

THE OBSERVATION OF INTERNAL MOTION OF LINEAR POLYSTYRENE CHAINS IN CYCLOHEXANE AROUND θ TEMPERATURE*

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Abstract A high molecular weight ($M_w = 1.85 \times 10^7$) polystyrene (PS) with narrow distribution was prepared by high vacuum anionic polymerization in tetrahydrofuran. By use of dynamic light scattering, the dynamics of PS chains in cyclohexane was studied around the θ temperature. For the first time, we have observed the internal motion of polymer chains in solutions below the θ temperature by using dynamic light scattering at smaller angles (even $qR_g < 1$).

Keywords: Dynamic light scattering; Internal motion; Relaxation time.

INTRODUCTION

As a fundamental problem in polymer physics, the dynamics of polymer chains in dilute solutions has been extensively studied both in theory and in experiments^[1–27]. The theory of the dynamics of non-charged flexible polymer chains was developed by Rouse^[1] and Zimm^[2]. Based on the Rouse-Zimm model, Pecora^[3], de Gennes^[4], Dubois-Violette^[5] established the equations about the dynamic structure factor $S(q, t)$ of flexible polymers in dilute solutions. Akcasu *et al.* developed the method to relate the initial slope of $S(q, t)$ to the cumulants fit results ($\langle \Gamma \rangle$, the initial decay or the average line-width of the correlation function) which was determined by dynamic light scattering (DLS)^[6–8]. Chu, Berne and Pecora *et al.* have established the data analysis methods to detect the internal motions of polymer chains in dilute solutions^[9–11].

In the region of $qR_g \ll 1$, where the scattering vector $q = 4\pi n \sin(\theta/2)/\lambda_0$ and n , θ , λ_0 are the solvent refractive index, the scattering angle and the wavelength of the light in vacuum, respectively, R_g is the radius of gyration. $S(q, t)$ is mainly contributed by translational diffusion of center of mass of polymer chains, which can be measured by DLS. When $ql > 1$, where l is the statistical length of the chains (*ca.* 0.5–5 nm), $S(q, t)$ can not be described by the Rouse-Zimm model, and the dynamic behavior is generally detected by neutron spin-echo or NMR technique. When $qR_g > 1$ and $ql < 1$, $S(q, t)$ is multi-exponential due to significant contributions from various internal motions, so that multi-peaks in the CONTIN fit results of correlation function ($G(q, t)$) can be observed. Such a region is called internal region or fractal region. In light scattering, for different solvent and wavelength of the light, $1/q$ is 30–1000 nm in the range of 12–155°, so we could observe the internal motion of a homopolymer chain with high molecular weight ($R_g \gg 30$ nm) at a large angle^[12–23]. Alternatively, the

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internal motion could be observed by using block copolymers with one decolorant block^[24–29], the typical example is polystyrene-*b*-polymethyl methacrylate (PS-*b*-PMMA) in benzene.

Most previous work deal with polymers in good solvent, the dynamics of a polymer in θ solvent below the θ temperature has not been examined because of the possible phase separation of the solution. Since the polymer chains are shrunk coils or globules when the temperature is above the lower critical solution temperature (LCST) or lower than the upper critical solution temperature (UCST) in extremely dilute solutions^[30–39], the R_g should be much smaller than that in good solvent. Thus, only the internal motion of long polymer chains in extremely dilute solutions could be observed by laser light scattering (LLS). In the present work, we have prepared long polystyrene chains by anionic polymerization and investigated their internal motion in cyclohexane in the bad solvent region by using LLS.

EXPERIMENTAL

Materials

PS was prepared by the high vacuum anionic polymerization in tetrahydrofuran (THF) with the initiation of sodium naphthalene. The molecular weight and its distribution were detected by static and dynamic laser light scattering in toluene^[40]. Cyclohexane was dried by CaH_2 and distilled before use.

Sample Preparation

After PS was dissolved in dust-filtered cyclohexane at 50°C for one week, the solution was further diluted with dust-filtered cyclohexane for several times. The solution was kept at 50°C for at least one week so that the polymer was completely dissolved, and the possible dust deposited on the bottom of the cell. The concentration was 6.49×10^{-6} g/mL. Finally, the solution was dropped into the scattering cell by burette. The solution was kept at each temperature point for 5 h before the LLS measurement.

