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Laser Light-Scattering Study of Novel Thermoplastics. 1. Phenolphthalein Poly(aryl ether ketone)

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ABSTRACT: Five different molecular weight phenolphthalein poly(aryl ether ketone) (PEK-C) fractions in $CHCl_3$ were studied by static and dynamic laser light scattering (LLS). The dynamic LLS revealed that the PEK-C samples contain some large polymer clusters. These large clusters can be removed by filtering the solution with a 0.1-μm filter. We found that the persistence length of PEK-C in $CHCl_3$ at 25 °C is ∼2 nm and the Flory characteristic ratio, C_∞, is ∼25. Our results showed that $\langle R_g^2\rangle_z^{1/2} = (3.50 \pm 0.20) \times 10^{-2} M_w^{0.54\pm0.01}$ and $\langle D\rangle = (2.37 \pm 0.05) \times 10^{-4} M_w^{-0.55\pm0.01}$, with $\langle R_g^2\rangle_z^{1/2}$, M_w, and $\langle D\rangle$ being the *z*-average radius of gyration, the weight-average molecular weight, and the *z*-average translational diffusion coefficient, respectively. A combination of static and dynamic LLS results enabled us to determine $D = (2.20 \pm 0.10) \times 10^{-4} M^{-0.555\pm0.015}$, where D and M correspond to monodisperse species. Using this calibration between D and M, we have determined molecular weight distributions of five PEK-C fractions from their corresponding translational diffusion coefficient distribution.

Introduction

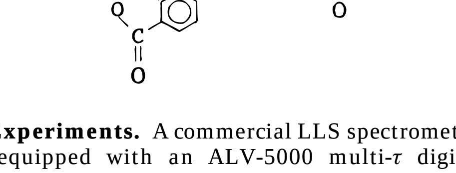
Poly(aryl ether ketone)s have been commercially introduced as a class of high-performance polymer materials with excellent heat resistance and high mechanical strength. Two of the most prominent members, poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK), are widely used as engineering thermoplastics or 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 CH_3SO_3H.[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(aryl ether ketone) (PEK-C) and phenolphthalein poly(aryl ether sulfone) (PES-C), have been successfully developed in the Changchun Institute of Applied Chemistry, Academy of Science, China.[5] PEK-C is not only similar to poly(aryl ether ketone)s with excellent physical and mechanical properties but also is soluble in polar organic solvents, such as chloroform ($CHCl_3$), *N*,*N*-dimethylformamide (DMF), *N*-methylpyrrolidinone (NMP), and chlorohydrocarbons, which renders its solutions castable. It has been recommended for high temperature and solvent resistant membranes.[6] Some dilute solution properties of PEK-C, 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 study of the chain conformation and flexibility of PEK-C in $CHCl_3$ on the basis of the molecular weight (M) 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, and the relationship between the translational diffusion coefficient, $\langle D\rangle$, from dynamic laser light scattering (LLS) and the weight-average molecular weight, M_w, from static LLS, together with the molecular weight distribution (MWD) of PEK-C calculated from its diffusion coefficient distribution, $G(D)$. The study of PES-C will be reported in a separate paper.

Experimental Section

Preparation of PEK-C. The PEK-C samples were synthesized by the following nucleophilic substitution polycondensation. First, equal molar phenolphthalein and dichlorodiphenyl ketone were dissolved in cyclobutane sulfone ($TMSO_2$); then, an excess amount of dehydrated K_2CO_3 was added as a catalyst; finally, the solution mixture was heated to 220 °C, and reaction was carried out under N_2 for 8 h. A 2% solution of PEK-C 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 h. The details of the sample preparation can be found elsewhere.[5] Five fractions were obtained and denoted as PK1−PK5 thereafter. As shown below, the structure of PEK-C is similar to PEEK.



