Dynamic Light-Scattering Characterization of the Molecular Weight Distribution of Unfractionated Polyimide

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ABSTRACT: Using a developed laser light-scattering (LLS) procedure, we accomplished the characterization of an unfractionated polyimide (UPI) in $CHCl_3$ at 25°C. The Laplace inversion of precisely measured intensity–intensity time correlation function from dynamic LLS leads 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 a previously established calibration of D (cm^2/s) $= 3.53 \times 10^{-4} M^{-0.579}$, we were able to convert $G(D)$ into a molecular weight distribution. The weight-average molecular weight M_w, calculated from the molecular weight distribution, agrees well with that directly measured in static LLS. Our results indicate that both the calibration and LLS procedure used in this study are ready to be applied as a routine method for the characterization of the molecular weight distribution of polyimide. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1670–1674, 2001

Key words: dynamic laser light scattering; unfractionated polyimide; poly(BCPOBDA/DMMDA); Rayleigh ratio; intensity–intensity time correlation

INTRODUCTION

Polyimides, in particular those derived from fully aromatic monomers, represent a very important class of high-performance synthetic polymers because of their excellent mechanical, optical, and chemical properties.[1] It is well known that a fully thermoimidized polyimide is normally insoluble in common organic solvents. On the one hand, this insolubility leads to chemical resistance; on the other hand, this insolubility becomes a major obstacle in studying the solution properties, such as the chain flexibility and conformation. In the past, the solution properties and molecular parameters of these insoluble polyimides had to be estimated from their precursor, for example, poly-amic acid formed by the first-stage reaction of aromatic diamines with an anhydride. This approach has some intrinsic and serious problems, including effects of polyelectrolytes and the differences in chain rigidity between a poly(amic acid) and its corresponding polyimide chain.[2–4] Moreover, information obtained from the study of those soluble poly(amic acids) can be strongly influenced by both the nature of imidization and the reversible reaction.[5]

To tailor a polyimide to satisfy specific requirements in various industries, a careful examination and control of its chain conformation are of great importance. Practically, a correlation between the chain flexibility and bulk properties is still missing. Recently, a soluble high-performance polyimide was synthesized: poly[1,4′-bis(3,4-carboxyphenoxy) benzene dianhydride/2,2′-dimethyl-4,4′-methylene dianiline], termed

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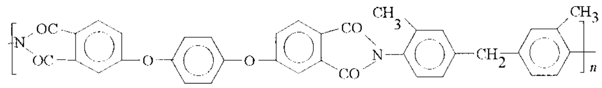
as poly(BCPOBDA/DMMDA), having the following structure:



It is worth noting that poly(BCPOBDA/DMMDA) has two flexible ether linkages in its repeating unit. It is soluble in organic solvents such as chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and dimethyl acetamide (DMAc). This enhanced solubility provides us an opportunity to directly study their solution properties. Previously, we[6] studied the chain conformation of five narrowly distributed polyimide fractions in $CHCl_3$ in terms of the molecular weight dependence of $\langle R_g \rangle$ and $\langle R_g \rangle / \langle R_h \rangle$, where $\langle R_g \rangle$ and $\langle R_h \rangle$ are the average radius of gyration and average hydrodynamic radius, respectively. We also determined the calibration between the translational diffusion coefficient D and the molecular weight M for polyimides in $CHCl_3$ at 25°C. We will demonstrate that, on the basis of our previously determined calibration,[6] we are able to characterize the molecular weight distribution of unfractionated polyimide by a combination of static and dynamic LLS. This method was previously used for unfractionated phenolphthalein polyether sulfone[7] and phenolphthalein polyether ketone.[8]

EXPERIMENTAL

Solution Preparation

The preparation of polyimide was previously detailed.[6] Analytical-grade chloroform $CHCl_3$ from Merck (Rahway, NJ) as a solvent was used without further purification. Five solutions, with their concentrations ranging from 8.72×10^{-4} to 4.36×10^{-3} g/mL, were prepared by successively diluting a stock solution of 4.36×10^{-3} g/mL. All polymer solutions were clarified by using a 0.1-μm Whatman filter (Whatman, Clifton, NJ) to remove dust and multichain aggregates.