Laser Light Scattering

A commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-digital time correlation (ALV5000) and a cylindrical 22 mW He-Ne laser ($\lambda_0 = 632$ nm, Uniphase) as the light source was used. In static LLS^[41], we can obtain the weight-average molecular weight (M_w) and the z-average root-mean square radius of gyration ($\langle R_g^2 \rangle^{1/2}$ or written as $\langle R_g \rangle$) of scattering objects in a dilute solution/dispersion from the angular and concentration dependence of the excess absolute scattering intensity (Rayleigh ratio $R_{vv}(q)$, and $qR_g \ll 1$) as,

$$\frac{Kc}{R_{vv}(q)} = m_0 S(q) + 2A_2 c \approx \frac{1}{M_w} \left(1 + \frac{1}{3} \langle R_g^2 \rangle q^2 \right) + 2A_2 c \quad (1)$$

where $K = 4\pi n^2 (dn/dc)^2 / (N_A \lambda_0^4)$ and $q = (4\pi n / \lambda_0) \sin(\theta/2)$ with N_A , dn/dc , n , λ_0 and m_0 being the Avogadro number, the specific refractive index increment, the solvent refractive index, the wavelength of the light in vacuum and the molecular weight of the monomer, respectively. $S(q)$ is the structure factor; and A_2 is the second virial coefficient. For the Gauss chain, the structure factor is fitted with Debye equation as follow^[9]:

$$S(q) = N \times 2(qR_g)^{-2} [1 - (qR_g)^{-2} (1 - \exp(-(qR_g)^2))] \quad (2)$$

Where N is the polymerization degree of the chain. At $qR_g \ll 1$, $S(q) \approx 1 - (qR_g)^2/3$ which is in agreement with Eq. (1). In this experiment, PS has a narrow distribution and $\langle R_g^2 \rangle^{1/2} \equiv R_g$, the polydisperse influence is not considered.

In DLS^[10], the Laplace inversion (the CONTIN program in the correlator was used) of each measured intensity-intensity-time correlation function $G^{(2)}(q, t)$ in the self-beating mode can lead to a characteristic relaxation time distribution $G(\tau)$. Laplace inversion analysis of a measured intensity-intensity time correlation function $G^{(2)}(q, t)$ in the self-beating mode can lead to an average line width ($\langle \Gamma \rangle$), for a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by $(1/\tau q^2)_{c \rightarrow 0, q \rightarrow 0} \rightarrow D$. In this case, $G(\tau)$ can be converted into a translational diffusion coefficient distribution $G(D)$ or further to a hydrodynamic radius distribution $f(R_h)$ via the Stokes-Einstein equation, $R_h = (k_B T / 6\pi\eta) / D$, where k_B , T and η are the Boltzmann

constant, the absolute temperature, and the solvent viscosity, respectively. The cumulant analysis of $G^{(2)}(t)$ can actually result in an accurate average characteristic relaxation time $\langle\tau\rangle$ ($\tau = 1/\Gamma$) and its polydispersity index (PDI). The molecular weight distribution of the scattering object can be estimated from PDI by the following equation.

$$M_z / M_w = 1 + \left(\frac{1}{\nu}\right)^2 \times \text{PDI} \quad (3)$$

Where ν is the Flory factor of the scattering object, and the value of the linear chain should be 0.6 or 0.5 in good or θ solvent, respectively. Note that the laser used is relatively weak so that there is no local heating and degradation^[42]. In each DLS measurement, the time correlation function was accumulated until the maximum difference between the measured and calculated data points was less than 0.1%, which spent 0.5 h to 7 h as the angle was increased from 12° to 155°.

RESULTS AND DISCUSSION

The molecular weight of PS used in this study could not be characterized by gel permeation chromatography (GPC) because it is too high. We used LLS to measure the molecular weight and distribution of polystyrene in toluene. Figure 1 shows the SLS results, where the concentrations used are $c = 1.15 \times 10^{-4}$, 2.39×10^{-4} , 3.32×10^{-4} and 4.84×10^{-4} g/mL. After the least square fitting with Eq. (2), we can get the results that M_w was 1.85×10^7 , R_g was 270 nm and A_2 was 2.3×10^{-4} mL·mol·g⁻². The results are consistent with those in reference [43].