LLS Experiments. A commercial LLS spectrometer (ALV/SP-150 equipped with an ALV-5000 multi-τ 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 was no angular dependence of the scattered light from toluene. The spatial coherence constant, β, was ∼0.9, somewhat large for an LLS spectrometer capable of doing both static and dynamic LLS

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

sample	$10^{-5}M_w$ (g/mol)	$\langle R_g\rangle$ (nm)	10^4A_2 (mol mL/g^2)	$10^8\langle D\rangle$ (cm^2/s)	R_h (nm)	$\langle R_g\rangle/\langle R_h\rangle$	$10^{-5}(M_w)_{calcd}$	M_w/M_n
PK1	11.0	95.4	2.63	8.09	44.9	2.10	10.7	5.64
PK2	6.56	71.6	3.11	10.8	37.3	1.90	6.41	5.33
PK3	1.21	32.3	9.49	27.2	14.8	2.20	1.36	3.64
PK4	0.53	17.7	15.1	48.0	8.39	2.10	0.52	1.81
PK5	0.25	10.7	21.6	75.8	5.31	2.00	0.24	1.85

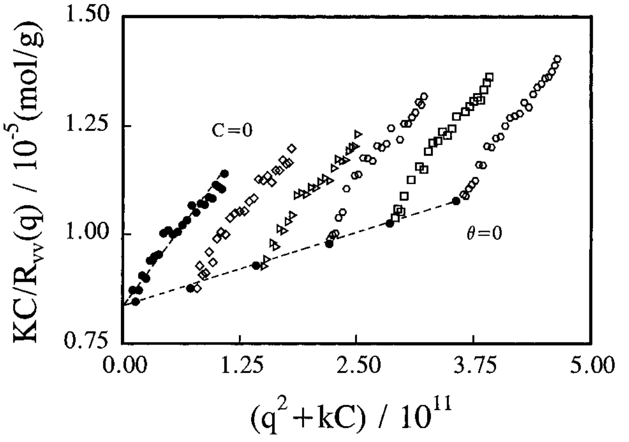

Figure 1. Typical Zimm plot of PK3 in $CHCl_3$ at 25 °C, after using 0.22-μm filters, where C ranges from 1×10^{-3} to 2.5×10^{-3} g/mL.

simultaneously. Using this apparatus, we were able to carry out both 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]

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

where $K = 4\pi^2n^2(dn/dC)^2/(N_A\lambda_o^4)$ and $q = 4\pi n/\lambda_o \sin(\theta/2)$, with N_A, dn/dC, n, and λ_o being 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; $\langle R_g^2\rangle_z^{1/2}$ (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 were able to 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,[16] 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 of PEK-C in $CHCl_3$ at $T = 25$ °C and $\lambda_o = 532$ nm is 0.231 ± 0.001 mL/g. In this study, a differential refractometer was used not only to measure the refractive index increment but also to determine the PEK-C 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]

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

Where A is a measured base line, β is, 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

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

Using a Laplace inversion program, CONTIN,[13] supplied with the correlator, we were able to calculate $G(\Gamma)$ from $G^{(2)}(t,\theta)$.

In this study, analytical grade $CHCl_3$ was used as a solvent without further purification. For each PEK-C fraction, five concentrations ranging 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 of "PK1 and PK2" and "PK3, PK4, and PK5" were clarified by 0.5- and 0.22-μm Millipore filters, respectively, and in the second stage, 0.1-μm Whatman filters were used for all PEK-C solutions.

Results and Discussion

Figure 1 shows a typical Zimm plot of PEK-C in $CHCl_3$ at 25 °C, where a 0.22-μm filter was used with C ranging from 2.75×10^{-4} to 1.37×10^{-3} g/mL. Using eq 1, we obtained values of M_w, R_g, and A_2 respectively from $[KC/R_{vv}(\theta)]_{\theta\to 0, c\to 0}$, $[KC/R_{vv}(\theta)]_{c\to 0}$ vs q^2, and $[KC/R_{vv}(\theta)]_{\theta\to 0}$ vs C. The static LLS results are summarized in Table 1. The positive values of A_2 indicate that $CHCl_3$ is a good solvent for PEK-C at 25 °C. It should be noted that for samples PK4 and pK5 there are large errors associated with the $\langle R_g\rangle$ values which should be interpreted only as a reference, i.e., <10 nm.

Modeling PEK-C as a wormlike chain, we estimate the persistence length, l, on the basis of $\langle R_g^2\rangle = l^2\{1/3(L/l) - 1 + (2l/L) - (2l^2/L^2)[1 - \exp(-L/l)]\}$,[21] where L ($=nl_u$) is the contour length with l_u being the projected length of the segments between two ether linkages and n ($=M_w/M_o$) being the number of the segments. In the case of PEK-C, the average values of l_u and M_o are ~1.1 nm and ~248 g/mol, respectively, from its chemical structure. Strictly speaking, $n = M_z/M_o$. The value of l estimated from five PEK-C samples is ~2 nm for PEK-C in $CHCl_3$ at 25 °C, which leads to a value of $C_\infty \sim 25$, using the formula $C_\infty = (2l/l_o) - 1$,[22] where l_o is the average bond length.