Laser Light Scattering (LLS)

A modified commercial LLS spectrometer (ALV/SP-125 equipped with an ALV-5000 multi-tau digital time correlator; Lamgen, Hessen, Germany) was used with a solid-state laser (ADLAS DPY425II; output power is ~ 400 mW at $\lambda_0 = 532$ nm) as the light source. The incident beam was vertically polarized with respect to the scattering plane. For static LLS, the instrument was calibrated with toluene to ensure that the scattering intensity from toluene had no angular dependence in the angular range of 6–150°. The detail of LLS instrumentation and theory can be found elsewhere.[9,10]

The angular dependence of the excess absolute time-averaged scattered intensity (known as the excess Rayleigh ratio) $R_{vv}(q)$ was measured. For a dilute polymer solution at a relatively low scattering angle θ, $R_{vv}(q)$ can be expressed as[11]

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^2 \rangle q^2\right) + 2A_2C \qquad (1)$$

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 representing the Avogadro number, the specific refractive index increment, the solvent refractive index, and the wavelength of the light *in vacuo,* respectively. M_w is the weight-average molecular weight, A_2 is the second virial coefficient, and $\langle R_g^2 \rangle_z^{1/2}$ (simply 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 were able to determine M_w, $\langle R_g \rangle$, and A_2 from a Zimm plot that incorporates θ and C extrapolation on a single grid.

The differential refractive index increment dn/dC (0.189 ± 0.002) for PI in $CHCl_3$ at $T = 25$°C and $\lambda_0 = 532$ nm was determined by a high-precision differential refractometer, which was incorporated as one part of our LLS spectrometer,[12] so that we were able to measure dn/dC and $R_{vv}(q)$ under identical experimental conditions. No wavelength correction was necessary.

RESULTS AND DISCUSSION

Figure 1 shows a typical plot of the measured intensity–intensity time correlation function for an unfractionated PI sample in $CHCl_3$ at $\theta = 20°$ and $T = 25$°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[9,10]

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

where A is a measured baseline, β is a parameter that depends on the coherence of the detection,

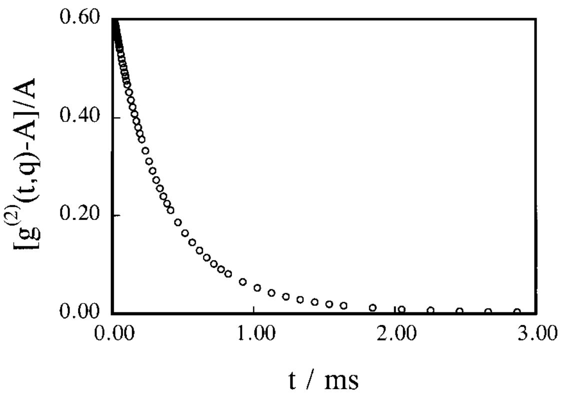


Figure 1 Typical measured intensity–intensity time correlation function for the unfractionated PI in $CHCl_3$ at $\theta = 20°$ and $T = 25°C$, where the polyimide concentration was 8.72×10^{-4} g/mL.

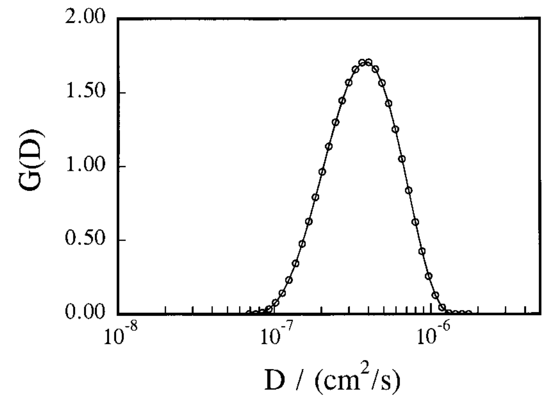


Figure 2 Translational diffusion coefficient distribution $G(D)$ of the unfractionated PI in $CHCl_3$ at $T = 25°C$.

