# Dilute Solution Properties of Phenolphthalein Poly(aryl ether ketone)

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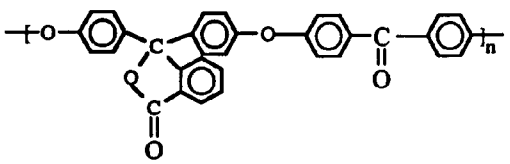
**Summary:** Five narrow molecular weight distributed fractions of Phenolphthalein poly (aryl ether ketone) were studied in chloroform by static laser light scattering (LLS) and viscometry at 25 °C. From static LLS, the weight-average molecular weights ($M_w$), z-average radii of gyration; $\langle R_g^2\rangle_z^{1/2}$ (or written as $\langle R_g\rangle$) and second virial coefficients, $A_2$ of the PEK-C fractions were determined. Our results showed that $\langle R_g^2\rangle_z^{1/2} = 3.50 \times 10^{-2} M_w^{0.54}$. From viscometry, the reduced and inherent viscosities of all the fractions were measured and the corresponding intrinsic viscosities were determined. The intrinsic viscosities scaled with the molecular weights obtained through static LLS yielding a Mark-Houwink equation of $[\eta] = 4.42 \times 10^{-2} M_w^{0.686}$. The exponent values indicate that PEK-C in $CHCl_3$ at 25 °C has a coil chain conformation.

## 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 at high-temperature. 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) [1, 2]. On the other hand, their chemical resistance and crystalline structure make them soluble only in strong acids or solvents with a boiling point higher than the melting temperature of these polymer crystals. Therefore, the processing and applications of these thermoplastics have been greatly hindered by their insolubility in common solvents. So far, very few studies on dilute solution properties of PEEK have been reported mainly because it is soluble only in concentrated $H_2SO_4$, $HSO_3Cl$, and $CH_3SO_3H$ [3, 4]. However, various extent of sulfonation of PEEK in $H_2SO_4$ has certainly complicated its characterization [5]. A novel thermoplastic, phenolphthalein poly (aryl ether ketone) (PEK-C), with the following chemical structure has been synthesized [6].



PEK-C is not only similar to PEEK in physical and mechanical properties but is also soluble in several polar organic solvents, such as chloroform, N,N-dimethyl-formamide (DMF), N-methyl pyrrolidinone (NMP), 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 [7].

Previously, we studied the chain conformation of five narrowly distributed PEK-C fractions in $CHCl_3$ at 25 °C and determined the calibration between the translational diffusion coefficient D and the molecular weight M for it [8]. We also demonstrated that on the basis of our previously established calibration, it was possible to characterise the molecular weight distribution from of broadly distributed unfractionated PEK-C in $CHCl_3$ using only one dynamic LLS measurement [9]. In this work, we want to extend the scope of our investigation on PEK-C, namely, (1) to study its chain conformation and (2) flexibility in $CHCl_3$ on the basis of molecular weight dependence of its intrinsic viscosity .

## Results and Discussion

Fig. 1 shows a plot of the refractive index increment ($\Delta n$) versus concentration (C) for PEK-C in $CHCl_3$ at 25 °C and $\lambda_o$ = 532 nm, whereas $\Delta n$ was measured by a novel high-precision differential

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refractometer [10], which enables us to measure dn/dC and the scattered light intensity under identical experimental conditions, so that the wavelength correction was eliminated. The relative error associated with the specific refractive index increment (dn/dC) of 0.231 ± 0.001 mL/g calculated from the Fig. 1 is less than ± 1%. It is vital in static light scattering to have a precise value of differential refractive index increment, dn/dC, because the measured $M_w$ is proportional to $(dn/dC)^{-2}$.

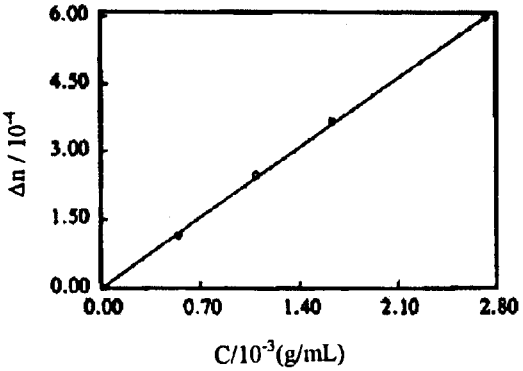


Fig. 1. Plot of the refractive index increment (Δn) versus concentration (C) for PEK-C-1 in $CHCl_3$ at 25 °C and $\lambda_o$ = 532nm, where the slope is the refractive index increment (dn/dC) = 0.231 ± 0.001 mL/g.