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 0.22-μm filter. The fast relaxation (peak 1) corresponds to single PEK-C chains, and the slow relaxation (peak 2) in the bimodal distribution indicates that there exist some large species in the sample. The PEK-C samples are broadly distributed, which is inconsistent with the prediction of $M_w/M_n \leq 2$ for a polycondensation reaction.

Figure 3 shows plots of $\langle\Gamma\rangle/q^2$ vs q^2 for peaks 1 and 2, where $\langle\Gamma\rangle = \int G(\Gamma)\Gamma\, d\Gamma$. The linear q^2 dependence of $\langle\Gamma\rangle/q^2$ indicates that both the relaxation processes observed in Figure 2 are diffusive. For a diffusive relaxation, Γ can related to both C and θ as[14,15]

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

where D is the translational diffusion coefficient at $c \to 0$ and $\theta \to 0$, k_d is the diffusion second virial coefficient,

Table 2. Summary of Laser Light-Scattering Results for Five Samples of PEK-C Using 0.1-μm Filters

sample	$10^{-5}M_w$ (g/mol)	$\langle R_g\rangle$ (nm)	$10^8\langle D\rangle$ (cm^2/s)	$\langle R_h\rangle$ (nm)	$\langle R_g\rangle/\langle R_h\rangle$	$10^{-5}(M_w)_{calcd}$	$(M_w/M_n)_{calcd}$
PK1	1.30	19.9	28.6	14.1	1.41	1.25	1.96
PK2	0.92	16.4	35.0	11.5	1.42	0.92	1.57
PK3	0.51	12.1	50.3	8.01	1.51	0.54	1.50
PK4	0.39	~10	57.9	6.97	~1.4	0.37	1.55
PK5	0.22	~8	78.0	5.16	~1.5	0.25	1.49

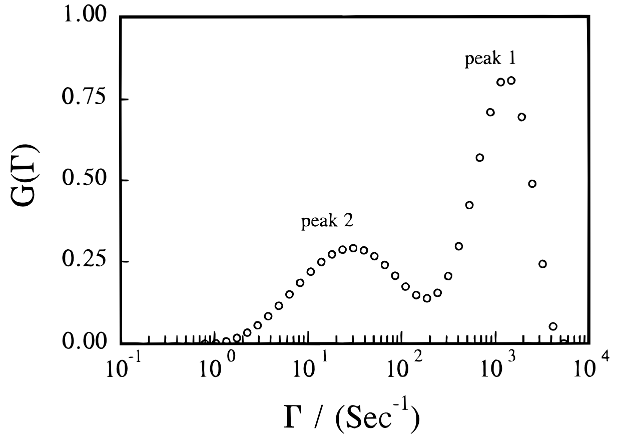

Figure 2. Typical line-width distribution, $G(\Gamma)$, of PK3 in CHCl$_3$ at 25 °C after using 0.5-μm filters.

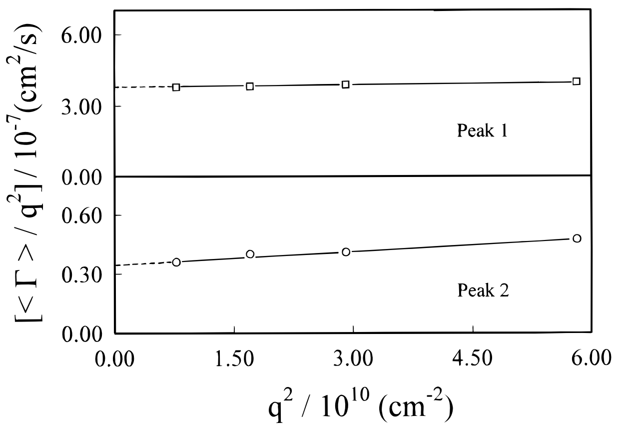

Figure 3. Typical q^2 dependence of Γ/q^2 of PK3 in CHCl$_3$ at 25 °C.

