

Characterization of Novel Thermoplastic Polymers With Phenolphthalein in Their Backbone Chains*

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Different molecular weight phenolphthalein poly(ether ketone) (PEK-C) and phenolphthalein poly(ether sulfone) (PES-C) fractions in chloroform (CHCl_3) were studied by static and dynamic laser light scattering (LLS). The dynamic LLS revealed that both the PEK-C and PES-C samples contain some large polymer clusters formed in the process of polymerization. These large clusters can be removed by filtering the solution with a 0.1- μm filter. The positive second virial coefficient (A_2) shows that CHCl_3 is a good solvent for these polymers at room temperature. The persistence length and the Flory characteristic ratio of these polymers in CHCl_3 at 25°C are ~ 2 nm and ~ 3 , respectively, which indicate that these polymer chains are flexible. A combination of static and dynamic LLS results, namely the weight-average molecular weight from static LLS and the line-width distribution from dynamic LLS, lead to two calibrations between the translational diffusion coefficient (D) and molecular weight (M): $D = 2.20 \times 10^{-4} M^{-0.56}$ for PEK-C and $D = 2.45 \times 10^{-4} M^{-0.55}$ for PES-C in CHCl_3 . Using these calibrations, we are able to estimate not only the molecular weight distributions of these fractionated polymers, but also unfractionated PEK-C and PES-C samples

INTRODUCTION

Both poly(ether ketones) and poly(ether sulfones) are commercial high-performance polymers with excellent heat resistance and high mechanical strength. Two of the most prominent members, poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK), are widely used as an engineering thermoplastics or as matrix resins in advanced composite materials (1, 2). However, these polymers are soluble only in strong acids or solvents with a boiling point higher than their melting points, mainly due to their insoluble crystalline structure. Therefore, the processing and application of these thermoplastics have been greatly hindered by their low solubility in common solvents. So far, few studies on dilute solution properties of PEEK have been conducted because PEEK can be sulfonated and dissolved only in concentrated H_2SO_4 , HSO_3Cl and $\text{CH}_3\text{SO}_3\text{H}$ (3, 4). In the past, much effort has been spent to develop a polymer with similar properties as PEEK or PEK, but a better solubility in common solvents.

Recently, two novel thermoplastics with an amorphous structure, phenolphthalein poly(ether ketone)

(PEK-C) and phenolphthalein poly(ether sulfone) (PES-C), have been successfully developed in the Changchun Institute of Applied Chemistry, Academy of Science, China (5). These polymers are not only similar to PEEK or PEK with excellent physical and mechanical properties, but also soluble in polar organic solvents, such as chloroform (CHCl_3), *N,N*-dimethyl formamide (DMF), *N*-methyl pyrrolidinone (NMP) and chlorohydrocarbons, which render its solutions castable. These polymers have been recommended for high temperature and solvent resistant membranes (6). Some dilute solution properties of these polymers, such as the interaction with organic solvents (7), the Mark-Houwink equations in CHCl_3 and DMF (8), and a θ -solvent composition (9), were previously determined.

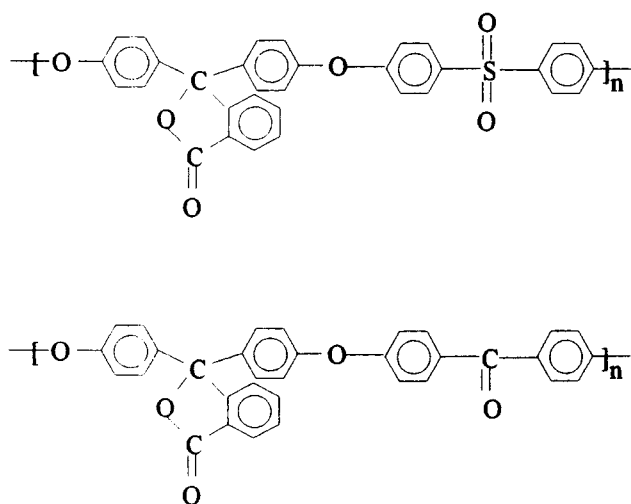
In this paper, we report the calibrations between the translational diffusion coefficient (D) and molecular weight (M) together with their molecular weight distributions (MWD) calculated from their corresponding translational diffusion coefficient distribution $G(D)$ measured in dynamic laser light scattering (LLS).