Fig. 2 shows a typical Zimm plot of PEK-C in $CHCl_3$ at 25 °C, where 0.22-μm filter was used and C ranges from 2.16 x $10^{-4}$ to 1.08 x $10^{-3}$ g/mL. On the basis of eq. 1, we have calculated the values of $M_w$, $\langle R_g \rangle$, and $A_2$ 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 respectively. The static LLS results of five fractions 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, but the decrease of $A_2$ values with the increase in molecular weight indicates that the solvent quality becomes poorer with increasing the molecular weight.

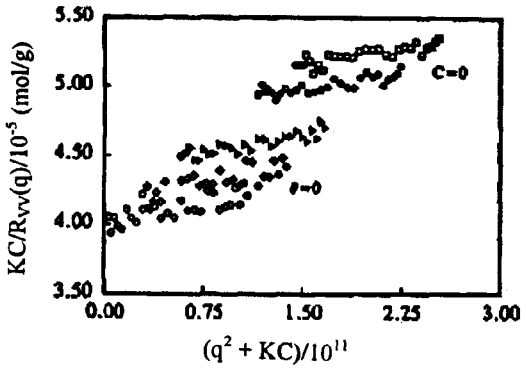


Fig. 2. Typical Zimm-plot of PEK-C-5 in $CHCl_3$ at 25° C, where the concentration, ranges from 2.162 x $10^{-4}$ to 1.08 x $10^{-3}$ g/mL.

Fig. 3 shows that the log of $\langle R_g \rangle$ is a linear function of log $M_w$ of PEK-C in $CHCl_3$ at 25 °C. The solid line represents the fitting of $\langle R_g \rangle = (3.52 \pm 0.20) \times 10^{-2} M_w^{0.54}$. The exponent value of 0.54 indicates that the PEK-C in $CHCl_3$ at 25 °C has a coil chain conformation.

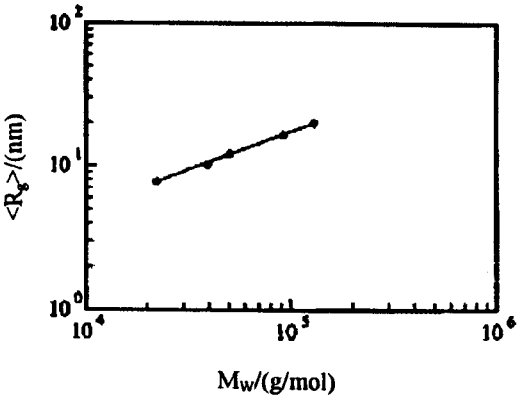


Fig. 3. Double logarithmic plot of $\langle R_g \rangle_z$ versus $M_w$ for PEK-C, where the solid lines represent the least square fitting of $\langle R_g^2 \rangle_z^{1/2} = (3.50 \pm 0.20) \times 10^{-2} M_w^{0.54}$

Table I. Summary of the viscometric and static Laser Light-scattering results of the five fractions of the PEK-C in $CHCl_3$ at 25 °C.

| Samples | $10^{-4} M_w$ g/mol | $\langle R_g^2 \rangle_z^{1/2}$ nm | $\langle R_o^2/6 \rangle^{1/2}$ nm | $\langle R_o^2 \rangle^{1/2}/M \times 10^4$ | $10^4 A_2$ mol.cm³/g² | [η] mL/g |
|---|---|---|---|---|---|---|
| PEK-C-1 | 13.0 | 19.9 | 20.5 | 1.58 | 2.63 | 121 |
| PEK-C-2 | 9.2 | 16.4 | 17.3 | 1.88 | 3.11 | 66 |
| PEK-C-3 | 5.1 | 12.1 | 12.9 | 2.53 | 9.49 | 56 |
| PEK-C-4 | 3.9 | 10.0 | 11.3 | 2.90 | 15.1 | 51 |
| PEK-C-5 | 2.23 | ~8.0 | 8.5 | 3.86 | 21.6 | 30 |

Fig. 4 shows the plots of the reduced and inherent viscosity for the PEK-C-5 as a function of concentration as described by eq. (2) and (3). It can be seen that the data can be fitted well to the Huggin and Kraemer relations given by eq. (5) and (6) respectively. The intrinsic viscosity, [η] was determined by extrapolating the data to zero polymer concentration, using linear regression and it was noted that both the eqs. (5) and (6) gave the same results as per extrapolations. The intrinsic viscosities so obtained for the five fractions with different molecular weights are given in Table 1.