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

$$|g^{(1)}(t, q)| = \langle E(t, q)E^*(0, q)\rangle = \int_0^\infty G(\Gamma)e^{-\Gamma t}\, d\Gamma \quad (3)$$

Using a Laplace inversion program CONTIN,[13] 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,[14]

$$\frac{\Gamma}{q^2} = D(1 + k_d C)(1 + f\langle R_g^2\rangle_z q^2) \quad (4)$$

where D is the translational diffusion coefficient at $C \to 0$ and $q \to 0$; k_d is the diffusion second virial coefficient; and f is a dimensionless number that depends on the chain conformation, solvent quality, and internal motions. On the basis of eq. (4), D, f, and k_d can be calculated from $(\Gamma/q^2)_{c\to 0,\theta\to 0}$, $(\Gamma/q^2)_{c\to 0}$ versus q^2, and $(\Gamma/q^2)_{\theta\to 0}$ versus C, respectively. For a flexible polymer chain in a good solvent, f is in the range of 0.1–0.2.[14] Therefore, in comparison with $KC/R_{vv}(q)$ in eq. (1), Γ/q^2 is less dependent on the scattering angle. Our previous study[8] showed that $f \sim 0.1$ and $k_D \sim 10$ for PI in $CHCl_3$ at 25°C. The very small value of k_D is attributed to the cancellation between the thermodynamic ($2A_2M_w$) and hydrodynamic ($C_DN_AR_h^3/M_w$) interactions when $A_2 > 0$, that is,[15]

$$k_d = 2A_2M_w - C_DN_AR_h^3/M_w \quad (5)$$

where C_D is a constant. Therefore, Γ/q^2 is less dependent than $KC/R_{vv}(q)$ is on C. With the values of k_D and f, we were able to convert $G(\Gamma)$, measured at a finite C and q, to $G(D)$.

Figure 2 shows a typical translational diffusion coefficient distribution $G(D)$ for the unfractionated polyimide sample in $CHCl_3$ at 25°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 $\langle R_h\rangle$ [$=k_BT/(6\pi\eta\langle D\rangle)$], where k_B, T, and η are the Boltzmann constant, the absolute temperature,

Table I Summary of Static and Dynamic Laser Light-Scattering Results for Unfractionated PI Sample in $CHCl_3$ at 25°C

Samples	10^{-4} M_w (g/mol)	$\langle R_g\rangle$ (nm)	10^3 A_2 (mol cm^{-3} g^{-2})	10^8 $\langle D\rangle$ (cm^2/s)	$\langle R_h\rangle$ (nm)	$\langle R_g\rangle/\langle R_h\rangle$	$(M_w/M_n)_{calcd}$
UPI	8.60	19	1.33	35.60	11	1.72	1.75

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

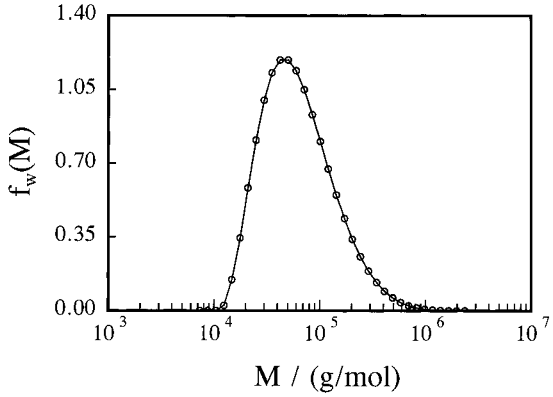


Figure 3 Differential weight distribution $f_w(M)$ of the unfractionated PI, which was calculated from the $G(D)$ in Figure 2.

and solvent viscosity, respectively. The values of $\langle D\rangle$ and $\langle R_h\rangle$ for the polyimide sample are listed in Table I. The ratio of $\langle R_g/R_h\rangle$ (1.72) suggests that the polyimide chains have a coil conformation in $CHCl_3$ at 25°C. Further, using our previously established calibration[6] of D (cm^2/s) $= 3.53 \times 10^{-4}$ $M^{-0.579}$, we were able to transform $G(D)$ into a molecular weight distribution. The principle is as follows.[16–18] From the definition of $|g^{(1)}(t)|$, when $t \to 0$,