EXPERIMENTAL

Preparation of PEK-C and PES-C. The PEK-C and PES-C samples were synthesized by a nucleophilic substitution polycondensation: first, equal

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molar phenolphthalein and dichlorodiphenyl ketone or dichlorodiphenyl sulfone were dissolved in cyclobutane sulfone (TMSO₂); then, an excess amount of dehydrated K₂CO₃ was added as a catalyst; finally, the solution mixture was heated to 220°C and reaction was carried out under N₂ for 8 hours. A 2% solution of the produced polymers in DMF was fractionally precipitated with ethanol at room temperature. The precipitates were washed with ethanol and then dried in vacuo at 60°C for 48 hours. The details of the sample preparation can be found elsewhere (5). Five fractions were obtained for PEK-C and PES-C, respectively, and denoted as PEK-C1 → PEK-C5 and PES-C1 → PES-C5 thereafter. As shown below, the structures of PEK-C and PES-C are similar to PEEK.



LLS Experiments. A commercial LLS spectrometer (ALV/SP-150 equipped with an ALV-5000 multi-tau digital time correlator) was used with a solid state laser (ADLAS DPY425II, output power is ~400 mw at $\lambda = 532$ 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 make sure that there is no angular dependence of the scattered light from toluene. The spatial coherence constant β is ~0.9, somewhat large for an LLS spectrometer capable of doing both static and dynamic LLS simultaneously. Using this apparatus, we can carry out static and dynamic LLS in the angular range of 6–154°. Details of LLS instrumentation and theory can be found elsewhere (10, 11).

The angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio, $R_{vv}(\theta)$, was measured. For a dilute polymer solution at a relatively low scattering angle θ , $R_{vv}(\theta)$ can be expressed as (12)

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

where $K = 4\pi^2 n^2 \left(\frac{dn}{dc} \right)^2 / \left(N_A \lambda_0^4 \right)$ and $q = \frac{4\pi n}{\lambda_0} \sin \left(\frac{\theta}{2} \right)$

with N_A , dn/dc , n , and λ_0 being the Avogadro's number, the specific refractive index increment, the solvent refractive index, and the wavelength of light in vacuo, respectively. M_w is the weight average molecular weight; A_2 is the second virial coefficient; and $\langle R_g^2 \rangle^{1/2}$ (or written as $\langle R_g \rangle$) is the root-mean square z -average radius of the polymer chain in solution and C is the polymer concentration. After measuring $R_{vv}(\theta)$ for a set of C and θ , we can determine M_w , R_g , and A_2 from a Zimm plot, which incorporates the θ and C extrapolation on a single grid (12).

It is necessary in static light scattering to have a precise value of the differential refractive index increment dn/dc because the measured M_w is proportional to $(dn/dc)^{-2}$. A novel and high precision differential refractometer was incorporated into the light scattering spectrometer (13), enabling us to measure dn/dc and the scattered light intensity under identical experimental conditions, so that the wavelength correction was eliminated. The measured dn/dc values for PEK-C and PES-C in CHCl₃ at $T = 25^\circ\text{C}$ and $\lambda_0 = 532$ nm are (0.231 ± 0.001) and (0.204 ± 0.001) mL/g, respectively. In this study, the differential refractometer was used not only to measure the refractive index increment, but also to determine the polymer concentration after filtration.

