

Study of Viscosity Abnormality of PS/Toluene Solution in Extremely Dilute Concentration Regime

Deng-Xue Du,^{1,2} Ju Zuo,² Ying-Li An,² Lei Zhou,¹ Yun Liu¹

¹College of Chemical Engineering, Shandong Institute of Light Industry, Ji'nan 250100, People's Republic of China

²The State Key Laboratory of Functional Polymer Materials for Adsorption and Separation, Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

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ABSTRACT: The concentration dependence of the reduced viscosity η_{sp}/c and the translational diffusion coefficient D_t^0 as well as the radius of gyration R_g of polystyrene in toluene were studied by viscometry and laser light scattering (LLS), respectively. The influence of the experimental error on the determination of the η_{sp}/c was investigated and a quantitative relation was given out. Viscometric experiment found that the η_{sp}/c - c curve is clearly divided into two parts by dynamic contact concentration c_s . When $c > c_s$, it shows normal linearity as predicted by Huggins equation. But when $c < c_s$, i.e., in the extremely dilute regime, the η_{sp}/c - c curve is no longer linear and levels off considering the experimental uncertainty. This new finding was confirmed by the follow-

ing LLS experiment, which indicates that the size of the polymer chains no longer varies with concentration when $c < c_s$. As a result, we, for the first time, using the method of combination of viscometry and LLS, prove an important conclusion that in the extremely dilute concentration regime, the reduced viscosity of polymer solution, at least for PS/toluene, conforming to the Einstein viscosity equation is just the intrinsic viscosity and independent of the concentration. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4440–4446, 2006

Key words: viscosity; polystyrene; light scattering; extremely dilute concentration regime; concentration dependence

INTRODUCTION

As early as the 1950s, it was found that solution viscosity of single polymer in extremely dilute concentration region usually reveals some abnormalities, i.e., the reduced viscosity-concentration (η_{sp}/c - c) curves deviate from linear relationship predicted by Huggins equation and show either an upward or a downward turn as concentration is very low.¹ Even for the identical PMMA/toluene solution, there are two contrary results: one reported the curve bends upward,² while the other found it downward.³ To interpret this abnormal phenomenon, many efforts have been made to investigate it.^{4–11} Unfortunately, there are still contradictions among several theories for that so far. Over the last few decades, the hypothesis of adsorption^{8,12–14} and that of critical concentration^{5,10,15} are relatively representative ones. There is still another explanation¹⁶ that the abnormality is perhaps related to the experimental error. Furthermore, the experimental error is related to the concentration, but the quantitatively mathematical relationship between them was not given.

Recently, some advancement has been made about this problem. Cheng and coworkers^{1,3,17–21} investigated this question systematically and proposed a quantitative adsorption theory that could interpret many experimental data: it's obviously considerable progress in solving the hard problem that has troubled people for half a century. However, the conclusion¹⁸ that the abnormality of the reduced viscosity appearing in the extremely dilute concentration region was solely due to the effect of adsorption of polymer chains on the viscometer inner surface seems a little absolute as several causes may exist simultaneously.

So what is the truth behind this abnormal phenomenon? It attracted us into further investigations. In this article, one polystyrene standard sample was studied with a conventional glass capillary viscometer, and the experimental result was new and corroborated by the dynamic light scattering (DLS) experiment in terms of the conformation of polymer chains. The result of this article, for the first time, by the method of combination of viscometry and DLS, provides authentic evidence for the prediction suggested by Pan and Cheng²² that in the extremely dilute concentration regime, the reduced viscosity is the intrinsic viscosity and independent of polymer concentration.

THERORETICAL BACKGROUND

Viscometry

The experimentally determined reduced viscosity of a dilute polymer solution is usually a linear func-

Correspondence to: D.-X. Du (dudengxue@sdili.edu.cn).

