Vol. 18 高等学校化学学报 No. 7
1 9 9 7年7月 CHEMICAL JOURNAL OF CHINESE UNIVERSITIES 1236～1239

[Letter]

Concentration Dependence of the Radius of Gyration and Translational Diffusion Coefficient of Linear Polystyrene Chains in Cyclohexane

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Keywords Polystyrene, Laser scattering, Hydrodynamic radius, Radius of gyration

1 Introduction

The dependence of the translational diffusion coefficient(D) of linear flexible polymer chains on concentration is controversial because theoretical predications and experimental results are contradictory. For example, Fixman has predicted that k_d, the second virial coefficient of D, is a non-zero constant at the Flory θ-point[1], while Yamakawa has predicted that k_d should vanish at the θ point[2]. The sedimentation experiments showed that k_d was a non-zero constant at the θ point[3], while the others found that it did vanish at the θ-point even for the same polymer sample used[4]. More experiments are needed to clarify this fundamental and controversial question. Another interesting problem related to the solution dynamics of a linear flexible chain at the θ-point is the concentration dependence of its radius of gyration(R_g). The SANS results show that the R_g of a flexible linear chain in a dilute θ-solution is the same as that in bulk[5,5]. It should be noted that in a good solvent k_d contains both thermodynamic and hydrodynamic contributions, while R_g contains only a thermodynamic contribution. This study was designed to find the concentration dependence of k_d and R_g, if there is any, in the dilute and semidilute solutions under the θ-condition.

2 Experimental

A polystyrene(PS) sample($M_w = 1.05 \times 10^6$ g/mol and $M_w/M_n = 1.08$) from Nanjing University and analytical grade cyclohexane were used without further purification. The polymer concentration was in the range of $2.08 \times 10^{-5} \sim 3.78 \times 10^{-3}$ g/mL. The solution was kept at 40 ℃ for at least three days to ensure a complete dissoluton and clarified with a 0.22 μm Millipore filter inside an oven to avoid precipitation. The samples were kept at 40 ℃ before the Laser Light Scattering(LLS) experiment at a lower θ-temperature of 34.5 ℃.

A modified commercial LLS spectrometer(ALV/SP-150, Germany) equipped with an

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Received on January 27, 1997.

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ALV-5000 multi-Γ digital correlator was used with a solid-state laser(ADLAS DPY42511, Germany; output power = 400 mW at $\lambda = 532$ nm) as the light source. The incident light beam was vertically polarized with respect to the scattering plane, and the laser light intensity was regulated with a beam attenuator(Newport M-925B) so that possible localized heating in the light-scattering cuvette can be avoided. In our present setup, the coherent factor β in dynamic LLS is about 0.87, a rather high value for an LLS spectrometer capable of doing both static and dynamic LLS simultaneously.

In static LLS, the excess scattering intensity, known as Rayleigh ratio $R_{vv}(\theta)$, is related to the scattering angle θ and polymer concentration c as[7]

$$Kc/R_{vv}(\theta) = 1/M_w[1 + (1/3)q^2\langle R_g\rangle] + 2A_2c \qquad (1)$$

where $K=4\pi^2n^2(\mathrm{d}n/\mathrm{d}c)^2/(N_A\lambda_0^4)$, $q=4\pi n\sin(\theta/2)/\lambda_0$ with n, $\mathrm{d}n/\mathrm{d}c$, λ_0 and N_A being the refractive index of the solvent, the specific refractive index increment, the wavelength of the light and Avogadro's number, respectively. In order to obtain a precise value of $\langle R_g\rangle$, a wide angular range of 20°～150° with a small step increment of 2° was used. The experimental value of M_w is 1.05×10^6 g/mol, very close to the literature value[8]. In dynamic LLS, the intensity-intensity time correlation function $G^{(2)}(t)$ was measured. Since the sample is very narrowly distrubuted, using the first-order cumulants analysis is sufficient to obtain the average transitional diffusion coefficient($\langle D\rangle$) from $G^{(2)}(t)$. The detail of dynamic LLS can be found elsewhere[9].

3 Results and Discussion

Fig. 1 shows the concentration dependence of the radius of gyration $\langle R_g\rangle$ of the polystyrene in cyclohexane, where the solution temperature is 34.5 ℃ at which the second virial coefficient A_2 is vanished and there is no indication of the presence of A_3 in the same concentration range studied. Within the experimental uncertainty, $\langle R_g\rangle$ is independent of the polymer concentration. It should be noted that the present results are different from the previous light scattering data of slight decrease of the coil dimension with increasing concentrations for polystyrene in a θ-solvent of *trans*-decalin at 20 ℃[10] and the theroretical interpretation of the concentration dependence based on spherical reflecting walls[12] cannot be confirmed by the present study.