Figure 2 shows the average line-width $\langle\Gamma\rangle$ has a linear dependence on q^2 at small angles. The extrapolation of $q \rightarrow 0$ passes the origin, revealing that it is diffusive. Thus, we can get the apparent translational diffusion coefficient and R_h of the polymer. The ratio of z -average root-mean square radius of gyration to hydrodynamic radius (R_g/R_h) at this concentration is 1.79. This is consistent with the theoretical prediction (1.78) for monodisperse Gaussian coils in good solvents^[42]. The PDI value at the angle of 12° was smaller than 0.01, indicating that the molecular weight distribution (M_z/M_w) was smaller than 1.04. Thus, the PS sample used has a very high molecular weight (1.85×10^7) and narrow distribution ($M_z/M_w < 1.1$). Note that the PDI value increases with the scattering angle. This is because the internal motion coupled into the pure diffusion motion.

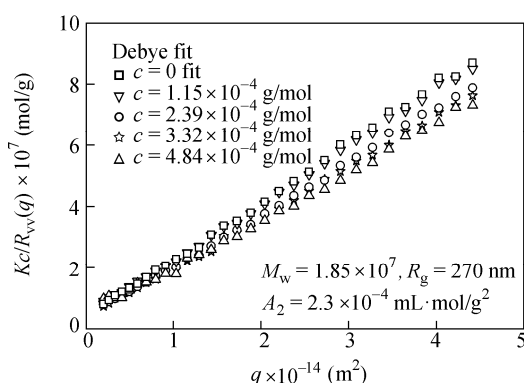


Fig. 1 Debye plot of polystyrene in toluene at 25°C. The concentration (c) ranges from 1.15×10^{-4} g/mL to 4.84×10^{-4} g/mL

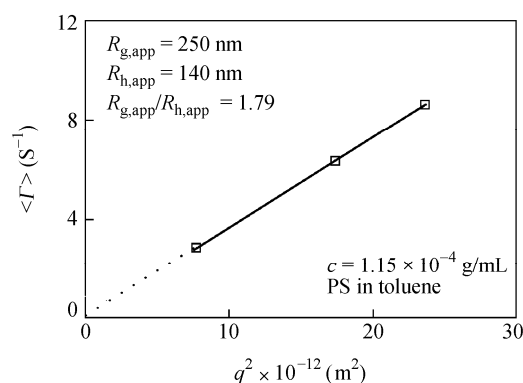


Fig. 2 Scattering vector (q) dependence of average characteristic line-width ($\langle\Gamma\rangle$) of polystyrenes in toluene at 25°C. $c = 1.15 \times 10^{-4}$ g/mL

Figure 3 shows that the apparent molecular weight ($M_{w,app}$) of PS almost does not change with temperature, indicating that no aggregation occurs, so it is possible for us to investigate the internal motion. Note that the slight decrease of the molecular weight at the lowest temperature can be attributed to the decrease of dn/dc . Figure 4 shows the form factor in different temperatures is close to the curve predicted by the Debye equation.

The inset shows R_g decreases with lowering temperature, clearly revealing that the chains have shrunk but not collapsed into globules.

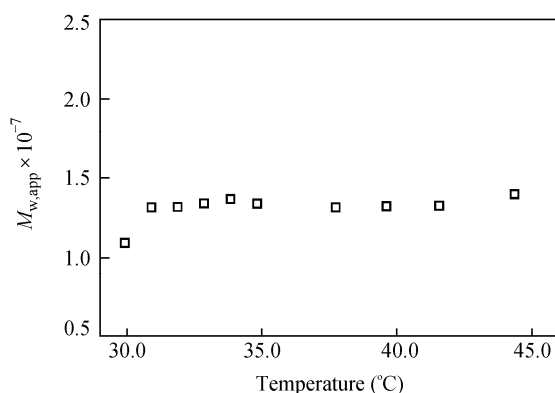


Fig. 3 Temperature dependence of apparent molecular weight for PS in cyclohexane in the range of 30–45°C
 $c = 6.49 \times 10^{-6}$ g/mL