In the dynamic LLS experiments, the intensity-intensity time correlation function $G^{(2)}(t, \theta)$ in the self-beating mode was measured. $G^{(2)}(t, \theta)$ is related to the normalized first-order electric field time correlation function, $g^{(1)}(t, \theta)$ as (10, 11)

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

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

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

Using a Laplace inversion program CONTIN (14) supplied with the correlator, we were able to calculate $G(\Gamma)$ from $G^{(2)}(t, \theta)$. It is worth noting that the inversion is not unique because of the data noise. This is why we insisted that the measured and calculated baselines agree with each other within 0.1%.

In this study, analytical grade CHCl₃ was used as a solvent without further purification. For each sample, five concentrations ranged from 2×10^{-4} to 2.5×10^{-3} g/mL were prepared by dilution. In the first stage of the LLS experiments, the solutions were clarified by 0.5 μm or 0.22 μm Millipore filters, depending on the molecular weight of the sample. Later, all samples were clarified by 0.1 μm Whatman filters in order to remove dust and very small amounts of larger polymer clusters.

RESULTS AND DISCUSSION

Table 1 summarizes the static LLS results, such as M_w , R_g , and A_2 for PEK-C in CHCl₃, which were obtained from the Zimm plot, that is, respectively from

Table 1. Summary of Laser Light Scattering Results for Five Samples of PEK-C Using 0.5 μm Filters.

Samples	$10^{-5}M_w$ (g/mol)	$\langle R_g \rangle$ (nm)	$10^4 A_2$ (mol.mL/g ²)	$10^8 \langle D \rangle$ (cm ² /s)
PEK-C1	11.0	95.4	2.63	8.09
PEK-C2	6.56	71.6	3.11	10.8
PEK-C3	1.21	32.3	9.49	27.2
PEK-C4	0.53	17.7	15.1	48.0
PEK-C5	0.25	10.7	21.6	75.8

$[KC/R_{v(\theta)}]_{\theta \rightarrow 0, c \rightarrow 0}$, $[KC/R_{v(\theta)}]_{c \rightarrow 0}$ vs. q^2 and $[KC/R_{v(\theta)}]_{\theta \rightarrow 0}$ vs. C , where all solutions were clarified with a 0.5- μm filter. The positive values of A_2 indicate that CHCl_3 is a good solvent for these polymers at 25°C. It should be noted that for the sample PEK-C4 and PEK-C5 there are large errors associated with the values of $\langle R_g \rangle$, which should be interpreted only as a reference, i.e., less than 10 nm. We also noted that for PEK-C1 and PEK-C2 the values of M_w are much higher than those ($< 1 \times 10^5$ g/mol) normally observed for polymers made by polycondensation. The persistence length and the Flory characteristic ratio of these polymers calculated from M_w and $\langle R_g \rangle$ are ~ 2 nm and ~ 3 , respectively, which indicate that these polymer chains are flexible in CHCl_3 at 25°C.

Figure 1 shows a typical plot of the measured intensity-intensity time correlation function of PES-C3 in CHCl_3 at $\theta = 20^\circ$ and $T = 25^\circ\text{C}$. The Laplace inversion of the measured time correlation function can lead to the line-width distribution $G(\Gamma)$ on the basis of Eqs 2 and 3. The line width Γ usually depends on both C and q . This dependency can be expressed as (15, 16)

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

where D is the translational diffusion coefficient at $C \rightarrow 0$, and $q \rightarrow 0$; k_d is diffusion second virial coefficient and f is a dimensionless number depending on the chain structure, polydispersity, and solvent quality. $\langle D \rangle$, f and k_d can be calculated from $(\Gamma/q^2)_{c \rightarrow 0, \theta \rightarrow 0}$,