and f is a dimensionless number depending on the chain conformation, solvent, and internal motions. Using eq 4, D, f, and k_d can be calculated from $(\Gamma/q^2)_{C\to0,\theta\to0}$, $(\Gamma/q^2)_{C\to0}$ vs q^2, and $(\Gamma/q^2)_{\theta\to0}$ vs C, respectively. In this study, we found that k_d is very small. With a pair of values for k_d and f, $G(\Gamma)$ can be converted into $G(D)$. Further, we can calculate an average translational diffusion coefficient, $\langle D\rangle$ [$= \int_0^\infty G(D)D\,dD$], and an 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, and the solvent viscosity, respectively. The values of $\langle D\rangle$, $\langle R_h\rangle$, and $\langle R_g\rangle/\langle R_h\rangle$ of five PEK-C samples are also listed in Table 1. The ratios of $\langle R_g\rangle/\langle R_h\rangle$ are slightly higher than the value (1.4−1.8) observed for a flexible polymer chain in good solvent,[17] possibly because the PEK-C samples are broadly distributed. Later, we found experimentally that the slow relaxation peak is removed by filtering the solution with a small pore size filter, which further indicates that the slow relaxation peak in Figure 2 is related to some large species in the PEK-C 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.

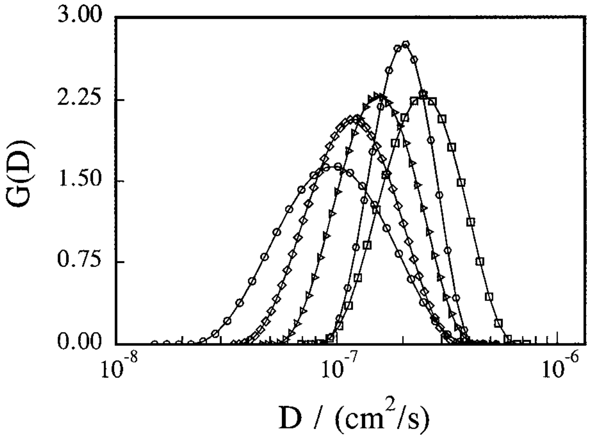

Figure 4. Five translational diffusion coefficient distributions of PEK-C samples (PK1 (○), PK2 (◇), PK3 (△), PK4 (○), and PK5 (□)) in CHCl$_3$ at 25 °C after using 0.1-μm filters.

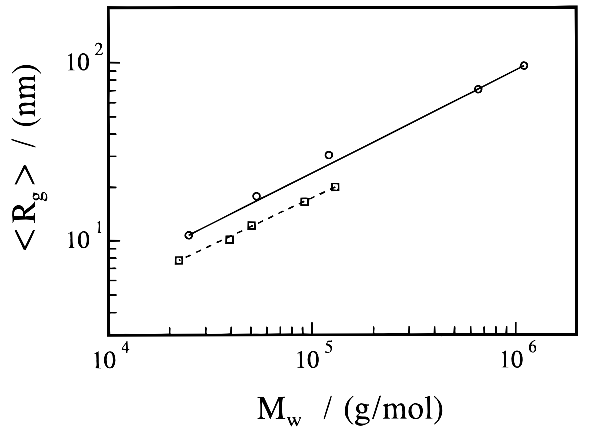

Figure 5. Double-logarithmic plots of $\langle R_g\rangle$ vs M_w: (□) the PEK-C solution clarified with 0.5-μm filters and (○) solution clarified with 0.1-μm filters.

Figure 4 shows the translational diffusion coefficient distributions, $G(D)$, of the five PEK-C samples in CHCl$_3$ at 25 °C, where 0.1-μm filters were used. In comparison with Figure 2, the large species in the samples have been removed, so that $G(D)$ is now a monomodal distribution. The large clusters did not reappear after 15 days, which leads us to believe that the clusters are not PEK-C aggregates. In this case $\langle D\rangle$ is independent of the scattering angle. The values of $\langle D\rangle$ and $\langle R_h\rangle$ together with M_w and $\langle R_g\rangle$ from static LLS are summarized in Table 2. The ratios of $\langle R_g\rangle/\langle R_h\rangle$ (~1.5) are close to the value predicted for a random coil in a good solvent, which further indicates that the PEK-C chain is flexible in CHCl$_3$ at 25 °C.

