Laser Light Scattering of the Molecular Weight Distribution of Unfractionated Phenolphthalein Poly(aryl ether sulfone)

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SYNOPSIS

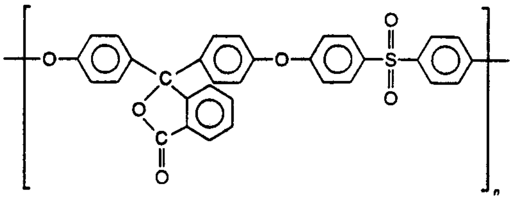
Two unfractionated samples of phenolphthalein poly(aryl ether sulfone) (PES-C) were characterized in $CHCl_3$ at 25°C by applying a recently developed laser light-scattering (LLS) procedure. The Laplace inversion of precisely measured intensity–intensity time correlation function lead us first to an estimate of the characteristic line-width distribution $G(\Gamma)$ and then to the translational diffusion coefficient distribution $G(D)$. A combination of static and dynamic LLS results enabled us to determine $D = (2.69 \times 10^{-4})M^{-0.553}$, which agrees with the calibration of $D = (2.45 \times 10^{-4})M^{-0.55}$ previously established by a set of narrowly distributed PES-C samples. Using this newly obtained scaling between D and M, we were able to convert $G(D)$ into a differential weight distribution $f_w(M)$ for the two PES-C samples. The weight-average molecular weights calculated from $f_w(M)$ are comparable to that obtained directly from static LLS. Our results showed that using two broadly distributed samples instead of a set of narrowly distributed samples have provided not only similar final results, but also a more practical method for the PES-C characterization. © 1997 John Wiley & Sons, Inc.

Keywords: light scattering • phenolphthalein poly(aryl ether sulfone) • molecular weight distribution • translational diffusion coefficient • calibration between D and M

INTRODUCTION

Poly(aryl ether ketones) (PEKs) as a new class of high-performance polymers were currently used in aerospace and electronic applications because of their high strength, toughness, good electrical properties, thermooxidative stability, and solvent resistance. Poly(aryl ether ether ketone) (PEEK) as one typical example has gained a significance commercial success because it can to be fabricated by conventional extrusion and molding techniques.[1] However, the lack of solubility for PEEK in common solvent has limited its many other applications.[2,3] So far few studies on dilute solution properties of PEEK has been conducted, mainly because it is only soluble in concentrated H_2SO_4, HSO_3Cl, and CH_3SO_3H.[5,7]

To solve this solubility problem, functional groups are normally added as a side groups or directly onto the polymer backbone to reduce or suppress the crystalline structure. However, a gain in solubility is frequently accompanied by a loss in thermal stability.[4] Recently, a new type of linear aromatic polymer, phenolphthalein poly(aryl ether sulfone) (PES-C) whose structure is as follows,



was developed in the Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Academia of Sinica, China. PES-C is not only similar as PEEK and PEK in its physical and mechanical properties, but also soluble in polar organic sol-

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vents, such as $CHCl_3$, *N,N*-dimethyl formamide (DMF), dimethyl acetamide (DMAc) and *N*-methyl pyrrolidinone (NMP). Some solution properties of PES-C, such as the Mark–Houwink equations in several solvents[8] and Flory characteristic ratio,[9] have been previously determined.

In our previous study,[10] we showed that PES-C contains 94 wt % of individual chains and 6 wt % of high molecular weight clusters; we investigated how the conformation and flexibility of the PES-C chain in $CHCl_3$ changes with the polymer molecular weight; and we also established a calibration 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 narrowly distributed samples.[11] Considering that the fractionation of PES-C is a very time-consuming process, we intend in this study to demonstrate that using two broadly distribution samples, we are also able to characterize the molecular weight distribution of PES-C by a combination of static and dynamic LLS.

EXPERIMENTAL

Sample Preparation

The PES-C samples were synthesized by a nucleophilic substitution polycondensation. The outline of the synthesis is as follows: (1) equimolar phenolphthalein and 4,4′-dichlorodiphenyl sulfone were dissolved in cyclobutane sulfone ($TMSO_2$); (2) excess amount of dehydrated K_2CO_3 was added as a catalyst; and (3) the solution mixture was heated to 220°C and reaction was carried under N_2 for 8 h. The final PES-C products were dried in vacum at 60°C for 48 h. Two unfractionated PES-C with different weight-average molecular weights were used in this study and they were labeled as UPES-C-1 and UPES-C-2 hereafter. The detail of sample preparation can be found elsewhere.[12]

Solution Preparation

Chloroform ($CHCl_3$) as a good solvent (Merck, analytical grade) was used without further purification. Five concentrations ranged from 1.2×10^{-3} to 5.12×10^{-3} g/mL were prepared by dilution. All polymer solutions were clarified by using a 0.1 μm Whatman filter in order to remove dust and multichain aggregates.