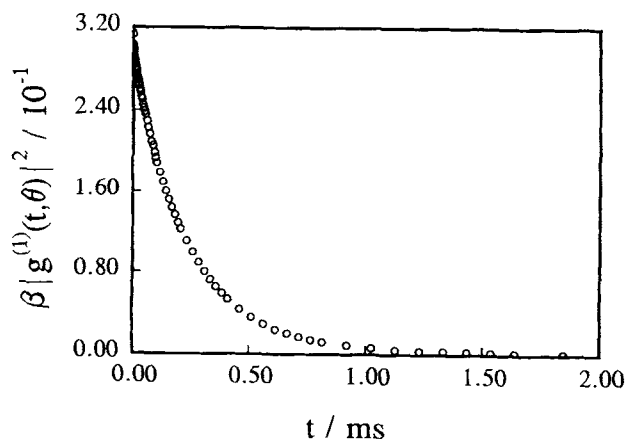


Fig. 1. Typical measured intensity-intensity time correlation function of PES-C3 in CHCl_3 at $\theta = 20^\circ$ and $T = 25^\circ\text{C}$.

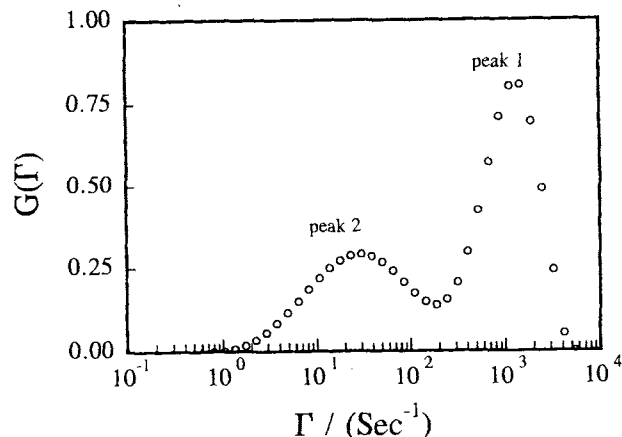


Fig. 2. Typical line-width distribution $G(\Gamma)$ of PEK-C3 in CHCl_3 at 25°C, where the solution was clarified with a 0.5- μm filter. Peak 1 represents individual PEK-C molecules, while peak 2 is related to some larger species produced during polymerization.

$(\Gamma/q^2)_{c \rightarrow 0}$ vs. q^2 and $(\Gamma/q^2)_{\theta \rightarrow 0}$ vs. C , respectively. In this study, we found that k_d is very small. With a pair of values of k_d and f , $G(\Gamma)$ can be converted into $G(D)$.

Figure 2 shows a typical line-width distribution $G(\Gamma)$ of PEK-C in CHCl_3 at 25°C after the solution was clarified with a 0.5- μm filter. The fast relaxation (peak 1) can be attributed to correspondences to individual PEK-C chains, and the slow relaxation (peak 2) in the bimodal distribution indicates that there exist some large species in the sample. It should be emphasized that these large species cannot be attributed to dust since they consistently appear at the same position of the line-width distribution. The broad distribution of PEK-C is also inconsistent with the prediction of $M_w/M_n \leq 2$ for a polycondensation reaction. Later, we found that the peak related to larger species could be removed by filters with a smaller pore size, which indirectly shows that these larger species are not due to either association or aggregation.

Figures 3 and 4 show translational diffusion coefficient distributions $G(D)$ of PES-C and PEK-C samples in CHCl_3 at $T = 25^\circ\text{C}$, $C \rightarrow 0$, and $q \rightarrow 0$, respectively, where all solutions were clarified with a 0.1- μm filter. It clearly shows that the peak related to the larger species was removed. From $G(D)$, we can calculate the z-average translational diffusion coefficient $\langle D \rangle = \int_0^\infty G(D) D dD$. The values of $\langle D \rangle$ and static LLS results (M_w , A_2 , and R_g) for PEK-C and PES-C in CHCl_3 at 25°C are, respectively, listed in Tables 2 and 3. It can be seen that after using a 0.1- μm filter the values of M_w are more reasonable and within the right range for polymers made by polycondensation.