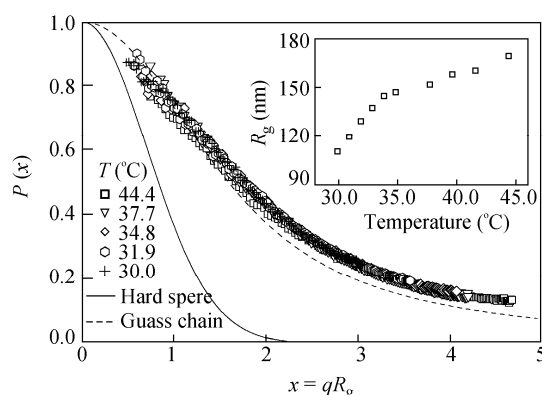


Fig. 4 Temperature dependence of the form factor ($P(x)$) of PS in cyclohexane at $c = 6.49 \times 10^{-6}$ g/mL
The dash line and solid line are the predictions of the form factor for Guass chain and hard sphere, respectively;
The inset shows the temperature dependence of R_g for PS in cyclohexane

Figure 5 shows the reduced first cumulant ($\Gamma\eta_0/q^3K_bT$) as a function of qR_g for PS dilute solutions, where the cumulant has been divided by q^3 so that it is a constant in the intermediate q region if Γ has a q^3 dependence^[13]. At a temperature above θ temperature, as qR_g increases, the reduced first cumulant decreases and approaches a constant at $qR_g = 2$. Clearly, the first cumulant is scaled with q^3 . This is consistent with the non-free-draining bead-spring theoretical model for flexible polymer chains^[12]. Such a dependence has also been reported before^[13, 20]. It has been predicted that the constant value of the reduced first cumulant is 0.053 for non-free-draining flexible coils with a preaveraged Oseen tensor and 0.0625 for that without a preaveraged Oseen tensor in θ solvent^[12]. In the present study, the constant value (0.050) is lower than the theoretical values but is consistent with the experimental value reported before^[13]. At a temperature below θ temperature, the first cumulant no longer has the q^3 dependence even $qR_g > 2$.

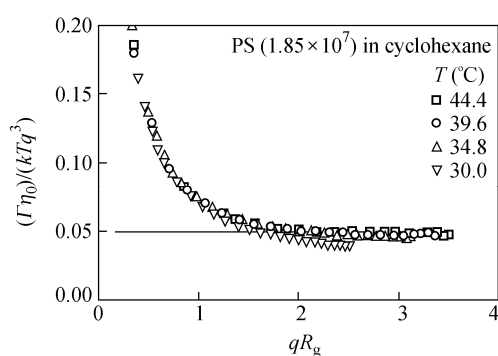


Fig. 5 Plot of $\Gamma\eta_0/q^3K_bT$ versus qR_g for PS in cyclohexane at different temperature
 η_0 is the solvent viscosity, and Γ was obtained from the cumulant analysis

We also used CONTIN program to analyze the results, which allows a much improved appraisal of the decay time distribution. Figure 6 shows the typical CONTIN analysis results of PS in cyclohexane at 44.4°C at different scattering angles. Obviously, there is only one peak at a small scattering angle (12°). However, as the angle increases, multi-peaks can be observed, and each of them becomes broader with the increasing angle.

Figure 7 shows the τq^2 dependence of the relaxation time distribution $f(\tau)$. The shift of peak positions suggests that different internal motions have coupled.