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TABLE I
Summary of M_w , M_w/M_n , and D_{t0}^0 of Polystyrene Standard Sample in Toluene

M_w (10^4 g/mol)		M_w/M_n	μ_2/Γ^2	D_{t0}^0 (10^{-7} cm ² /s)	
Nominal	Measured	Nominal	Measured	Extrapolated	Level off
34.1	33.2	1.07	0.078	2.44	2.49

tion of concentration expressed by Huggins equation as

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \quad (1)$$

where k_H is termed the Huggins coefficient or slope constant. The intercept $[\eta]$ is defined as intrinsic viscosity:

$$[\eta] \equiv \lim_{c \rightarrow 0} (\eta_{sp}/c) \quad (2)$$

which is related to the size of an isolated polymer chain in solution.²² The theory of intrinsic viscosity has been firmly established in the past half-century and has become a cornerstone of modern polymer science.²³

Static light scattering

In static light scattering (SLS), the excess scattering intensity, known as Rayleigh ratio $R_{vv}(\theta)$, is related to weight-average molecular weight M_w , mean-square radius of gyration $\langle R_g^2 \rangle$, the second virial coefficient A_2 , and polymer concentration c as²⁴

$$Kc/R_{vv}(\theta) = 1/M_w \left(1 + (1/3)q^2 \langle R_g^2 \rangle \right) + 2A_2c \quad (3)$$

where optical constant $K = 4\pi^2 n^2 (dn/dc)^2 / (N_A \lambda_0^4)$, wavevector $q = 4\pi n \sin(\theta/2) / \lambda_0$ with n , dn/dc , λ_0 , N_A , and θ being the refractive index of the solvent, the specific refractive index increment, the wavelength of light in vacuum, Avogadro's number, and scattering angle, respectively. The basic parameters of M_w , $\langle R_g^2 \rangle$, and A_2 of a polymer can be obtained simultaneously by Zimm plot in light of eq. (3).

Dynamic light scattering

In DLS, 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 relation²⁵

$$G^{(2)}(q, \tau) = A(1 + \beta |g^{(1)}(q, \tau)|^2) \quad (4)$$

where A , τ , and q are the baseline, delay time, and scattering wavevector, respectively. 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

$$g^{(1)}(q, \tau) = \int_0^\infty G(\Gamma) e^{-\Gamma\tau} d\Gamma \quad (5)$$

where $G(\Gamma)$ is the line-width distribution function. Further, Γ can be related to the translational diffusion coefficient D_t by

$$\Gamma/q^2 = D_t = D_t^0(1 + f \langle R_g^2 \rangle q^2) \quad (6)$$

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 . In the dilute solution, D_t^0 is normally expressed as a linear function of c by

$$D_t^0 = D_{t0}^0(1 + K_d c) \quad (7)$$

where superscript "0" and subscript "0" indicate that $q = 0$ and $c = 0$, respectively. K_d is the second virial coefficient of translational diffusion, which includes both the thermodynamic and hydrodynamic contributions.

EXPERIMENTAL

A narrowly distributed polystyrene (PS) standard sample from Nanjing University (China) was used. Some parameters including the polydispersity (M_w/M_n) by SEC and the value of poly (μ_2/Γ^2 , the measure of distribution of z-average diffusion coefficient, measured by DLS of the sample are listed in Table I. As we can see, the agreement between the nominal weight-average molecular weight M_w and the measured one by SLS is within the experimental error of $\pm 4\%$. The distribution of the hydrodynamic diameter of the sample determined by DLS is shown in Figure 1, from which and the value of μ_2/Γ^2 we can see that the distribution of the standard sample is fairly narrow.

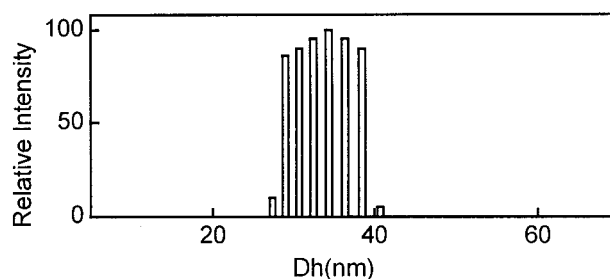


Figure 1 The distribution of hydrodynamic diameter of the PS sample.

Dust-free toluene of analytical purity was used as solvent after being filtered by a 0.2 μm Millipore filter.

Solution preparation

To compare with the results of the viscosity and the laser light scattering (LLS) measurements, the same stock solutions of PS/toluene with an exactly known concentration were prepared by weighing. Both the experiments of viscosity and the LLS demand "absolute" clean solutions—one or two little fibers or dust particles will dominate the measured signal, especially in the extremely dilute regime. So we took the following precautions in the preparation of solutions according to the method given in the literature.²⁵ Briefly, the procedure involves: (1) clean all needles, syringes, volume flasks and prepare the stock solutions with dust-free toluene, (2) dilute the stock solutions with dust-free toluene to desired concentration, (3) before the LLS measurement, clean carefully the final solutions once more with the 0.2 μm Millipore filter until the scattering intensity fluctuation at 15° is less than ± 3 (by examined 200 points with the program of BI9000AT v6.4 provided by Brookhaven Company at the same conditions as solution measuring).