Fitting the results with $\langle D \rangle = \langle k_D \rangle M_w^{-\langle \alpha_D \rangle}$, we have $\langle k_D \rangle = (2.26 \pm 0.02) \times 10^{-4}$ and $\langle \alpha_D \rangle = (0.54 \pm 0.01)$ for PES-C; and $\langle k_D \rangle = (2.37 \pm 0.02) \times 10^{-4}$ and $\langle \alpha_D \rangle = (0.55 \pm 0.01)$ for PEK-C in CHCl_3 at 25°C, where $\langle \rangle$ means the values of $\langle k_D \rangle$ and $\langle \alpha_D \rangle$ were obtained from $\langle D \rangle$ and M_w rather than D and M

Table 2. Summary of Static and Dynamic Laser Light Scattering Results for Five PES-C Samples.

Samples	$10^{-4} M_w$ (g/mol)	$\langle R_g^2 \rangle_z^{1/2}$ (nm)	$10^4 A_2$ (mol.cm ³ /g ²)	$10^8 \langle D \rangle$ (cm ² /s)	$10^{-4} (M_w)_{calcd}$ (g/mol)	$(M_w/M_n)_{calcd}$
PES-C1	8.52	13	3.9	53.9	8.48	1.33
PES-C2	6.15	~10	4.5	65.0	6.04	1.32
PES-C3	5.01	~10	8.6	70.0	5.24	1.21
PES-C4	4.15	<9	—	82.0	4.11	1.17
PES-C5	2.50	<9	—	103	2.48	1.17

Table 3. Summary of Laser Light Scattering Results for Five Samples of PEK-C Using 0.1 μm Filters

Samples	$10^{-5} M_w$ (g/mol)	$\langle R_g \rangle$ (nm)	$10^8 \langle D \rangle$ (cm ² /s)	$10^{-5} (M_w)_{calcd}$ (g/mol)	$(M_w/M_n)_{calcd}$
PEK-C1	1.30	19.9	28.6	1.25	1.96
PEK-C2	0.92	16.4	35.0	0.92	1.57
PEK-C3	0.51	12.1	50.3	0.54	1.50
PEK-C4	0.39	~10	57.9	0.37	1.55
PEK-C5	0.22	~8	78.0	0.25	1.49

for monodisperse species. In principle, we can use the scaling relationship between D and M to transfer $G(D)$ into a molecular weight distribution (MWD) by using the following procedure. From dynamic LLS, by the definition of $g^{(1)}(t)$, when $t \rightarrow 0$,

$$[g^{(1)}(t)]_{t \rightarrow 0} = \langle E(t)E^*(0) \rangle_{t \rightarrow 0} = \int_0^\infty G(\Gamma) \propto \langle I \rangle \quad (5)$$

while from static LLS, when $C \rightarrow 0$, and $q \rightarrow 0$, the net scattering intensity is given by

$$\langle I \rangle \propto \int_0^\infty f_w(M) M dM \quad (6)$$

A comparison of Eqs 5 and 6 leads to

$$\int_0^\infty G(\Gamma) d\Gamma \propto \int_0^\infty f_w(M) M dM \propto \int_0^\infty G(D) dD \quad (7)$$

This equation can be written as

$$\int_0^\infty G(D) D d(\ln D) \propto \int_0^\infty f_w(M) M^2 d(\ln M) \quad (8)$$

where $d(\ln D) \propto d(\ln M)$ since $D = k_D M^{-\alpha_D}$. Equation 8 leads to

$$f_w(M) \propto \frac{G(D)D}{M^2} \propto G(D)D^{1+\frac{2}{\alpha_D}} \quad (9)$$

From $f_w(M)$, we can calculate M_w by its definition,

$$(M_w)_{calcd} = \frac{\int_0^\infty f_w(M) M dM}{\int_0^\infty f_w(M) dM} = \frac{k_D^{1/\alpha_D} \int_0^\infty G(D) dD}{\int_0^\infty G(D) D^{1/\alpha_D} dD} \quad (10)$$