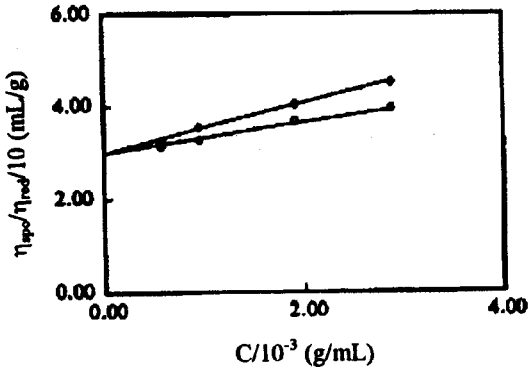


Fig. 4. Typical plots of the reduced (□) and inherent (O) viscosities of the PEK-C-5 in $CHCl_3$ at 25 °C where concentration ranges from 2.162 x $10^{-4}$ to 1.08 x $10^{-3}$ g/mL.

Fig. 5 shows the double logarithmic plot of the intrinsic viscosity as a function of the molecular weight of the five fractions of PEK-C. The solid line shows the least square fitting of the data and the relation obtained between intrinsic viscosity and molecular weight of $[\eta] = 4.42 \times 10^{-2} M_w^{0.686}$. The exponent value of (~0.686) further shows the polymer chain possesses a coil chain conformation in $CHCl_3$ at 25 °C. According to Flory's results for a polymer coil, $\alpha_D = (1+\alpha_\eta)/3$ [11], where $\alpha_D$ is the scaling constant in $\langle D \rangle = k_D M_w^{\alpha D}$ with <D>, the average translational diffusion coefficient coefficient distribution. Our previous LLS results showed that $\alpha_D \sim 0.555$ for this system [8]. This leads to $\alpha_\eta = 0.67$, which shows that our results from viscosity are consistent with the previous laser light scattering results.

For finding the unperturbed chain dimensions of the polymer, the results obtained for $M_w$ and [η] are plotted in Fig. 6 as per S.F equation [12]. The

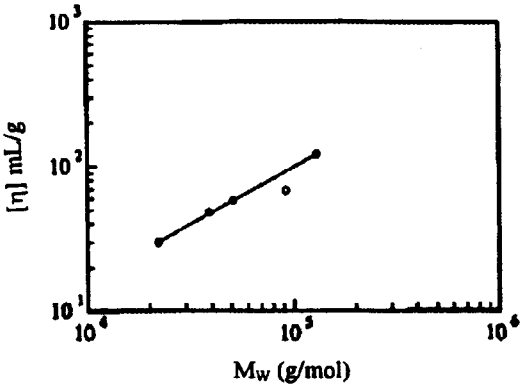


Fig. 5. Plot of the intrinsic viscosities as a function of molecular weight of the five fractions of PEK-C.

required parameter, $K_0$ was calculated directly from the intercept, which is 0.115 only. Since we know that $K_0 = \phi_0 A$ where $\phi_0$ is universal constant having value equal to 2.80 x $10^{21}$ $mol^{-1}$ and $A = (\langle R_0^2 \rangle / M)^{1/2}$ where $\langle R_0^2 \rangle$ is the mean square end to end distance of the polymer molecule at unperturbed state. Since $\langle R_g^2 \rangle_z^{1/2} = (\langle R_0^2 \rangle / 6)^{1/2}$ The values of $(\langle R_0^2 \rangle / 6^{1/2})$ were calculated and are listed in Table 1. The value of $\langle R_0^2 \rangle^{1/2}$ are slightly greater than the values $\langle R_g^2 \rangle_z^{1/2}$ as obtained from the static LLS results. This is due to the fact that S.F. equation overestimate the chain dimension in good solvent [13]. The values of $(\langle R_0^2 \rangle^{1/2}/M)$ are also listed in the Table 1. We see that these values increase with the decrease in molecular weight. This is due to the fact that the solvent quality increases with the decrease in molecular weight for a particular polymer and hence it will be stretched more.