Laser Light Scattering (LLS)

A modified commercial light-scattering spectrometer (ALV/SP-125 equipped with an ALV-5000 multi-τ digital time correlator) was used with a solid-state laser (ADLAS DPY 425II, output power $\approx$ 400 mW at $\lambda = 532$ nm) as the light source. The primary beam is vertically polarized with respect to the scattering plane (the optical table surface in this case). The detail of the LLS instrumentation and theory can be found elsewhere.[13,14] All the measurements were carried out at 25 ± 0.1°C.

The angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio, $R_{vv}(q)$, of a dilute polymer solution was measured for different concentrations C (g/mL) and scattering angles θ. $R_{vv}(q)$ is related to the weight average molecular weight M_w as[15]

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

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 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 incorporate q and C extrapolation on a single grid.

A novel and high precision differential refractometer[16] was used to determine the differential refractive index increment dn/dC (=0.204 mL/g) for PES-C in $CHCl_3$ at $T = 25$°C and $\lambda = 532$ nm. In this study, the differential refractometer was also used for determining the polymer concentration after the filtration.

In dynamic LLS, a precise intensity–intensity time correlation function $G^{(2)}(t, q)$ in the self-beating mode was measured. $G^{(2)}(t, q)$ is related to the normalized first-order electric field time correlation function $|g^{(1)}(t, q)|^2$ as[13,14]

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

where A is a measured base line; β a parameter

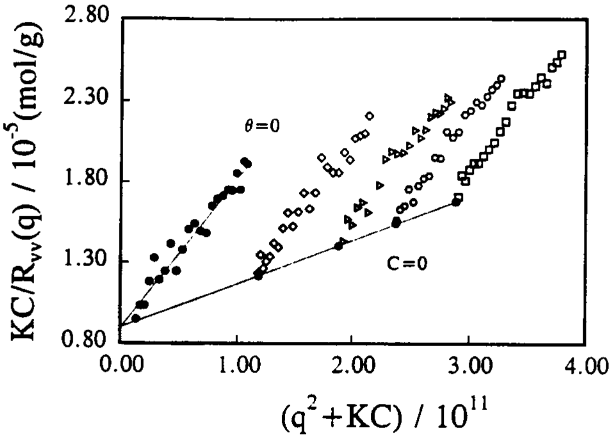

Figure 1. Typical static Zimm-plot for an unfractionated PES-C sample (UPES-C-1) in CHCl$_3$ at $T = 25°C$, where C ranged from 1.2×10^{-3} to 5.12×10^{-3} g/mL and all solutions were clarified with a 0.1 μm filter.

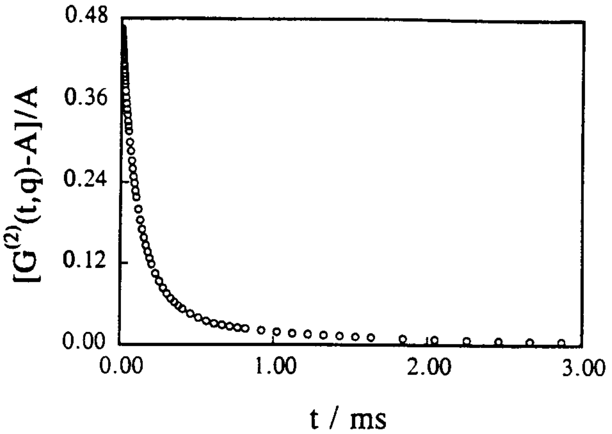

Figure 2. Typical measured intensity–intensity time correlation function $G^{(2)}(t, q)$ for an unfractionated PES-C sample (UPES-C-1) in CHCl$_3$ at $\theta = 20°$ and $T = 25°C$.

depending on the coherence of the detection; t, the delay time.