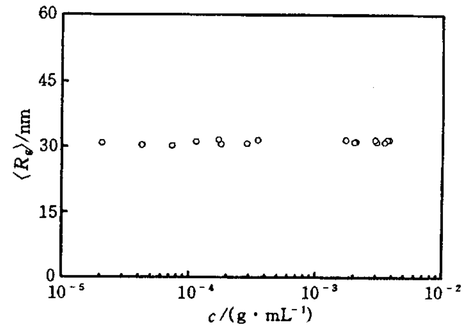

Fig. 1 Concentration dependence of the average radius of gyration $\langle R_g\rangle$ of polystyrene in cyclohexane at 34.5 ℃

Fig. 2 shows a concentration dependence of the apparent translational diffusion coefficient $\langle\Gamma\rangle/q^2$ of polystyrene in cyclothexane at $t=34.5$ ℃ and $\theta=15°$. When c is lower than 2×10^{-4} g/mL, $\langle\Gamma\rangle/q^2$ is indpendent of c; while c is higher than 2×10^{-4} g/mL, $\langle\Gamma\rangle/q^2$ decreases as c increases. If a linear axis of concentration is adopted as shown in Fig. 3, $\langle\Gamma\rangle/q^2$ is a linear function of c, supporting the Fixman's theory[1], *i. e.*, $k_d\neq0$ even under the θ-

condition. For polymer chains in a good solvent, Stockmayer showed that[13,14]

$$\langle \Gamma \rangle / q^2 = \langle D \rangle (1 + k_d c)(1 + f \langle R_g^2 \rangle q^2) \qquad (2)$$

where $\langle D \rangle$ is the average translational diffusion coefficient at $c \to 0$ and $q \to 0$; and f is a dimensionless number between 0.1 and 0.33. $k_d$contains a thermodynamic term and a hydrodynamic term, *i.e.* [15],

$$d_d = 2A_2 M_w - c_D N_A R_h^3 / M_w \qquad (3)$$

where c_D, N_a and R_h are a semi-empirical positive constant, the Avogadro's constant and the hydrodynamic radius, respectively. For a small q, $1 + f \langle R_g^2 \rangle q^2 \approx 1$. A combination of eq. (2) and eq. (3) leads to

$$\langle \Gamma \rangle / q^2 = \langle D \rangle [1 - (c_D N_A R_h^3 / M_w) c] \qquad (4)$$

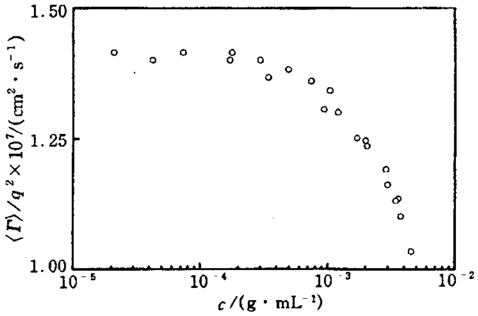

Fig. 2 Semi-logarithmic plot of $\langle \Gamma \rangle / q^2$ *vs* c for polystyrene in cyclohexane at 34.5 ℃

$\langle \Gamma \rangle$ and c are the average line width and polystyrene concentration, respectively.

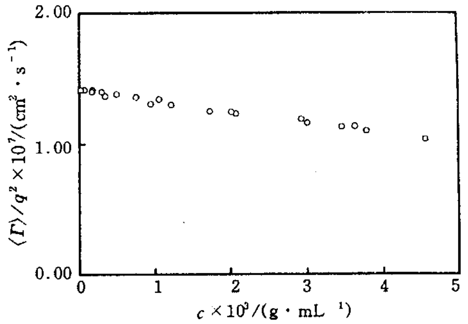

Fig. 3 Concentration dependence of $\langle \Gamma \rangle / q^2$ of polystyrene in cyclohexane at 34.5 ℃

$\langle \Gamma \rangle$ is the average line width.

A least-square fitting of the data in Fig. 3 shows that $c_D = 2.82$, close to 2.23 calculated on the basis of the soft sphere model proposed by Fixman[1]. It should be noted that the predication of $k_d = 0$ at $A_2 = -6.4 \times 10^{-4}$ mL · mol/g^{-2} is difficult to prove because the precipitation of polymer chains occurs under this poor solvent condition. When c is higher than 2×10^{-4} g/mL, the decrease of $\langle \Gamma \rangle / q^2$ might also be interpreted in terms of the intercoil association recently discussed by Cheng[16].

In summary, our results support the Flory's predication, namely $\langle R_g \rangle$ is independent of c under the θ-condition. The concentration dependence of $\langle D \rangle$ under the θ condition can be well described by the soft sphere model proposed by Fixman[1].

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θ条件下线性聚苯乙烯链的旋转半径及平动扩散系数的浓度依赖性

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摘要 研究了线性聚苯乙烯链在稀和半稀的θ溶液中平动扩散系数(D)和均方旋转半径(R_g)的浓度依赖性. 在θ条件下，R_g无浓度依赖性，而D的浓度依赖性可由Fixman软球模型理论描述.

关键词 聚苯乙烯，光散射，流体力学半径，旋转半径

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(Ed.: H, X)

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* 摘自“科技日报”1997年2月13日第二版。