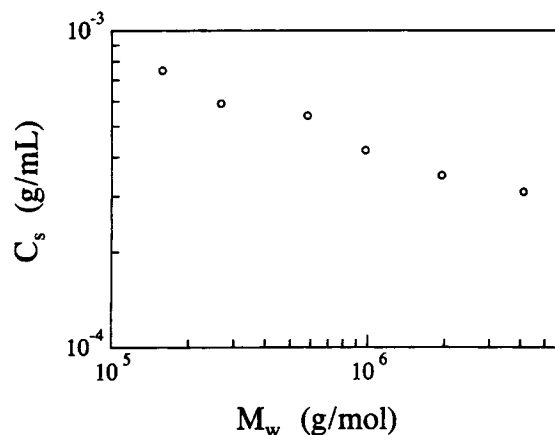


Figure 5. Plot of C_s vs M_w for six narrowly distributed polystyrene standards in toluene at 25°C.

shrinking in the dilute solution in dynamic light scattering experiment. When polymer concentration is lower than C_s , the diffusivity of polymer coil levels off. It will be more interesting in the future to theoretically predict how C_s changes with the size and size distribution of polymer coil; how C_s can be scaled to the average distance between polymer coils; how C_s depends on the nature of polymer; and how C_s can be related to the diffusion of polymer coils, such as the temperature and viscosity effects.

This work was initiated from a fruitful discussion with Profs. R. Cheng and R. Qian. The financial support of this work by the RGC Earmarked Grant 1993/94 (CUHK 79/93E, 221600140), the Research Grants Council of Hong Kong Government, is gratefully acknowledged.

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Received September 27, 1993

Revised December 13, 1993

Accepted January 3, 1994