RESULTS AND DISCUSSION

Figure 1 shows a typical static Zimm plot for UPES-C-1 in CHCl$_3$ at 25°C. On the basis of eq. (1), we were able to determine the values of M_w, R_g, and A_2, from the extrapolation of "$[KC/R_{vv}(q)]_{q\to 0, c\to 0}$," "$[KC/R_{vv}(q)]_{c\to 0}$ vs. q^2" and "$[KC/R_{vv}(q)]_{q\to 0}$ vs. C," respectively. The results are summarized in Table I. The positive values of A_2 shows that CHCl$_3$ is a good solvent for PES-C at room temperature.

Figure 2 shows a typical plot of the measured intensity–intensity time correlation function for UPES-C-1 in CHCl$_3$ at $\theta = 20°$ and $T = 25°C$. For a polydisperse sample, $|g^{(1)}(t, \theta)|$ is related to the line width distribution $G(\Gamma)$ by

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

The computer program CONTIN[17] was used in this work to calculate $G(\Gamma)$ from $G^{(2)}(t, \theta)$. In dynamic light-scattering field, it is known that when the molecular weight distribution of a given polymer sample is relatively low, such as $M_w/M_n < 2$, and the distribution has only one peak, the Laplace inversion of the time correlation function by using CONTIN method is quite reliable as long as the measured time correlation function does not contain too much noise. In this study, we have enforced that the difference between the measured and calculated baselines is less than 0.1% to insure that no serious noise was introduced in the measured time correlation function. The line width Γ usually depends on both C and q. This dependency can be expressed as,[18,19]

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

where D is the translational diffusion coefficient at $C \to 0$, and $q \to 0$; k_d is diffusion second virial coefficient; and f is dimentionless number. On the basis of eq. (4), D, f and k_d can be calculated from

Table I. Summary of Static and Dynamic Laser Light-Scattering Results for Two Unfractionated PES-C Samples in CHCl$_3$ at 25°C

Samples	$10^{-4} M_w$ (g/mol)	$\langle R_g\rangle$ (nm)	$10^4 A_2$ (mol.cm^3/g^2)	$10^8 \langle D\rangle$ (cm^2/s)	$\langle R_h\rangle$ (nm)	$\langle R_g\rangle/\langle R_h\rangle$	$\mu_2/\langle D\rangle^2$	$(M_w/M_n)_{calcd}$
UPES-C-1	11.7	14	2.2	39.5	10	1.40	0.20	1.75
UPES-C-2	4.65	11	3.6	72.9	6.0	1.83	0.17	1.74

The relative errors: M_w, ±5%; $\langle R_g\rangle$, ±10%; A$_2$, ±15%; $\langle D\rangle$, ±1%.

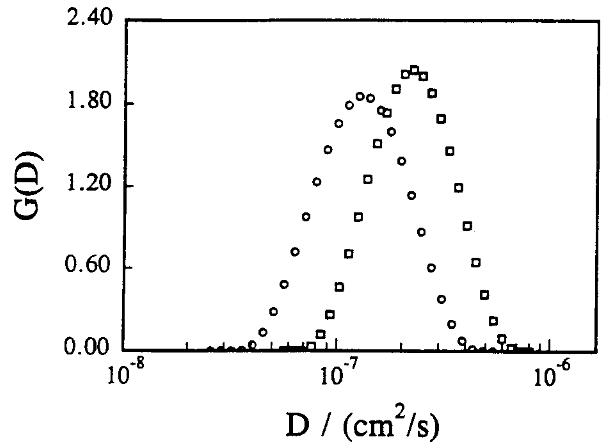

Figure 3. Translational diffusion coefficient distributions of two unfractionated PES-C samples in $CHCl_3$ at T = 25°C, where ○ UPES-C-1, and □ UPES-C-2.