Measurements of viscosity

Two conventional dilution-type Ubbelohde viscometers with capillary length of 110.0 mm and diameters of 0.30 and 0.40 mm respectively were used. A stopwatch with an accuracy of 0.01 s was used manually to measure the flow times. All measurements were performed in a water bath of $(30 \pm 0.01)^\circ\text{C}$. The flow time of pure solvent, named t_0 , was firstly measured by using a thoroughly cleaned viscometer, then pouring out the solvent and drying the viscometer. For measuring the flow times of polymer solutions, named t , of different concentrations, the concentrated PS solution with known mass and exact concentration was first measured. Afterward, weighed solvents were added to the viscometer successively for decreasing the solution concentration. The weight concentration was converted to a weight-volume one (in g/mL) by applying the density correction. For the purpose of accuracy, we do at least five parallel determinations for each concentration and the maximum difference among the flow times is required to be no larger than 0.2 s, which is in accordance with conventional practice. For each sample, we do several repeated experiments, observe and compare the data carefully to find the law of the variation of the $\eta_{\text{sp}}/c-c$ curves.

Measurements of LLS

All the LLS measurements of PS/toluene solutions were carried out at the same temperature of $(30$

$\pm 0.1)^\circ\text{C}$ by using a BI-200SM light scattering spectrometer with a BI-9000AT correlator (Brookhaven Instruments Corp.), the light source being an argon-ion laser (Coherent INNOVA 300, λ 514.5 nm, single-line power 1 w, with power-track). The incident light beam was vertically polarized with respect to the scattering plane. To obtain the precise values of the hydrodynamic radius R_h^0 and the radius of gyration R_g by the method of angular extrapolation for each concentration, we selected 7 angles from a wide angular range of 15 – 120° in DLS measurements and 22 angles from a range of 30 – 135° with a small step increment of 5° in SLS measurements, respectively.

RESULTS AND DISCUSSION

Finding of viscometry and discussion of the experimental error

The concentration dependence of the reduced viscosity of the PS sample in toluene with three repeated measurements strictly on the same conditions are shown in Figure 2. The semilogarithmic plot is drawn to scatter the data points in the extremely dilute concentration regime.

From Figure 2, we can see that, although the deviation of flow times for each concentration is < 0.2 s, the repeatability of the data grows worse rapidly along with the decrease of the concentration. Especially in the extremely dilute regime, it is hard to find the variation law of $\eta_{\text{sp}}/c-c$. Why is there such a great experimental error for the measurement of reduced viscosity although the repeatability of the flow times is satisfactory considering the manual operation? It is analyzed as follows. In our experimental condition, dilute and extremely dilute polymer solutions are operated, so the density correction should be ignored. Furthermore,

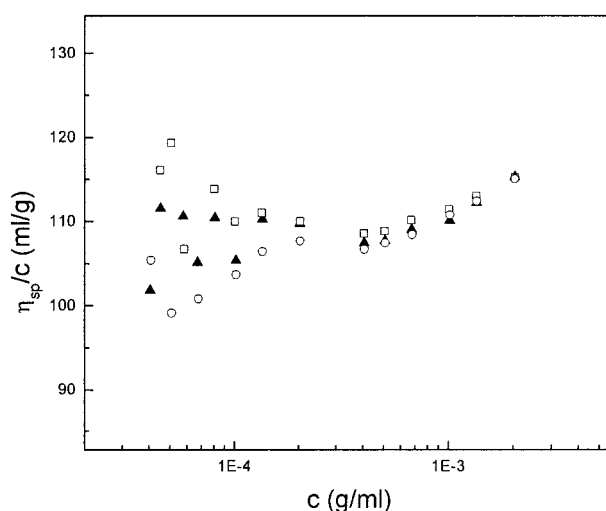


Figure 2 The relationship of $\eta_{\text{sp}}/c-c$ for the PS sample with three repeated measurements.

the flow times of both the solvent and the solution are much longer than 100 s and a sufficiently high length/diameter ratio is reached, so the kinetic energy corrections and end-effects should also be negligible. Hence, the relative viscosity can be calculated as

$$\eta_r = t/t_0 \quad (8)$$

where t and t_0 are, respectively, the flow time of the solution and the solvent.

