

# Dynamic Light-Scattering Characterization of the Molecular Weight Distribution of a Broadly Distributed Phenolphthalein Poly(aryl ether ketone)

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## SYNOPSIS

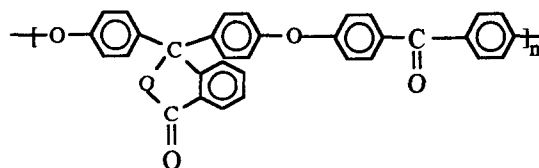
Using a recently developed laser light-scattering (LLS) procedure, we accomplished the characterization of a broadly distributed unfractionated phenolphthalein poly(aryl ether ketone) (PEK-C) in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ . The laplace inversion of precisely measured intensity-intensity 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  $D$  ( $\text{cm}^2/\text{s}$ ) =  $2.37 \times 10^{-4} M^{-0.57}$ , we were able to convert  $G(D)$  into a differential weight distribution  $f_w(M)$ . The weight-average molecular weight  $M_w$  calculated from  $f_w(M)$  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 PEK-C. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Poly(aryl ether ketones) as high-performance engineering thermoplastics have received considerable commercial interest because of their high chemical resistance and excellent mechanical properties, especially their high-temperature performance. They are widely used as matrix resins for high-performance reinforced composites. Two of the most prominent members are poly(ether ether ketone) (PEEK) and poly(ether ketone).<sup>1,2</sup> On the other hand, their chemical resistance and crystalline structure make them only soluble in strong acids or solvents with a boiling point higher than the melting temperature of their crystalline structure. Therefore, the process and application of these thermoplastics have been greatly hindered by their insolubility in common solvents. So far, few studies on dilute solution properties of PEEK have been reported mainly because it is only soluble in concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_3\text{Cl}$ , and  $\text{CH}_3\text{SO}_3\text{H}$ .<sup>3,4</sup> However, various

extents of sulfonation of PEEK in  $\text{H}_2\text{SO}_4$  has certainly complicated its characterization.<sup>5</sup>

Considering this solubility problem, Zhang et al.<sup>6</sup> recently developed a novel thermoplastic, phenolphthalein poly(aryl ether ketone) (PEK-C), which is a linear aromatic polymer with the following chemical structure:



PEK-C is not only similar to PEEK in physical and mechanical properties but also soluble in several polar organic solvents, such as chloroform, *N,N*-dimethylformamide, *N*-methylpyrrolidinone, and chlorohydrocarbones. In addition to matrix resins for high-performance reinforced composites, it has also been recommended for making a high-temperature and solvent-resistant membrane.<sup>7</sup>

Previously, we<sup>8</sup> studied the chain conformation of five narrowly distributed PEK-C fractions in  $\text{CHCl}_3$  in terms of the molecular weight dependence

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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, and we also determined the calibration between the translational diffusion coefficient  $D$  and the molecular weight  $M$  for PEK-C in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ . We demonstrate that on the basis of our previously determined calibration,<sup>8</sup> we are able to characterize the molecular weight distribution of a broadly distributed unfractionated PEK-C in  $\text{CHCl}_3$  from only one dynamic laser light-scattering (LLS) measurement.

## EXPERIMENTAL

### Solution Preparation

The preparation of PEK-C has been detailed before.<sup>6</sup> Analytical grade chloroform  $\text{CHCl}_3$  from Merck as a solvent was used without further purification. Five solutions with their concentrations ranged from  $8.72 \times 10^{-4}$  to  $4.36 \times 10^{-3}$  g/mL were prepared by successively diluting a stock solution of  $4.36 \times 10^{-3}$  g/mL. The polymer solutions were clarified by a  $0.1\text{-}\mu\text{m}$  Whatman filter to remove dust.

### Laser Light-Scattering

A modified commercial LLS spectrometer (ALV/SP-125 equipped with an ALV-5000 multi-tau digital time correlator) was used with a solid-state laser (ADLAS DPY425II, output power is  $\sim 400$  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  $6\text{--}150^\circ$ . The detail of LLS instrumentation and theory can be found elsewhere.<sup>9,10</sup>

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  $\theta$ ,  $R_{vv}(q)$  can be expressed as<sup>11</sup>

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

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  $\lambda_0$  being 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-aver-

aged 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  $\theta$ , we were able to determine  $M_w$ ,  $\langle R_g \rangle$ , and  $A_2$  from a Zimm plot that incorporates  $\theta$  and  $C$  extrapolation on a single grid.