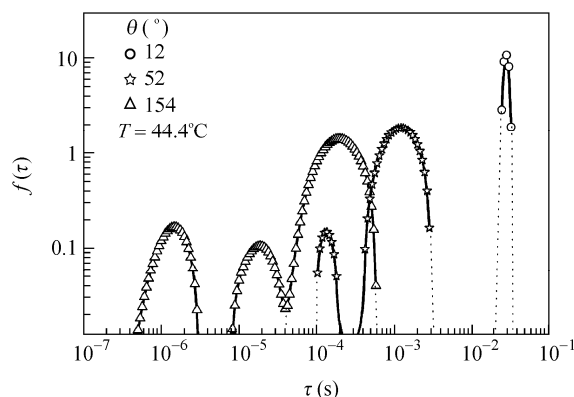


Fig. 6 Relaxation time distribution ($f(\tau)$) from the CONTIN analysis of PS in cyclohexane at 44.4°C at different scattering angles

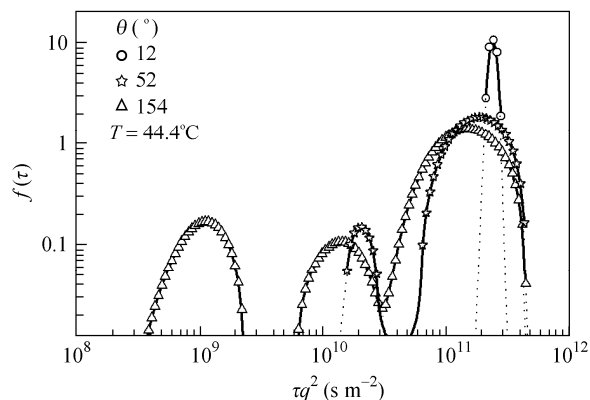


Fig. 7 Plots of relaxation time distribution ($f(\tau)$) versus τq^2 at 44.4°C at different scattering angles τ and q are relaxation time and scattering vector, respectively

Now, we define the motion with the largest relaxation time as the slow mode and all the others as the fast modes. Figure 8 shows a typical intensity contribution of the fast mode at the temperature of 44.4°C. As the qR_g increases, the contribution fluctuatedly increases. As shown in Fig. 7, this is because some fast modes couple with the slow mode^[20, 21]. At this temperature, only when the value of qR_g increases to about 1.0, multi-peaks can be observed by CONTIN fit^[20, 22]. As the temperature decreases, multi-peaks can be observed by CONTIN fit in smaller angles, and the intensity contribution of the fast mode is much larger than the predicted value for Gaussian chain^[44]. The inset shows the qR_g value for the first point where we observed the fast mode decreases with the temperature. When the temperature is below 32°C, a bimodal peak at the smallest angle can be observed. It indicates that the internal motion of the chain in bad solvent region is more obviously than it in good solvent region.

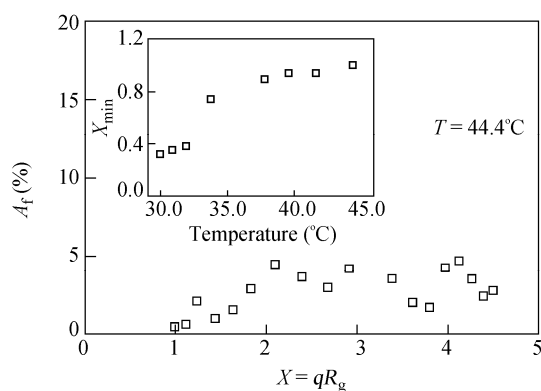


Fig. 8 The intensity contributions of the fast mode at different scattering angles. The inset shows the temperature dependence of the qR_g value of the first point where multi-peaks can be observed by CONTIN fit

It is known that when the size of the chain decreases as the temperature decreases, the concentration of monomer in each chain actually increases because the concentration is related to the concentration $c = 3N/4\pi R_g^3$, where N is the polymerization degree. Thus, the local viscosity of the chain increases, which slows down the relaxation of the internal motion. Consequently, the chain conformation cannot fully relax within the

measurement time. Moreover, the relaxation of internal motion has a q^3 dependence. That is why we can observe the internal motion at a small angle. However, how to describe the chain motion in bad solvent region in theory is still a challenge. Simulation and calculation about the internal motion are needed.

CONCLUSIONS

In conclusion, we have observed the internal motion of high molecular weight polystyrene chains in cyclohexane by use of dynamic laser light scattering. The internal motion will become more obviously as the solvent quality become worse because the relaxation time of the internal motion increases.

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