Our previous studies (17–19) have shown that using $\langle k_D \rangle$ and $\langle \alpha_D \rangle$ instead of k_D and α_D can introduce a large error in the final MWD. Therefore, we have to use the measured M_w from static LLS as constraints

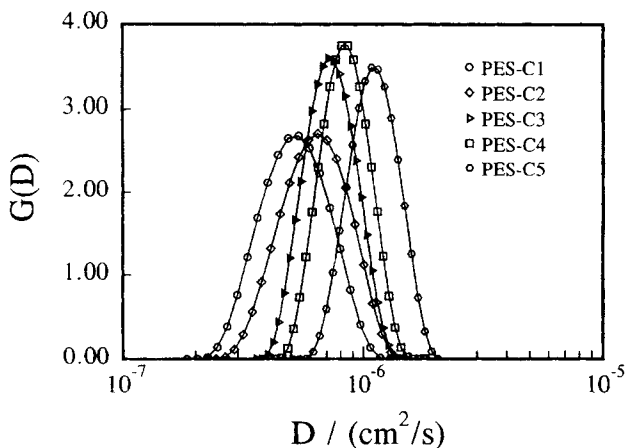


Fig. 3. Translational diffusion coefficient distributions of five PES-C samples in CHCl₃ at T = 25°C, where the solutions were clarified with a 0.1-μm filters.

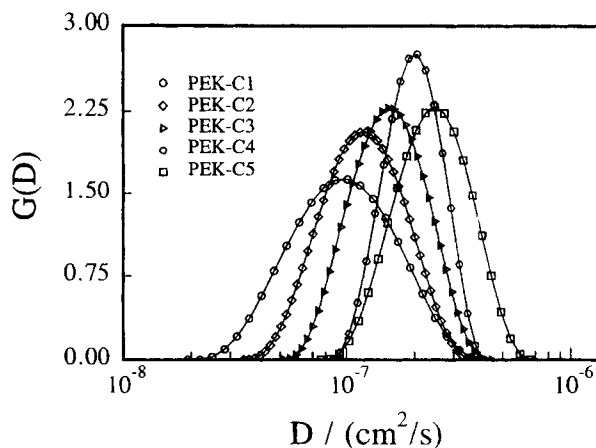


Fig. 4. Translational diffusion coefficient distributions of five PEK-C samples in CHCl₃ at T = 25°C, where the solutions were clarified with a 0.1-μm filters.

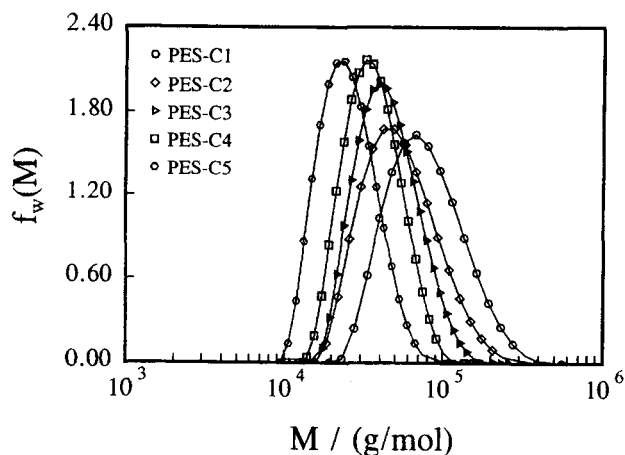


Fig. 5. Differential molecular weight distributions of five PES-C samples. The calculated weight average molecular weight and polydispersity index are listed in Table 2.