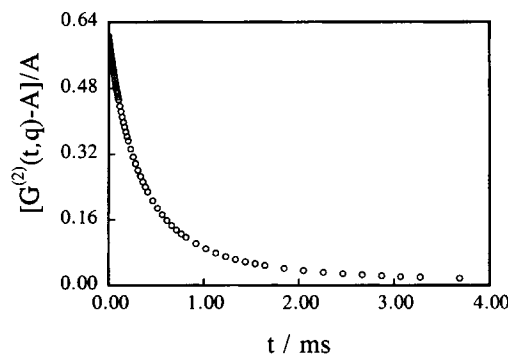
The differential refractive index increment  $dn/dc$  ( $0.231 \pm 0.001$ ) for PEK-C in  $\text{CHCl}_3$  at  $T = 25^\circ\text{C}$  and  $\lambda_0 = 532$  nm was determined by a novel and high-precision differential refractometer, which was incorporated as one part of our LLS spectrometer,<sup>12</sup> 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

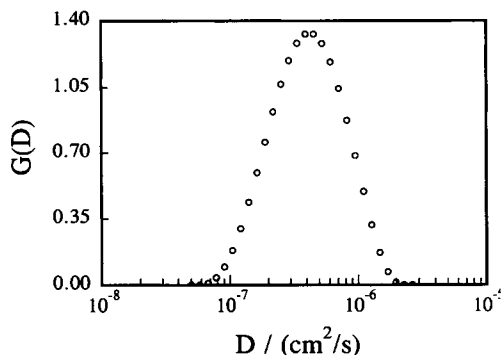
Figure 1 shows a typical plot of the measured intensity-intensity time correlation function for a broadly distributed unfractionated PEK-C sample in  $\text{CHCl}_3$  at  $\theta = 20^\circ$  and  $T = 25^\circ\text{C}$ . In dynamic LLS,  $G^{(2)}(t, q)$  can be related to the normalized first-order electric field time correlation function  $g^{(1)}(t, q)$  as<sup>9,10</sup>

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

where  $A$  is a measured baseline,  $\beta$  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



**Figure 1** Typical measured intensity-intensity time correlation function for the unfractionated PEK-C in  $\text{CHCl}_3$  at  $\theta = 20^\circ$  and  $T = 25^\circ\text{C}$ , where the PEK-C concentration was  $8.72 \times 10^{-4}$  g/mL.



**Figure 2** Translational diffusion coefficient distribution  $G(D)$  of the unfractionated PEK-C in  $\text{CHCl}_3$  at  $T = 25^\circ\text{C}$ .

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

Using a Laplace inversion program CONTIN<sup>13</sup> equipped with the correlator, we were able to calculate  $G(\Gamma)$  from  $G^{(2)}(t, q)$ . Generally,  $\Gamma$  is a function of both  $C$  and  $q$ . For a diffusive relaxation,<sup>14</sup>

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

where  $D$  is the translational diffusion coefficient at  $C \rightarrow 0$  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  $(\Gamma/q^2)_{C \rightarrow 0, q \rightarrow 0}$ ,  $(\Gamma/q^2)_{C \rightarrow 0}$  versus  $q^2$ , and  $(\Gamma/q^2)_{q \rightarrow 0}$  versus  $C$ , respectively. For a flexible polymer chain in a good solvent,  $f$  is in the range of 0.1–0.2.<sup>14</sup> Therefore, in comparison with  $KC/R_{vv}(q)$  in eq. (1),  $\Gamma/q^2$  is less dependent on the scattering angle. Our previous study<sup>8</sup> showed that  $f \sim 0.1$  and  $k_d \sim 10$  for PEK-C in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ . The very small value of  $k_d$  is due to the cancellation between the thermodynamic ( $2A_2M_w$ ) and hydrodynamic ( $C_D N_A R_h^3/M_w$ ) interactions when  $A_2 > 0$ , i.e.,<sup>15</sup>

$$k_d = 2A_2M_w - C_D N_A R_h^3/M_w \quad (5)$$

where  $C_D$  is a constant. Therefore,  $\Gamma/q^2$  is less dependent on  $C$  in comparison with  $KC/R_{vv}(q)$ . 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 PEK-C sample in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ , 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  $\langle R_h \rangle [= k_B T / (6\pi\eta\langle D \rangle)]$ , where  $k_B$ ,  $T$ , and  $\eta$  are the Boltzmann constant, the absolute temperature, and solvent viscosity, respectively. The values of  $\langle D \rangle$  and  $\langle R_h \rangle$  for the PEK-C sample are listed in Table I. The ratio of  $\langle R_g \rangle / \langle R_h \rangle$  ( $\sim 1.5$ ) suggests that the PEK-C chains have a coil conformation in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ . Further, using our previously established calibration<sup>8</sup> of  $D$  ( $\text{cm}^2/\text{s}$ ) =  $(2.37 \times 10^{-4})M^{-0.57}$ , we were able to transform  $G(D)$  into a molecular weight distribution. The principle is as follows.<sup>16–18</sup> From the definition of  $|g^{(1)}(t)|$ , when  $t \rightarrow 0$ ,

$$\begin{aligned} |g^{(1)}(t \rightarrow 0)| &= \langle E(t)E^*(0) \rangle_{t \rightarrow 0} \\ &= \int_0^\infty G(\Gamma) d\Gamma \propto I \end{aligned} \quad (6)$$