$(\Gamma/q^2)_{c\to 0,\theta\to 0}$, $(\Gamma/q^2)_{c\to 0}$ vs. q^2 and $(\Gamma/q^2)_{\theta\to 0}$ vs. C, respectively. The value of f depends on the chain structure, polydispersity, and solvent quality. For a flexible polymer chain in a good solvent, f is in the range of 0.1–0.2.[18,19] Therefore, in comparison with $KC/R_{vv}(q)$ in eq. (1), Γ/q^2 is less dependant on the scattering angle. Our results showed that $f \sim 0.1$ and $k_d \sim 20$ for PES-C in $CHCl_3$ at 25°C. The small value of k_d is due to the cancellation between the thermodynamic $(2A_2/M_w)$ and hydrodynamic $(C_D N_A R_h^3/M_w)$ interactions when $A_2 > 0$, namely

$$k_d = 2A_2 M_w - C_D N_A R_h^3 / M_w \tag{5}$$

where C_D is a positive constant. Therefore, Γ/q^2 is less dependant on C in comparison with $KC/R_{vv}(q)$ in eq. (1). 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 3 shows two typical translational diffusion coefficient distributions $G(D)$ for two unfractionated PES-C samples in $CHCl_3$ at $C \to 0$ and $q \to 0$. From $G(D)$, we can calculate the z-average translational diffusion coefficient $\langle D\rangle$ $(= \int_0^\infty G(D) D dD)$, the relative distribution width $(\mu_2/\langle D\rangle^2 = [\int_0^\infty G(D)(D - \langle D\rangle)^2 dD]/\langle D\rangle^2)$ and the average hydrodynamic radius $\langle R_h\rangle$ by replacing D in the Stokes–Einstein equation with $\langle D\rangle$, i.e., $\langle R_h\rangle$ $[= k_B T/(6\pi\eta\langle D\rangle)]$, where k_B, T, and η are the Boltzmann constant, the absolute temperature, and solvent viscosity, respectively. The values of $\langle D\rangle$, $\mu_2/\langle D\rangle^2$, $\langle R_h\rangle$, and $\langle R_g\rangle/\langle R_h\rangle$ of two unfractionated PES-C samples are also listed in Table I. The ratio $\langle R_g\rangle/\langle R_h\rangle$ is in the range of (1.4–1.8), normally observed for a flexible polymer chain in a good solvent.[19] There are two ways to convert $G(D)$ into a molecular weight distribution. One way is to use a set of narrowly distributed samples wherein their corresponding $\langle D\rangle$ and M_w are measured and used to establish the calibration $D = K_D M^{-\alpha_D}$; *and the other is to use two or more broadly distributed samples according to the following principles. In dynamic LLS,*

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

On the other hand, in static LLS, when $C \to 0$, and $q \to 0$,

$$R_{vv}(q \to 0) \propto I \propto M_w = \int_0^\infty f_w(M) M\, dM \tag{7}$$

A comparison of eqs. (6) and (7) leads to

$$\int_0^\infty G(\Gamma)\, d\Gamma \propto \int_0^\infty f_w(M) M\, dM \tag{8}$$

where $G(\Gamma) \propto G(D)$ since $\Gamma \propto D$. eq. (8) can be rewritten as

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

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

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

where all proportional constants are omitted since they are irrelevant to a given distribution. From $f_w(M)$, M_w can be calculated by its definition;

$$(M_w)_{\text{calcd}} = \frac{\int_0^\infty f_w(M) M\, dM}{\int_0^\infty f_w(M)\, dM} = \frac{k_D^{1/\alpha_D} \int_0^\infty G(D)\, dD}{\int_0^\infty G(D) D^{1/\alpha_D}\, dD}$$
$$= \frac{k_D^{1/\alpha_D}}{\int_0^\infty G(D) D^{1/\alpha_D}\, dD} \tag{11}$$

because $\int_0^\infty G(D)\, dD = 1$. For two samples 1 and 2, we have

$$\frac{(M_w)_{\text{calcd},1}}{(M_w)_{\text{calcd},2}} = \frac{\left[\int_0^\infty G_1(D)\,dD\right]\left[\int_0^\infty G_2(D)D^{1/\alpha_D}\,dD\right]}{\left[\int_0^\infty G_1(D)D^{1/\alpha_D}\,dD\right]\left[\int_0^\infty G_2(D)\,dD\right]} \quad (12)$$

For a given polymer, $(M_w)_{\text{calcd}}$ should be equal to M_w if α_D and k_D are properly chosen, and we can find a minimum difference between $[(M_{w,1})/(M_{w,2})]_{\text{calcd}}$ and $(M_{w,1})/(M_{w,2})]_{\text{staticLLS}}$. On the basis of above discussion, the error function is defined as

$$\text{ERROR}(k_D) = \left[\frac{(M_{w,1}) - (M_{w,1})_{\text{calcd}}}{M_{w,1}}\right]^2 + \left[\frac{(M_{w,2}) - (M_{w,2})_{\text{calcd}}}{M_{w,2}}\right]^2 \quad (13)$$

