

Characterization of a Single Sample of Polymer by Dynamic Light-Scattering Technique

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Summary: This article describes the characterization of a single sample of polystyrene in toluene using laser light-scattering (LLS) technique. In dynamic LLS the Laplace inversion of precisely measured intensity-intensity time correlation function lead us first to an estimate of the characteristic line-width distribution $G(\Gamma)$ and then to the translational diffusion coefficient distribution $G(D)$. By using previously established calibration of $D = (3.64 \times 10^{-4}) M^{-0.577}$, we were able to convert $G(D)$ into a differential weight distribution $f_w(M)$ for the single sample of polystyrene. The weight-average molecular weights calculated from $f_w(M)$ are comparable to that obtained directly from static LLS. Our results showed that using single polystyrene sample instead of a set of narrowly distributed samples provided not only similar final results, but also a more practical method for polystyrene characterization.

Introduction

The properties of polymers and the articles manufactured from them are determined in great measure by molecular parameters. In many cases, where polymers are soluble both viscosity measurement and gel permeation chromatography (GPC) offer a rapid, simple and routine method for the determination of both weight average molar mass (M_w) and molecular mass distribution (M_wD). However, it is known, that the molar mass estimated from viscosity has a large uncertainty because of the errors associated with the Mark-Houwink-Sakurada parameters. As for SEC, a proper calibration of the SEC columns requires narrowly distributed standard polymer samples which are difficult to obtain in practice. Moreover, a normal SEC is not able to characterize a sample with an average molar mass higher than $\sim 5 \times 10^6$. Often these data are not available or are difficult or time-consuming to obtain. Moreover, a chemist may have only a single sample of polymer for characterization. In the present investigation we used the previously established calibration [1] between the translational diffusion coefficient (D) from dynamic laser light scattering (LLS) and the weight-average molecular weight (M_w) from static LLS by using a set of M and D to characterize a single sample of a polymer. This

method has been previously used for the characterization of phenolphthalein poly aryl (ether ketone) and polyimide [2,3].

Results and Discussion

Fig. 1 shows a typical plot of the measured intensity-intensity time correlation function for the polystyrene sample in toluene at $\theta = 20^\circ$ and $T = 20^\circ\text{C}$. In dynamic LLS, $G^{(2)}(t, q)$ can be related to the normalized first-order electric field time correlation function $g^{(1)}(t, q)$ as [4,5].

$$G^{(2)}(t, q) = \langle I(t, q)I(0, q) \rangle = A[1 + \beta |g^{(1)}(t, q)|^2] \quad (1)$$

where A is a measured base line; β is a parameter depending on the coherence of the detection; and t is the delay time. For a polydisperse sample, $g^{(1)}(t, q)$ is further related to the line-width distribution $G(\Gamma)$ by

$$|g^{(1)}(t, q)| = \langle E(t, q)E^*(0, q) \rangle = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma \quad (2)$$

Using a Laplace inversion program CONTIN [6] equipped with the correlator, we were able to calculate $G(\Gamma)$ from $G^{(2)}(t, q)$. Generally, Γ is a function of both C and q . For a diffusive relaxation [7,8]

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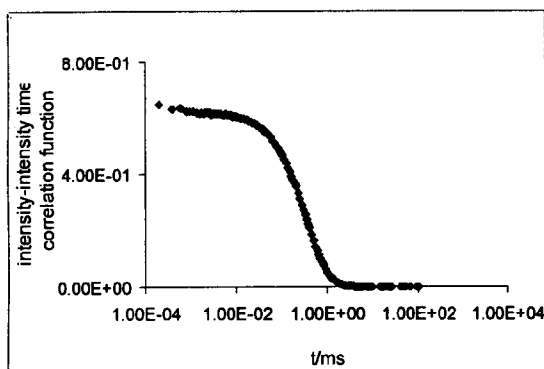


Fig. 1: Typical measured intensity-intensity time correlation function for the polystyrene in toluene at $\theta = 20^\circ$ and $T = 20^\circ\text{C}$, where the polystyrene concentration was 8.72×10^{-4} g/mL.

$$\frac{\Gamma}{q^2} = D(1 + k_d C)(1 + f \langle R_g^2 \rangle_z q^2) \quad (3)$$

where D is the translational diffusion coefficient at $C \rightarrow 0$ and $q \rightarrow 0$; k_d is the diffusion second virial coefficient; and f is a dimensionless number depending on the chain conformation, solvent quality and internal motions. On the basis of eq. 4, D , f and k_d can be calculated from $(\Gamma/q^2)_{C \rightarrow 0, \theta \rightarrow 0}$, $(\Gamma/q^2)_{C \rightarrow 0}$ versus q^2 and $(\Gamma/q^2)_{\theta \rightarrow 0}$ versus C , respectively. For a flexible polymer chain in a good solvent, f is in the range of 0.1 - 0.2 [9]. With the values of k_D and f , we were able to convert $G(\Gamma)$ measured at a finite C and q to $G(D)$.

