

## Characterization of Phenolphthalein Poly(aryl ether Sulfone)

<sup>1</sup>M. SIDDIQ\*, <sup>2</sup>K. MAHMOOD AND <sup>2</sup>M. K. BALOCH

<sup>1</sup>Department of Chemistry, Quaid-I-Azam University, Islamabad, Pakistan

<sup>2</sup>Department of Chemistry, Gomal University, D.I.Khan, Pakistan

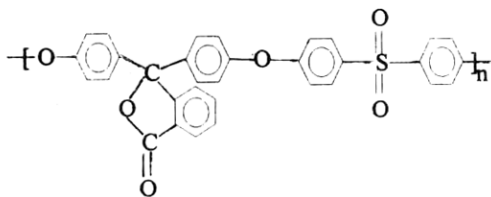
(Received 23<sup>rd</sup> October, 2001, revised 30<sup>th</sup> March, 2005)

**Summary:** Four narrow molecular weight distributed fractions of Phenolphthalein Poly(aryl ether sulfone) (PES) were studied in CHCl<sub>3</sub> 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;  $\langle R_g^2 \rangle_z^{1/2}$ , second virial coefficients  $A_2$  of the PES samples were determined. 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 their molecular weight obtained through static LLS, yielding a Mark-Houwink equation of  $[\eta] = 4.42 \times 10^{-2} M^{0.686}$ . The exponent value indicates that PES in CHCl<sub>3</sub> has a coil chain conformation. The value of  $\alpha_n$  obtained from viscosity is comparable with  $\alpha_D$  obtained previously from dynamic LLS.

### Introduction

Both Poly (aryl ether ketones) (PEEK) and Poly (ether ketone) (PEK) are receiving considerable interest because of their high mechanical properties, excellent thermal stability and good chemical resistance [1,2]. However, both PEEK and PEK have several limitations in preparation processing and low thermoxidative stability [3-5]. These polymers are only soluble in strong acids or solvents with boiling point higher than their melting points, mainly due to their insoluble crystalline structure [6,7]

On the other hand thermoplastic Phenolphthalein poly (ether sulfone) (PES) has been developed with the following chemical structure [8].



PES has not only outstanding physical and mechanical properties, but is also soluble in polar organic solvents, such as CHCl<sub>3</sub>, *N,N*-dimethyl formamide (DMF), dimethyl acetamide (DMAc) and *N*-methyl pyrrolidinone (NMP). Previously, we characterised a linear chain of PES in the presence of large polymer cluster [9]. We have also characterized the chain conformation and flexibility of the PES chain in CHCl<sub>3</sub> at 25 °C and established a calibration between translational diffusion coefficient (*D*) and molecular weight (*M*) [10].

In this work we want to extend the scope of our investigation on PES, namely, to study the chain conformation and flexibility in CHCl<sub>3</sub> on the basis of molecular weight dependence of its intrinsic viscosity.

### Results and Discussion

Figure 1 shows a typical Zimm plot of PES-2 in CHCl<sub>3</sub> at 25 °C, where a 0.22- $\mu$ m filter was used and *C* range from  $2.16 \times 10^{-4}$  to  $1.08 \times 10^{-3}$  g/mL. On the basis of equation 1, we have calculated the values of  $M_w$ ,  $\langle R_g \rangle$ , and  $A_2$  respectively from  $[KC/R_{vv}(\theta)]_{\theta \rightarrow 0, c \rightarrow 0}$ ,  $[KC/R_{vv}(\theta)]_{c \rightarrow 0}$  vs  $q^2$ , and  $[KC/R_{vv}(\theta)]_{\theta \rightarrow 0}$  vs *C*. The static LLS results of four fractions are summarized in Table I. The positive values of  $A_2$  indicate that chloroform is a good solvent for PES at 25 °C.