Figure 5 shows that for PEK-C in CHCl$_3$ at 25 °C, $\log(\langle R_g\rangle)$ is a linear function of $\log(M_w)$. The continuous and dotted lines represent the fitting of $R_g(\mathrm{mm}) = (3.73 \pm 0.20) \times 10^{-2}M_w^{0.56\pm0.01}$ and $R_g(\mathrm{nm}) = (3.50 \pm 0.20) \times 10^{-2}M_w^{0.54\pm0.01}$, respectively. For a similar molecular weight, the value of $\langle R_g\rangle$ obtained without removing the large species is greater because $\langle R_g\rangle$ is a z-averaged value, while M_w is only a weight-averaged one. The exponent value of ~0.55 ± 0.01 also indicates that

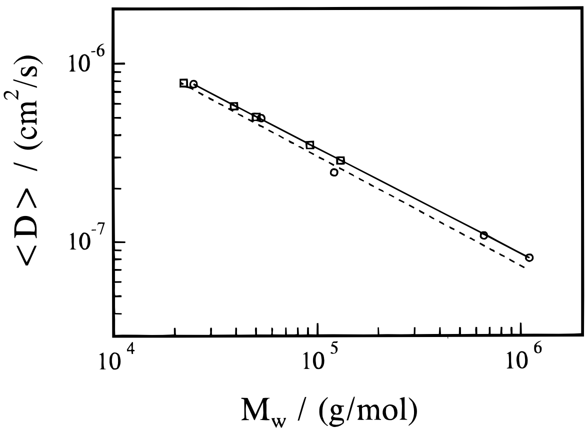

Figure 6. Double-logarithmic plot of $\langle D\rangle$ vs M_w: (□) the PEK-C solution clarified with 0.5-μm filters and (○) solution clarified with 0.1-μm filters.

PEK-C in $CHCl_3$ at 25 °C has a coil conformation and the PEK-C chain is flexible in $CHCl_3$. We will return to this point later.

Figure 6 shows that $\log(\langle D\rangle)$ is also a linear function of $\log(M_w)$ for PEK-C in $CHCl_3$ at 25 °C. The line shows a fitting of $D(\mathrm{cm^2/s}) = \langle k_D\rangle M_w^{-\langle\alpha_D\rangle}$, with $\langle k_D\rangle = (2.37 \pm 0.05) \times 10^{-4}$ and $\langle\alpha_D\rangle = 0.55 \pm 0.01$, where "$\langle\ \rangle$" indicates the values of $\langle k_D\rangle$ and $\langle\alpha_D\rangle$ were obtained using $\langle D\rangle$ and M_w rather than D and M. The value of $\langle\alpha_D\rangle$ (=0.55 ± 0.01) indicates that the PEK-C chain has a coil chain conformation in $CHCl_3$ at 25 °C. In principle, with $\langle\alpha_D\rangle$ and $\langle k_D\rangle$, we can transform $G(D)$ into a molecular weight distribution (MWD).[18] However, the PEK-C samples are broadly distributed even after using a 0.1-μm filter. Previous studies[17,19] have shown that using $\langle k_D\rangle$ and $\langle\alpha_D\rangle$ instead of k_D and α_D for a broadly distributed sample can introduce a large error in the final MWD. Therefore, it is preferable to combine both static and dynamic LLS results,[19] whereby values of M_w and $G(D)$ from more than one broadly distributed sample are used to find k_D and α_D. The principle of this method has been given before.[19] Using this method, we found that $\alpha_D = 0.555 \pm 0.015$ and $k_D = (2.20 \pm 0.10) \times 10^{-4}$. This pair of α_D and k_D defines a calibration between D and M for PEK-C in $CHCl_3$ at 25 °C, shown in Figure 6 by the dotted line. According to Flory's result for a polymer coil,[20] $\alpha_D = (1 + \alpha_\eta)/3$, where α_η is a scaling constant in $[\eta] = k_\eta M_w^{\alpha_\eta}$, with $[\eta]$ being the intrinsic viscosity. The previous results[8] showed that $\alpha_\eta = 0.66$. This leads to $\alpha_D = 0.552$, which agrees well with the $\alpha_D = 0.555$ from $G(D)$ and M_w.