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

$$\begin{aligned} \int_0^\infty G(\Gamma) d\Gamma &\propto \int_0^\infty f_w(M)M dM \\ &\propto \int_0^\infty G(D) dD \end{aligned} \quad (8)$$

which can be rewritten as

**Table I** Summary of LLS Results of Unfractionated PEK-C Sample

$10^{-4} M_w$ (g/mol)	$\langle R_g \rangle$ (nm)	$10^4 A_2$ (mol · mL/g <sup>2</sup> )	$10^8 \langle D \rangle$ (cm <sup>2</sup> /s)	$\langle R_h \rangle$ (nm)	$\langle R_g \rangle / \langle R_h \rangle$	$10^{-4} (M_w)_{\text{calcd}}$	$(M_w/M_n)_{\text{calcd}}$
6.25	21	8.2	42.6	14.1	1.5	6.15	1.98

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

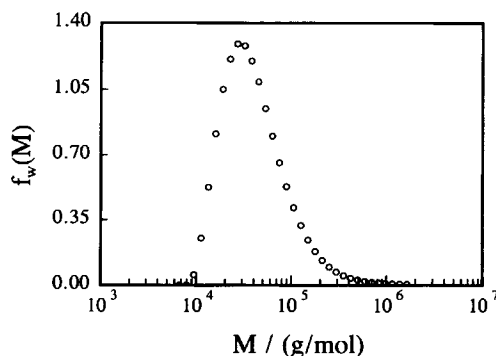
where  $d(\ln D) \propto d(\ln M)$  since  $D = k_D M^{-\alpha_D}$ . Therefore,

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

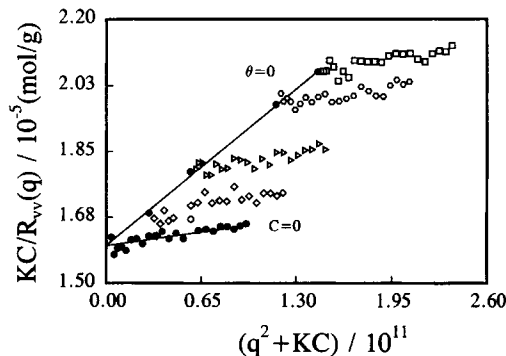
Using  $D$  ( $\text{cm}^2/\text{s}$ ) =  $2.37 \times 10^{-4} M^{-0.57}$  and eq. (10), we transformed  $D$  to  $M$  and  $G(D)$  into  $f_w(M)$ , where we used the fact that for a given solvent and temperature both  $k_D$  and  $\alpha_D$  are related to the polymer chain conformation but not strongly to the polydispersity of polymer chain; namely, we can apply  $D = k_D M^{-\alpha_D}$  obtained from a series of fractionated samples to a broadly distributed unfractionated sample.

Figure 3 shows a differential weight distribution for the unfractionated PEK-C 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 I. The calculated value of  $M_w/M_n$  ( $\sim 2$ ) is close to that predicted by polycondensation reaction kinetics. One way to check this calculated  $f_w(M)$  is to measured  $M_w$  directly from static LLS.

Figure 4 shows a typical Zimm plot for the unfractionated PEK-C in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ , where the solution were clarified by a  $0.1\text{-}\mu\text{m}$  filter and  $C$  ranged from  $8.72 \times 10^{-4}$  to  $4.36 \times 10^{-3}$  g/mL. On the basis of eq. (1), we obtained the values of  $M_w$ ,  $\langle R_g \rangle$ , and  $A_2$ , respectively, from  $[KC/R_{vv}(q)]_{\theta \rightarrow 0, c \rightarrow 0}$ ,  $[KC/R_{vv}(q)]_{c \rightarrow 0}$  versus  $q^2$ , and  $[KC/R_{vv}(q)]_{\theta \rightarrow 0}$  versus  $C$ . The static LLS results are also summarized in Table I. The positive value of  $A_2$  indicate that  $\text{CHCl}_3$



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



**Figure 4** Typical Zimm plot for the unfractionated PEK-C in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ , where the solution was clarified by a  $0.1\text{-}\mu\text{m}$  filters and  $C$  ranged from  $8.72 \times 10^{-4}$  to  $4.36 \times 10^{-3}$  g/mL.

is a fairly good solvent for PEK-C at  $25^\circ\text{C}$ . The measured  $M_w$  from static LLS is practically the 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.

In summary, the unfractionated PEK-C sample can be characterized in  $\text{CHCl}_3$  at  $25^\circ\text{C}$  by using dynamic LLS. The relatively small angular and concentration dependence and of the translational diffusion coefficient measured in dynamic LLS enable us to characterize PEK-C 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 PEK-C from the measured line-width distribution  $G(\Gamma)$ .

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