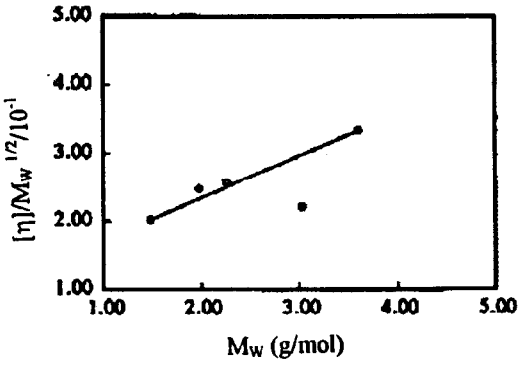


Fig. 6. Stockmayer-Fixman Plot of $[\eta]/M_w^{1/2}$ as a function of $M_w^{1/2}$ (eq. 8) of the PEK-C

## Experimental

*Solution Preparation*

The preparation of PEK-C sample has been detailed before [6]. Five fractions were obtained and denoted as PEK-C-1 — PEK-C-5 thereafter. Analytical grade chloroform $CHCl_3$ from Merck as a solvent was used without further purification. Five solutions with their concentrations ranged from 2.16 x $10^{-4}$ to 1.08 x $10^{-3}$ g/mL were prepared by successively diluting a stock solution of 1.08 x $10^{-3}$ g/mL. All polymer solutions were clarified by using a 0.2-μm Whatman filter in order to remove dust and multichain aggregates.

*Laser Light-Scattering Study*

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, having output power as ~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, rather high for a LLS spectrometer capable of doing both static and dynamic LLS simultaneously. At the present set-up, we were able to carry out both static and dynamic LLS in the angular range of 6° - 154°. The detail of LLS instrumentation and theory can be found elsewhere [14, 15].

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 [16].

$$\frac{KC}{R(vv)(\theta)} \approx \frac{1}{Mw}(1+\frac{1}{3}<R_g^2>q^2)+2A_2C \qquad (1)$$

Where $K = 4\pi^2 n^2 (\frac{dn}{dc})^2/(N_A\lambda_o^4)$ and $q = \frac{4\pi n}{\lambda_o}\sin(\frac{\theta}{2})$, with $N_A$, dn/dC, n, and $\lambda_o$ being Avogadro number, the specific refractive index increment, the solvent refractive index, and the wave length of light in vacuo, respectively. $M_w$ is the weight-average molecular weight; $A_2$ is the second virial coefficient; $<R_g^2>_z^{1/2}$ (or written as $<R_g>$) is the root-mean square z-average radius of the polymer chain in solution, and C is the polymer concentration.

*Viscometric Study*

Dilute polymer solutions for viscosity measurements were prepared in Chloroform. The efflux times of the dilute polymer solutions were measured using Ubbelohde capillary viscometer at the temperature of 25 ± 0.1 °C maintained with the thermostat bath. The efflux times were converted to reduce viscosities according to the following formula.

$$[\eta_{red}] \approx \frac{\eta_{sp}}{C} = \frac{\eta-\eta_s}{\eta_s C} \approx \frac{(t-t_0)}{t_0 C} \text{ -------} \qquad (2)$$

And

$$\frac{\ln\eta_r}{C} = \frac{\ln\eta/\eta_s}{C} \approx \frac{\ln(t/t_0)}{C} \text{ -------} \qquad (3)$$

Where $\eta_{red}$ is the reduced viscosity, C is the solution concentration, $\eta$ the solution viscosities, $\eta_s$ the solvent viscosity, $\eta_{sp}$ the specific viscosity, t is the efflux time of solution and $t_o$ is the efflux time of solvent.

When the solution concentration C approaches zero, the intrinsic viscosity is defined by the following formula:

$$[\eta] = \lim_{c\to 0} = \frac{\eta_{sp}}{C} = \lim_{c\to 0} = \frac{\ln\eta_r}{C} \qquad (4)$$

The intrinsic viscosities of the five fractions were obtained by extrapolation of the reduced and inherent viscosity to zero polymer concentration using either the Huggin [17], or the Kraemer [18] equation, respectively:

$$\frac{\eta_{sp}}{C} = [\eta] + K_H[\eta]^2 C + \text{-----} \qquad (5)$$

And

$$\frac{\ln\eta_r}{C} = [\eta] + K_k[\eta]^2 C + \text{-----} \qquad (6)$$

Where $K_H$ and $K_K$ are the Huggins and the kraemer coefficients respectively. The intrinsic viscosity data can be scaled to the molecular weight using Mark- Houwink equation:

$$[\eta] = K_\eta M^{\alpha_\eta} \text{ --------} \quad (7)$$

The constants K and $\alpha_\eta$ in Eq. (7) are dependent on the polymer, solvent system and temperature.

To calculate the unperturbed chain dimensions in term of $K_o$ from the intrinsic viscosity, the Stockmayer-Fixman equation can be used [12], which has the following form.

$$[\eta]/M_w^{1/2} = K_o + 0.51\ \phi_o\ B\ M_w^{1/2} \text{ -------} \quad (8)$$

Here B is a constant and depends on the interactions of the system. $\phi_o$ is a universal constant. Though the value of $K_o$ is supposed to be constant but normally it depends upon the solvent quality.

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