Fig. 2 shows a typical translational diffusion coefficient distribution $G(D)$ for the polystyrene sample in toluene at 20°C , from which we were able to calculate the average translational diffusion coefficient $\langle D \rangle = \int_0^\infty G(D)D dD$ and the average hydrodynamic radius $\langle R_h \rangle = [\kappa_B T / (6\pi\eta \langle D \rangle)]$, where κ_B , T and η are the Boltzmann constant, the absolute temperature and solvent viscosity,

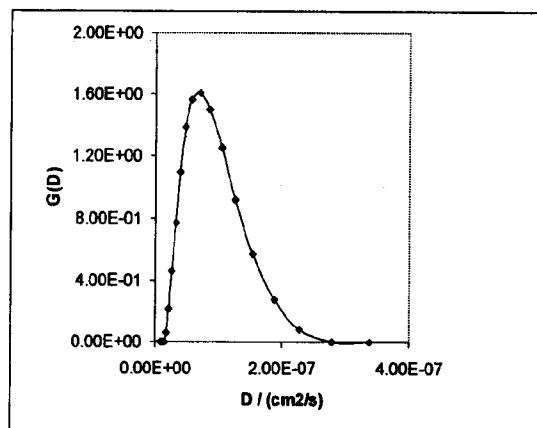


Fig. 2: Translational diffusion coefficient distribution $G(D)$ of the polystyrene in toluene at $T = 20^\circ\text{C}$.

respectively. The values of $\langle D \rangle$ and $\langle R_h \rangle$ for the polystyrene sample are listed in Table-1. The ratio of $\langle R_g \rangle / \langle R_h \rangle$ (~ 1.5) suggests that the polystyrene chains have a coil conformation in toluene at 20°C . Further, by using previously established calibration of D (cm^2/s) = $(2.37 \times 10^{-4}) M^{0.577}$, we were able to transform $G(D)$ into a molecular weight distribution. The principle is as follows [10-12]. From the definition of $|g^{(1)}(t)|$, when $t \rightarrow 0$,

$$|g^{(1)}(t \rightarrow 0)| = \langle E(t)E^*(0) \rangle_{t \rightarrow 0} = \int_0^\infty G(\Gamma) d\Gamma \propto I \quad (4)$$

whereas in static LLS, on the basis of eq. (9), when $C \rightarrow 0$ and $q \rightarrow 0$, we have

$$R_w(q) \propto I \propto \int_0^\infty f_w(M) M dM \quad (5)$$

where $f_w(M)$ is a differential weight distribution. A comparison of Eqs. (4) and (5) leads us to

$$\int_0^\infty G(\Gamma) d\Gamma \propto \int_0^\infty f_w(M) M dM \propto \int_0^\infty G(D) dD \quad (6)$$

This can be rewritten as

$$\int_0^\infty G(D) D d(\ln D) \propto \int_0^\infty f_w(M) M^2 d(\ln M) \quad (7)$$

Table-1: Summary of static and dynamic laser light-scattering results for polystyrene sample in toluene at 20°C .

Sample	$10^6 M_w$ (g/mol)	R_g (nm)	$10^4 A_2$ ($\text{mol.cm}^3/\text{g}^2$)	$10^8 \langle D \rangle$ (cm^2/s)	$\langle R_h \rangle$ (nm)	$R_g / \langle R_h \rangle$	$(M_w)_{\text{calcd}}$
PS-1	4.36	117	2.13	4.80	75	1.60	4.50

The relative errors: $M_w, \pm 5\%$; $\langle R_g \rangle, \pm 10\%$; $A_2, \pm 15\%$; $\langle D \rangle, \pm 1\%$.

where $d(\ln D) \propto d(\ln M)$ since $D = k_D M^{-\alpha_D}$
Therefore,

$$f_w(M) \propto \frac{G(D)D}{M^2} \propto G(D)D^{1+\frac{2}{\alpha_D}} \quad (8)$$

Using equation¹ D (cm^2/s) = $3.64 \times 10^{-4} M^{-0.577}$ and equation (8), we transformed D to M and $G(D)$ into $f_w(M)$, where we used the fact that for a given solvent and temperature both k_D and α_D are related to the polymer chain conformation but not strongly to the polydispersity of polymer chain; namely, we can apply $D = k_D M^{-\alpha_D}$ obtained from a series of fractionated polystyrene samples to a single polystyrene sample.

Fig. 3 shows a differential weight distribution for the polystyrene calculated from $G(D)$. Values of M_w and polydispersity index M_w/M_n calculated from $f_w(M)$ are also listed in Table-1. One way to check this calculated $f_w(M)$ is to measure M_w directly from static LLS.