The reduced viscosity η_{sp}/c can be calculated as

$$\eta_{sp}/c = (\eta_r - 1)/c \quad (9)$$

and combining eqs. (8) and (9), we have

$$\eta_{sp}/c = (t - t_0)/(t_0 c) \quad (10)$$

Provided the deviation of flow time of the solution is denoted as Δt ($\Delta t = t - \bar{t}$, \bar{t} is the mean value of flow times) as well as Δt_0 of the solvent, the deviation of the reduced viscosity, $\Delta(\eta_{sp}/c)$, could thence, by use of total differential, be

$$|\Delta(\eta_{sp}/c)| = |\Delta t|/(t_0 c) + t|\Delta t_0|/(t_0^2 c^2) \quad (11)$$

Generally, $|\Delta t|$ and $|\Delta t_0|$ are required to be <0.1 s.

Assuming there is hardly systematic error—and so is it in fact—the measurement error of the reduced viscosity may be expressed approximately as

$$E = |\Delta(\eta_{sp}/c)|/(\eta_{sp}/c) = (t|\Delta t_0| + t_0|\Delta t|)/(t_0^2 \eta_{sp}) \quad (12)$$

According to Huggins equation, we have

$$\eta_{sp} = [\eta] c + k_H [\eta]^2 c^2 \quad (13)$$

Then inserting eq. (13) into eq. (12), the quantitative relationship of E and c will be obtained as

$$E = |\Delta(\eta_{sp}/c)|/(\eta_{sp}/c) = (t|\Delta t_0| + t_0|\Delta t|)/(t_0^2([\eta]c + k_H[\eta]^2 c^2)) \quad (14)$$

In the dilute and extremely dilute concentration region, c^2 in eq. (14) can be neglected, so eq. (14) can be simplified as

$$E = |\Delta(\eta_{sp}/c)|/(\eta_{sp}/c) = (t|\Delta t_0| + t_0|\Delta t|)/(t_0^2[\eta]c) \quad (15)$$

For limit values to eqs. (14) and (15) we have

$$\lim_{c \rightarrow 0} E = \infty \quad (16)$$

At the condition tested, for a given sample, $[\eta]$, Δt , Δt_0 , and t_0 are constants, $t \geq t_0$, so E is in inverse

proportion to c . As the solution dilutes, the measuring error of the reduced viscosity will increasingly go up till infinity. Thus it is predictable that the fluctuation of the η_{sp}/c curve will be more and more evident with the decrease of the concentration, especially in the extremely dilute regime, just as shown in Figures 2 and 3. The error bars in Figure 3 intuitively demonstrate the deviation of η_{sp}/c with the concentration as $|\Delta t|$ and $|\Delta t_0|$ are equal to 0.1 s. So the fluctuation of the data is inevitable under conventional experimental conditions even for reliable experimental data. It should be emphasized that if the experimental conditions, especially the time-measuring precision, would be improved, the repeatability of the curves could be improved correspondingly. In other words, the time-measuring precision determines the extent of the fluctuation of data.

As data in Figure 2 are so scattered and there seems to be no obvious variation law in the extremely dilute regime, we computed the mean values of η_{sp}/c and the average η_{sp}/c - c curve is shown in Figure 3 (the error bars are also given out). From which we find that the curve can be clearly divided into two parts by a critical concentration c_s , which is about 4×10^{-4} g/mL. Experimentally, c_s might be addressed as the "dynamic contact concentration" presented by Qian^{26,27} rather than the "overlap concentration" c^* presented by de Gennes²⁸ in light of its order of magnitude. Qian has suggested that there exists a dynamic contact concentration c_s at which the chain segments of polymer coil start to feel the repulsive interaction between segments of neighboring coils, and the coils start to shrink in dimension when the solution concentration $c > c_s$. From the