$$|g^{(1)}(t \to 0)| = \langle E(t)E^*(0)\rangle_{t\to 0} = \int_0^\infty G(\Gamma)\, d\Gamma \propto I \quad (6)$$

whereas in static LLS, on the basis of eq. (1), when $C \to 0$ and $q \to 0$, we have

$$R_{vv}(q) \propto I \propto \int_0^\infty f_w(M)M\, dM \quad (7)$$

where $f_w(M)$ is a differential weight distribution. A comparison of eqs. (6) and (7) leads us to

$$\int_0^\infty G(\Gamma)\, d\Gamma \propto \int_0^\infty f_w(M)M\, dM \propto \int_0^\infty G(D)\, dD \quad (8)$$

which can be rewritten as

$$\int_0^\infty G(D)D\ d(\ln D) \propto \int_0^\infty f_w(M)M^2\ d(\ln M) \quad (9)$$

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

$$f_w(M) \propto \frac{G(D)D}{M^2} \propto G(D)D^{1+(2/\alpha_D)} \quad (10)$$

Using D (cm^2/s) $= 3.53 \times 10^{-4}$ $M^{-0.579}$ and eq. (10), 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; that is, we can apply $D = k_D M^{-\alpha_D}$, obtained from a series of fractionated samples, to a broadly distributed unfractionated PI sample.

Figure 3 shows a differential weight distribution for the unfractionated PI sample calculated from $G(D)$. Values of M_w and the polydispersity index M_w/M_n calculated from $f_w(M)$ are also listed in Table I. The calculated value of M_w/M_n (1.75) shows that the polymer is moderately distributed. One way to check this calculated $f_w(M)$ is to measure M_w directly from static LLS.

Figure 4 shows a typical Zimm plot for the unfractionated polyimide in $CHCl_3$ at 25°C, where the solutions were clarified by a 0.1-μm filter and C ranged from 8.72×10^{-4} to 4.36×10^{-3} g/mL. On the basis of eq. (1), we obtained the values of M_w, $\langle R_g\rangle$, and A_2, respectively, from $[KC/R_{vv}(q)]_{\theta\to 0, c\to 0}$, $[KC/R_{vv}(q)]_{c\to 0}$ versus q^2, and $[KC/R_{vv}(q)]_{\theta\to 0}$ versus C. The static LLS results are also summarized in Table I. The positive value of A_2 indicates that $CHCl_3$ is a fairly good solvent for the unfractionated PI at 25°C. The measured M_w from static LLS is practically the

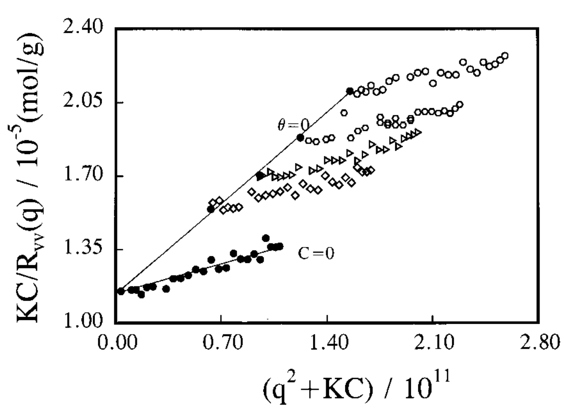


Figure 4 Typical Zimm plot for the unfractionated PI in $CHCl_3$ at 25°C, where the solution was clarified by a 0.1-μm filter and C ranged from 8.72×10^{-4} to 4.36×10^{-3} g/mL.

same as the calculated M_w from $f_w(M)$ obtained in dynamic LLS, which indirectly demonstrates that $f_w(M)$ in Figure 3 is reasonable.

CONCLUSIONS

In summary, this investigation showed that the unfractionated PI sample can be characterized in $CHCl_3$ at 25°C by using dynamic LLS. The relatively small angular and concentration dependencies and translational diffusion coefficients measured in dynamic LLS enable us to characterize PI from only one dynamic LLS measurement at a finite concentration and small scattering angle. In this way, dynamic LLS can be used as a quick and convenient routine method to characterize the molecular weight distribution of polyimide from the measured line-width distribution $G(\Gamma)$.

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