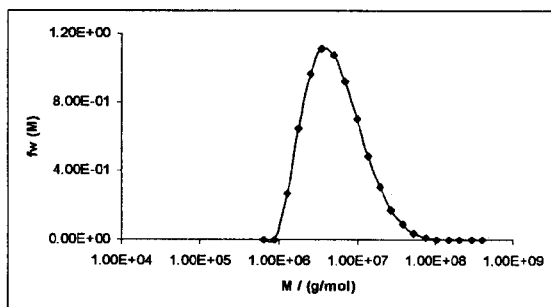


Fig. 3: Differential weight distribution $f_w(M)$ of the polystyrene, which was calculated from the $G(D)$ in Fig. 2.

Fig. 4 shows a typical Zimm plot for the polystyrene sample in toluene at 20 °C, where the solutions were clarified by a 0.5- μm filter and C ranged from 8.72×10^{-4} to 4.36×10^{-3} g/ mL. On the basis of Eq. (9), we obtained the values of M_w , $\langle R_g \rangle$ and A_2 , respectively, from $[KC/R_{wv}(q)]_{\theta \rightarrow 0, c \rightarrow 0}$, $[KC/R_{wv}(q)]_{c \rightarrow 0}$ vs q^2 and $[KC/R_{wv}(q)]_{\theta \rightarrow 0}$ vs C . The static LLS results are also summarized in Table-1. The positive value of A_2 indicates that toluene is a fairly good solvent for polystyrene at 20 °C. The measured M_w from static LLS is the same as the calculated M_w from $f_w(M)$ obtained in dynamic LLS,

which indirectly demonstrates that $f_w(M)$ in Fig. 3 is reasonable.

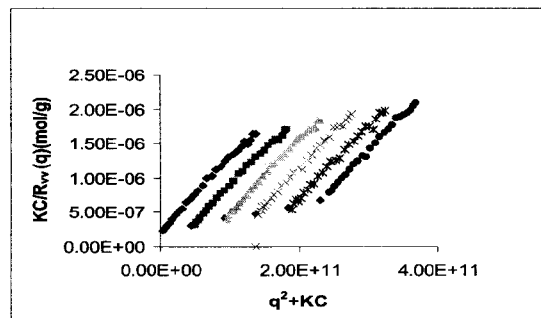


Fig. 4: Typical Zimm-plot for the polystyrene in toluene at 20 °C, where the solution was clarified by a 0.5- μm filter and C ranged from 8.72×10^{-4} to 4.36×10^{-3} g/ mL.

In short, the polystyrene sample can be characterized in toluene at 20 °C by using dynamic LLS only. The relatively small angular and concentration dependence and of the translational diffusion coefficient measured in dynamic LLS enable us to characterize polystyrene from only one dynamic LLS measurement at a finite concentration and small scattering angle. In this way, dynamic LLS can be used as a routine method to characterize the molecular weight distribution of polystyrene from the measured line-width distribution $G(\Gamma)$.

Experimental

Solution Preparation

Polystyrene sample of high molecular weight from Aldrich was used in this work. Toluene as a good solvent (Merck, analytical grade) was used without further purification. Five concentrations ranging from 4.36×10^{-3} to 8.72×10^{-4} g/ mL were prepared by dilution. All polymer solutions were clarified by using a 0.5- μm Whatman filter in order to remove dust.

Laser Light Scattering (LLS)

A commercial light-scattering spectrometer (ALV/SP-120 equipped with an ALV-5000 multi- τ digital time correlator) was used with a solid-state laser (ADLAS DPY 420II, output power ≈ 400 mW

at $\lambda = 532$ nm) as the light source. The primary beam is vertically polarized with respect to the scattering plane. The details of the LLS instrumentation and theory can be found in books [4,5]. All the measurements were carried out at 20 ± 0.1 °C.

The angular dependence of the excess absolute time-averaged scattered intensity, known as excess Rayleigh ratio, $R_{VV}(q)$, of a dilute polymer solution was measured for different concentrations C (g/mol) and scattering angles θ . $R_{VV}(q)$ is related to the weight average molecular weight M_w as [12]

$$\frac{KC}{R_{VV}(q)} \approx \frac{1}{M_w} \left(1 + \frac{1}{3} \langle R_g^2 \rangle q^2 \right) + 2A_2 C \quad (9)$$

where $K = 4\pi^2 n^2 (dn/dc)^2 / (N_A \lambda_0^4)$ and $q = (4\pi n / \lambda_0) \sin(\theta/2)$ with N_A , dn/dc , n and λ_0 being Avogadro number, the specific refractive index increment, the solvent refractive index and the wavelength of the light in vacuo, respectively; A_2 is the second virial coefficient; and $\langle R_g^2 \rangle_z^{1/2}$ (or written as $\langle R_g \rangle$) is the root-mean square z-average radius of gyration of the polymer chain in solution. After measuring $R_{VV}(q)$ at a set of C and θ , we are able to determine M_w , R_g and A_2 from a Zimm plot

which incorporates q and C extrapolation on a single grid.

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