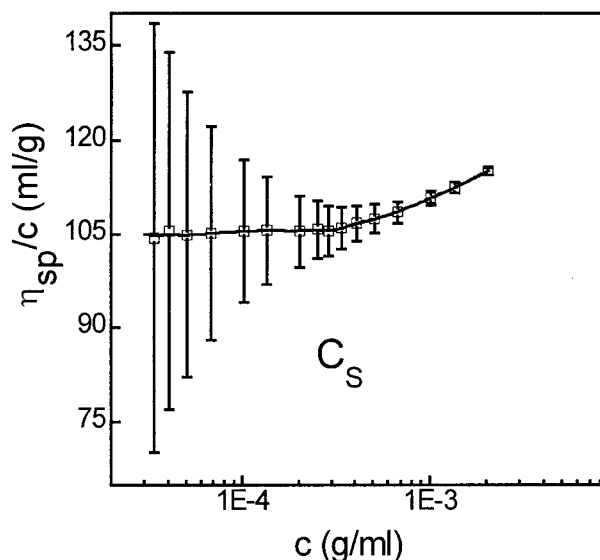


Figure 3 The concentration dependence of the reduced viscosity of the PS/toluene solution. The error bars are calculated from eq. (11) with $|\Delta t|$ and $|\Delta t_0|$ as 0.1 s.

definition of c_s , we can see that it is similar to the critical concentration c^{**} , presented by Dondos, who believes that in that concentration, entanglements emerge between the macromolecular chains, but the value of c_s we detected is lower than the c^{**} determined by Dondos with viscometry.²⁹ The existence of c_s has been confirmed later by precise SEC³⁰ and DLS²⁵ studies. Moreover, Wu²⁵ has suggested the variation of c_s as a function of M_w . From Figure 3, we can see that when $c > c_s$, namely, in the dilute concentration regime, the $\eta_{sp}/c-c$ curve shows a normal good linearity as predicted by Huggins equation; but when $c < c_s$, namely, in the extremely dilute concentration regime, it is no longer linear and appears to level off in the range of error considering the comparatively large experimental uncertainty of conventional Ubbelohde viscometry as analyzed above.

Our viscometric result is novel and different from the earlier reports by Ohrn^{12,13}—Most of his findings bend upward in the extremely dilute concentration regime, which is usually explained by the polymer adsorption in the inner wall of the viscometer. But in our study, there is no obvious evidence to confirm the existence of the adsorption. The reason for this difference about adsorption is perhaps due to the difference of the surface property of the inner wall of the capillary made by different kinds of glass. Pan and Cheng²² have predicted that in the extremely dilute concentration regime where polymer chains are isolated and do not suffer interchain interaction, the reduced viscosity will be equal to the intrinsic viscosity and independent of polymer concentration, that is,

$$|\eta_{sp}/C|_{C < c_s} = [\eta] \quad (17)$$

In other words, it conforms to the Einstein viscosity equation³¹ after $c < c_s$:

$$\eta_r = 1 + [\eta]c \quad (18)$$

This prediction is in accordance with the experimental findings reported by Haney³² who has used a bridge-type differential capillary viscometer rather than a conventional Ubbelohde viscometer. Our experimental results above too appear to prove this prediction.

However, because of the significant effect of the error in the measurement of the viscosity, it seems a little difficult to make an accurate judgment only by means of viscometry. Now that the intrinsic viscosity is a measure of the shape and size of the isolated macromolecule,³³ and the laser light scattering (LLS) happened to be a very suitable tool to measure the dimension of the polymer, it is a good choice to verify the results of viscometry by LLS experiments.

The confirmation of the DLS

In terms of the experimental procedure of DLS described in the "Experimental" section, the line-width distribution $[G(\Gamma)]$ and the average values of the line width ($\bar{\Gamma}$) were obtained using a Laplace inversion program (CONTIN), and then D_t can be obtained by eq. (6). The hydrodynamic radius of the polymer can then be determined from Stokes-Einstein equation

$$R_h D_t = k_B T / 6\pi\eta \quad (19)$$

where k_B , T , and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. So R_h is in inverse proportion to D_t under given experimental conditions. Figure 4 shows typical plots of D_t versus q^2 for eight concentrations of the PS/toluene solution at 30°C. In the ideal case, D_t does not depend on the square of the scattering vector q , but in fact, due to the influence of the factors such as polydispersity and nonsphere, the $D_t \sim q^2$ curves usually show negative or positive slope as in Figure 4 according to eq. (6). The lines in Figure 4 represent the least-square fitting and D_t^0 can be obtained from the intercept of the fitting lines on the basis of eq. (6). So the $D_t^0 \sim c$ curve of the PS/toluene solution can be obtained in Figure 5 with error bars of $\pm 5\%$ experimental error.