Figure 2 shows the typical plot of the reduced and inherent viscosity of the PES-2 as a function of concentration as described by equations 2 and 3. It can be seen that the data can be fitted to the Huggin's and Kraemer's relations given by equations 5 and 6 respectively. The intrinsic viscosity,  $[\eta]$  was determined by extrapolating the data to zero polymer concentration, using linear regression. The intrinsic viscosities so obtained for the four fractions with different molecular weights are given in Table 1.

Figure 3 shows the double logarithmic plot of the intrinsic viscosity as a function of the molecular weight of the four fractions of PES. The solid line shows the least square fitting of  $[\eta] = 4.42 \times 10^{-2}$

\*To whom all correspondence should be addressed.

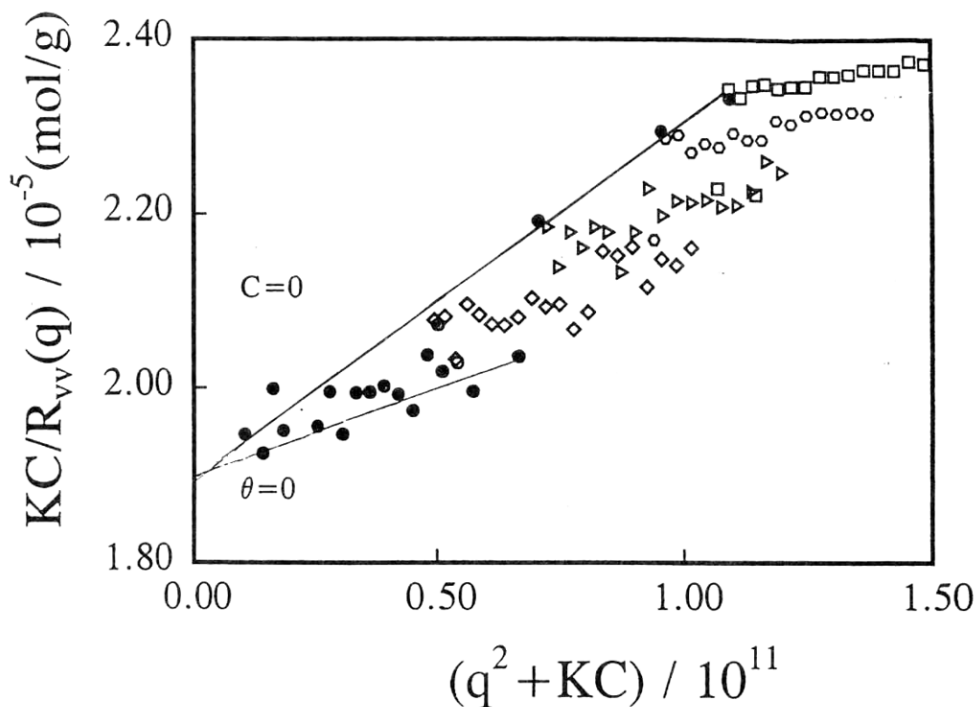


Fig. 1: Typical Zimm-plot of PES-2, where concentration ranges from  $2.16 \times 10^{-4}$  to  $1.08 \times 10^{-3}$  g/mL.