By iterating of α_D, we can first find a proper α_D to minimize the difference between the left hand side and right hand side of eq. (12), and then calculate k_D from eq. (11). Figure 4 shows typical plots of ERROR(k_D) vs. k_D for different values of α_D. It can be seen that there exist overall a minimum error ERROR(k_D) at $\alpha_D = 0.553$ and $k_D = 2.69 \times 10^{-4}$. The final result is D (cm^2/s) $= (2.69 \times 10^{-4})M^{-0.553}$, which reasonably agree well with D (cm^2/ses) $= (2.45 \times 10^{-4})M^{-0.55}$ previously determined from a set of fractionated PES-C samples. Using $D = 2.69 \times 10^{-4}M^{-0.553}$ and eq. (10), we transformed D to M and $G(D)$ into $f_w(M)$. It should be noted that in the above calculation we always use the integration values of $G(D)$ instead of individual values of $G(D)$.

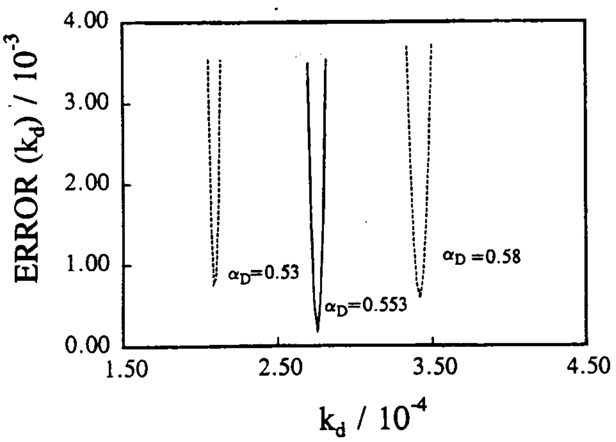

Figure 4. Plot of the relative ERROR (k_D) vs. k_D, where ERROR (k_D) is define as $= [\{(M_{w,1}) - (M_{w,1})_{\text{calcd}}\}/M_{w,1}]^2 + [\{(M_{w,2}) - (M_{w,2})_{\text{calcd}}\}/M_{w,2}]^2$.

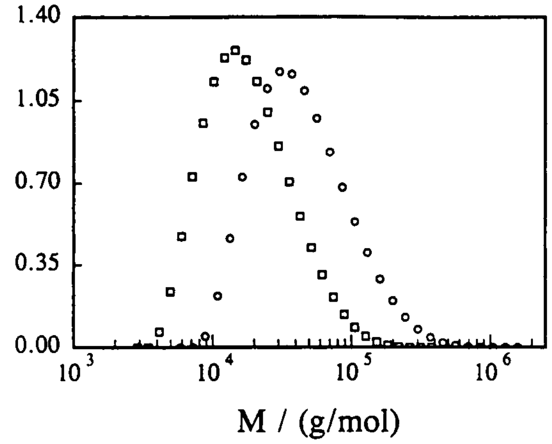

Figure 5. Differential weight distributions of two unfractionated PES-C samples, where ○ UPES-C-1, and □ UPES-C-2.

Figure 5 shows differential weight distributions $f_w(M)$ for two unfractionated PES-C samples. From each $f_w(M)$, we were able to calculate polydispersity index $(M_w/M_n)_{\text{calcd}}$, which is also listed in Table I. It is known that M_w/M_n can be estimated to the relative width by $M_w/M_n \sim 1 + 4\mu_2/\langle D\rangle^2$. The data in Table I has confirmed this estimation. It is known that for a polycondensation $M_w/M_n \leq 2$, so that the $M_w/M_n \sim 1.7-1.8$ is quite reasonable.

In summary, the unfractionated PES-C samples can be characterized in CHCl$_3$ at room temperature by a combination of static and dynamic laser light scattering (LLS). The calibration established in this study can be used in the future characterization of PES-C as long as CHCl$_3$ is used as a solvent and temperature is 25°C. On the other hand, the relatively small angular and concentration dependence of the translational diffusion coefficient measured in dynamic LLS enable us to characterize PES-C from only one dynamic LLS measurement at a finite concentration and small scattering angle.

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