Comparing Figures 3 and 5, we can find that the lines are quite alike. Figure 5 also clearly shows two regimes, and the boundary concentration is also c_s , the value of which is about 3.5×10^{-4} g/mL, a little lower than the value in Figure 3. This result is consistent with the conclusion made by Dondos and coworkers,²⁹ who found that the critical concentration is lower when determined by UV measurements in the static state compared with that determined in the dynamic state using viscometry. In Figure 5,

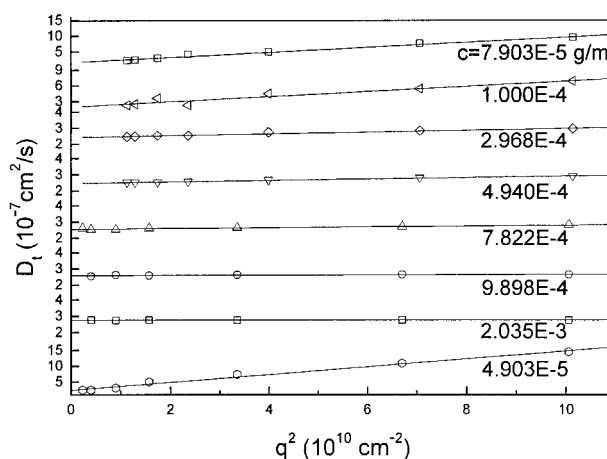


Figure 4 Plots of D_t versus q^2 for eight concentrations of PS sample in toluene at 30°C.

when $c > c_{sr}$, namely, in the dilute regime, D_t^0 is a linear function of c as predicted by eq. (7); but when $c < c_{sr}$, namely, in the extremely dilute regime, D_t^0 levels off considering $\pm 5\%$ experimental error. It might be right to consider that this level-off behavior of D_t^0 in the extremely dilute regime is an essential feature of polymer solution as predicted by the concept of the screening length.²⁵ The result of D_{t0}^0 extrapolated linearly from the $D_t^0 \sim c$ curve and the level-off value are summarized in Table I. From Figure 5 and eq. (19), we know that the hydrodynamic radius gradually increases as the concentration decreases at first; when $c = c_{sr}$, D_t^0 (R_h^0) reaches the minimum (maximum) value and levels off after $c < c_s$. This variation can be simply explained as follows: along with the decrease of the concentration, the distance among polymer molecules will increase, and the volume of the molecules will expand continuously. Till $c = c_{sr}$, the volume is up to the maximum value and hardly varies with diluting any longer. That is to say, in the extremely dilute concentration regime, polymer chains are isolated and almost do not suffer interchain interaction. Additionally, the intrinsic viscosity is dependent upon the volume occupied by the polymer chains,³⁴ so the reduced viscosity, i.e., the intrinsic viscosity as $c < c_s$, tends to be invariable. So far we have interpreted satisfactorily the viscosity abnormality of PS/toluene solution in extremely dilute concentration regime and adequately supported the prediction mentioned above.

Young et al.³⁴ have reported that for nonaggregating polymers in dilute solution, z-average diffusion coefficient is concentration-independent; if a polymer is aggregating, then it varies with concentration. From Figure 5 we can see that, in the dilute concentration regime, D_t^0 varies with c , but the variation range is relatively narrower, so we may conclude

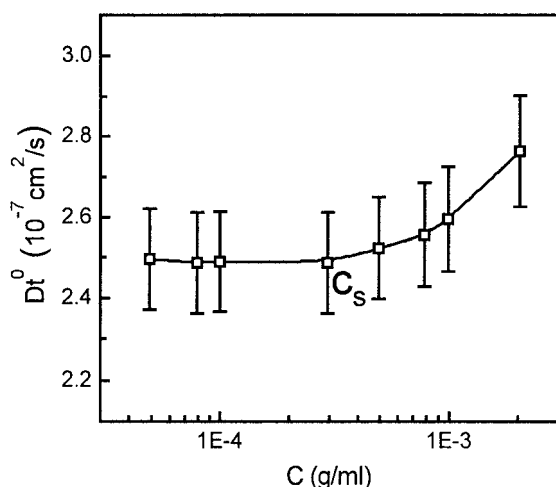


Figure 5 Plots of D_t^0 versus c for the PS/toluene solution. The error bars denote $\pm 5\%$ experimental uncertainty of the method.