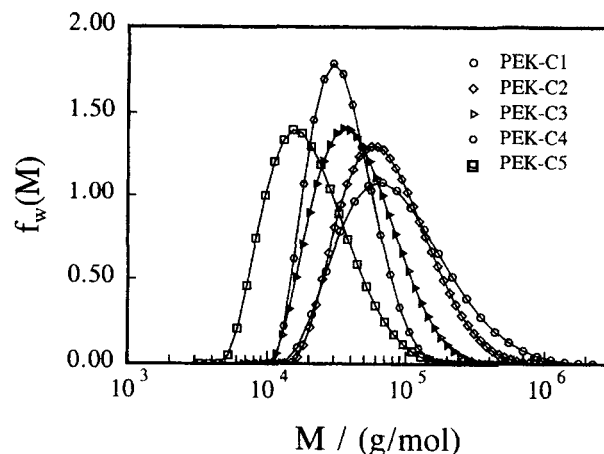


Fig. 6. Differential molecular weight distributions of five PEK-C samples. The calculated weight average molecular weight and polydispersity index are listed in Table 3.

to find k_D and α_D from $G(D)$ on the basis of Eqs 9 and 10. The detail of this method is reported in our previous studies (17-19). Here, we determined that $\alpha_D = 0.55$ and $k_D = 2.45 \times 10^{-4}$ for PES-C; and $\alpha_D = 0.56$ and $k_D = 2.20 \times 10^{-4}$ for PEK-C in CHCl_3 at 25°C , respectively. Each pair of k_D and α_D values defines a calibration between D and M , which enables us to convert each $G(D)$ to a corresponding MWD. It should be noted that these MWDs are estimated values, which are less accurate than those from GPC.

Figures 5 and 6 show differential molecular weight distributions $f_w(M)$ of the PES-C and PEK-C samples. From each $f_w(M)$, we were able to calculate the weight average molecular weight (M_w)_{calcd} and polydispersity index (M_w/M_n)_{calcd}, which are also listed in Tables 2 and 3. The values M_w/M_n show that the distribution of the PES-C samples after clarifying with a $0.1 \mu\text{m}$ filter are fairly narrow. It should be noted that these calibrations between D and M have already been used to measure the molecular weight distributions of unfractionated PES-C and PEK-C samples in practice.

CONCLUSION

A combination of static and dynamic laser light-scattering studies of phenolphthalein poly(ether sulfone) (PES-C) and phenolphthalein poly(ether ketone) (PEK-C) in chloroform (CHCl_3) at 25°C leads to calibrations between the translational diffusion coefficient (D) and molecular weight (M), namely, $D = 2.45 \times 10^{-4} M^{-0.55}$ for PES-C and $D = 2.20 \times 10^{-4} M^{-0.56}$ for PEK-C, respectively. Using these calibrations, we have determined not only the weight-average molecular weights of PES-C and PEK-C samples, but also their molecular weight distributions. The established calibration between D and M together with the values of A_2 will enable us to characterize PES-C with only one concentration in the future. Our results also showed that both the PES-C and PEK-C chains are flexible in CHCl_3 at 25°C , and CHCl_3 is a good solvent for these polymers.

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NOMENCLATURE

C:	polymer concentration
D:	translational diffusion coefficient
$\langle D \rangle$:	average translational diffusion coefficient
dn/dc :	specific refractive index increment
λ :	wavelength
k_d :	diffusion second virial coefficient
k_D :	prefactor in the calibration between D and M
Γ :	line width
$G(\Gamma)$:	line-width distribution
$G(D)$:	translational diffusion coefficient distribution
$G^{(2)}(t)$:	intensity-intensity time correlation function
LLS:	laser light scattering
n :	refractive index
M :	molecular weight
M_w :	weight-average molecular weight
M_w/M_n :	polydispersity index
MWD:	molecular weight distribution
PEK-C:	phenolphthalein poly(ether ketone)
PES-C:	phenolphthalein poly(ether sulfone)
$\langle R_g \rangle$:	z-average radius of gyration

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