Figures 7 and 8 respectively show differential weight distributions, $f_w(M)$, of five PEK-C samples. It is worth noting that in Figure 7 each $f_w(M)$ has only one broad peak, even though the $G(\Gamma)$ shown in Figure 2 is a bimodal distribution. This is because $G(D)$ is an intensity (z) distribution and is much more sensitive to large species in the sample than $f_w(M)$, namely $G(D) \propto I \propto f_N(M)M^2$, while $f_w(M) \propto f_N(M)M$, where $f_N(M)$ is a differential number distribution. The disappearance of the second peak in $f_w(M)$ indicates that the number of these large species in PEK-C is very small. From each $f_w(M)$ in Figures 7 and 8, we were able to calculate the corresponding weight-average molecular weight, $(M_w)_{\mathrm{calcd}}$, and polydispersity index, $(M_w/M_n)_{\mathrm{calcd}}$. They are listed in Tables 1 and 2, respectively. The PEK-C samples before removing the large species are broadly distributed. It should be stated that the presence of small amounts of larger species was not observed in gel permeation chromatography (GPC) studies because GPC is less sensitive to the trace amount of large species.

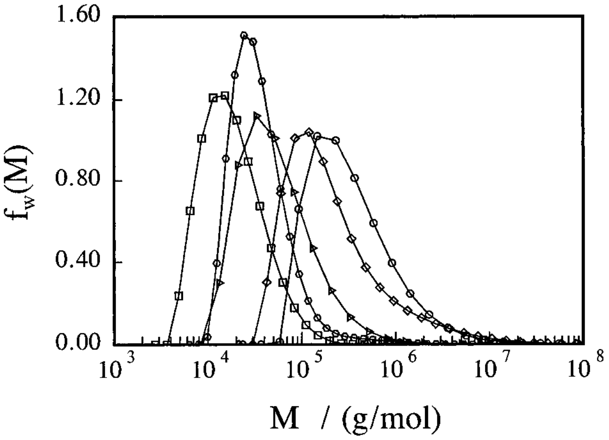

Figure 7. Differential molecular weight distributions of PK1 (○), PK2 (◇), PK3 (△), PK4 (○), and PK5 (□), where the PEK-C solutions were clarified with 0.1-μm filters.

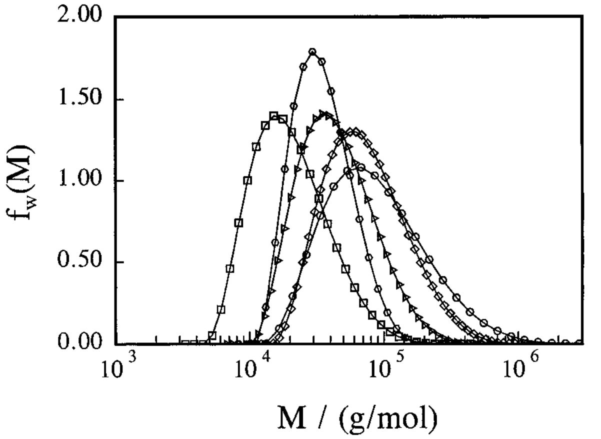

Figure 8. Differential molecular weight distributions of PK1–PK5 (the symbols are the same as in Figure 7), where the PEK-C solutions were clarified with 0.1-μm filters.

Conclusion

A study combining both static and dynamic laser light-scattering results has found that for phenolphthalein poly(aryl ether ketone) (PEK-C) in $CHCl_3$ at 25 °C the persistence length, l, is ~2 nm, the Flory characteristic ratio, C_∞, is ~25, the translational diffusion coefficient, D, is related to the molecular weight by $D = (2.20 \pm 0.01) \times 10^{-4}M^{-0.555\pm0.015}$, and the radius of gyration, $\langle R_g\rangle$, is related to the weight-average molecular weight, M_w, by $\langle R_g\rangle = (3.50 \pm 0.20) \times 10^{-2}M_w^{0.54\pm0.01}$. These results indicate that the PEK-C chain in $CHCl_3$ at 25 °C has a coil conformation. The dynamic LLS results also reveal that there exists a trace amount of large species in PEK-C. These large species lead to a higher apparent molecular weight of PEK-C, which was not observed in GPC studies. We have demonstrated that these large species can be removed from the solution by a 0.1-μm filter. Therefore, we believe that these large species were large PEK-C clusters formed during the polymerization. The study of the nature of these large clusters and their influence on PEK-C performance as a thermoplastic material is ongoing.

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