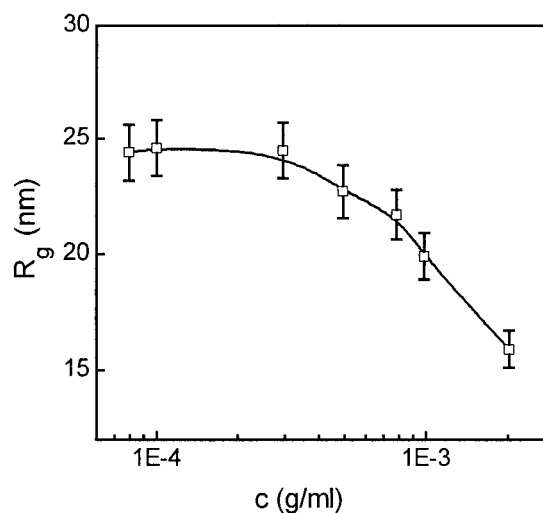


Figure 6 Plots of R_g versus c for the PS/toluene solution. The error bars denote $\pm 5\%$ experimental uncertainty of the method.

that PS molecules have slight aggregation in this regime. However, in the extremely dilute regime, D_t^0 has no concentration-dependence, so there is no aggregation among PS molecules.

In addition, from Figure 5, it seems reasonable to suggest, like the viscosity, that in the extremely dilute concentration regime, there exists:

$$|D_t^0|_{c < c_s} = D_{t0}^0 \quad (20)$$

In fact, from Table I, we can see that the extrapolated value of D_{t0}^0 is very close to the level-off one.

The confirmation of the SLS

In terms of the experimental procedure of SLS described in the experimental part, the $R_g \sim c$ curve for the PS sample was obtained as shown in Figure 6 considering $\pm 5\%$ experimental error. Comparing Figure 6 with Figure 5, the conclusion is made that the variation laws of R_g and R_h^0 (inverse proportional to D_t^0) are completely consistent. So the research results of the LLS are in accordance with those of the viscometry satisfactorily.

CONCLUSIONS

In summary, the variation of reduced viscosity (η_{sp}/c) with concentration has been studied with polystyrene sample in toluene. It is found that the system has no obvious adsorption and there is a larger experimental error caused by the manual time-measuring. Through mathematical analysis, a quantitative relation about the error is given. By the method of computing mean values from several repeated measurements, the variation law of η_{sp}/c - c curve can be found preliminarily.

There exists a dynamic contact concentration c_s which separates a dilute regime ($c > c_s$) into an extremely dilute regime ($c < c_s$). When $c > c_s$, the $\eta_{sp}/c-c$ curve shows a good linearity as predicted by Huggins equation; but when $c < c_s$, it is interesting that the $\eta_{sp}/c-c$ curve bends neither upward nor downward but levels off. This finding is interesting; nevertheless, considering the relatively larger experimental uncertainty, the laser light scattering investigation is performed to confirm it once more. The results of LLS show that the $D_t^0 \sim c$ and $R_g \sim c$ curves, resembling the $\eta_{sp}/c-c$ curve, are also divided into two parts by c_s . When $c > c_s$, the curves are normal and linear. When $c < c_s$, they level off in the range of experimental error. That means D_t^0 (R_h^0) and R_g are invariable and independent of polymer concentration in the extremely dilute concentration regime. That is to say, the polymer chains are isolated and unfold completely to be random coils, so their hydrodynamic volumes are not changeable any more, and thus the $\eta_{sp}/c-c$ curve would level off. Therefore, the LLS experiments corroborate the viscometric result in terms of the conformation of polymer chains. Furthermore, this article, for the first time, through a method of combination of conventional Ubbolohde viscometry with LLS, proves an important conclusion unambiguously, once predicted by Pan and Cheng,²² that the reduced viscosity is the intrinsic viscosity and independent of polymer concentration in the extremely dilute concentration regime. It is true at least for PS/toluene solution and it will be still true, we believe, for nonpolyelectrolyte solution.

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