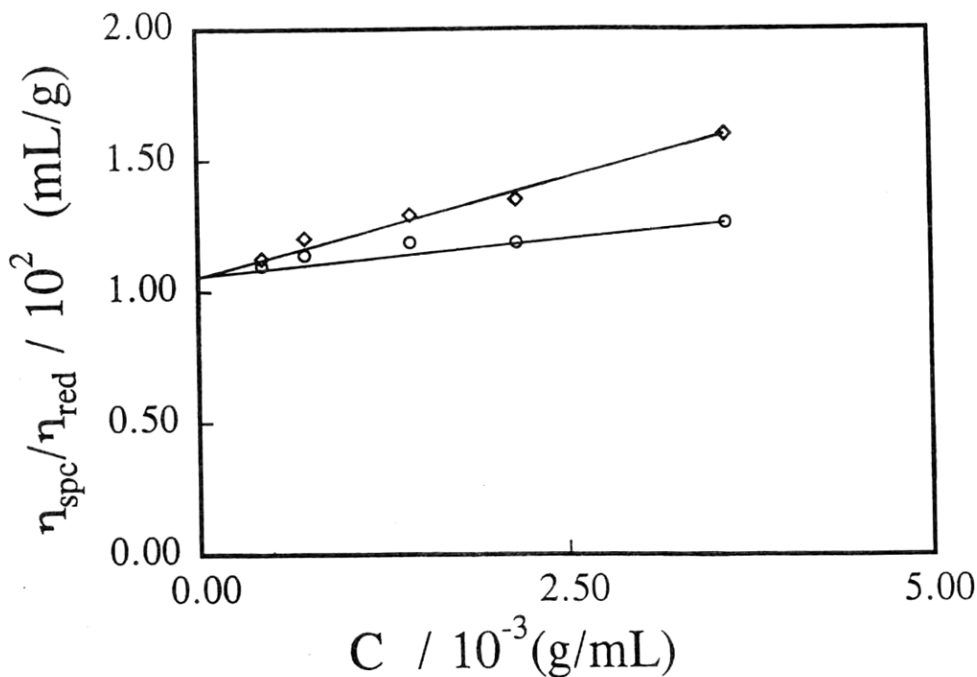


Fig. 2: Typical plots of the reduced ( $\square$ ) and ( $\circ$ ) viscosities of the PES-2 fraction in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ .

Table 1. Summary of the static LLS and viscometric results of the four fractions of PES in  $\text{CHCl}_3$  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)	$\langle R_o^2 \rangle / M^{1/2}$	$10^4 A_2$ (mol.cm <sup>3</sup> /g <sup>2</sup> )	$[\eta]$ (mL/g)	Activation Energy (Joules)
PES-1	6.20	~10	19.4	18.9	4.51	102	4212
PES-2	5.00	~10	17.5	23.2	8.95	89	3416
PES-3	4.20	<9	9.7	28.9	9.0	75	1978
PES-4	2.50	<9	8.27	54.4	---	50	1241

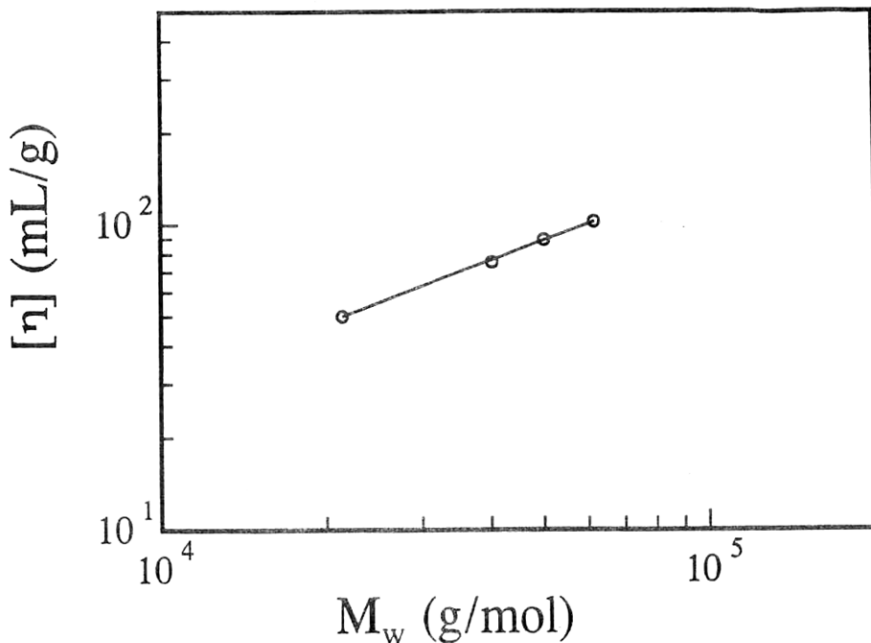


Fig. 3: Plot of the intrinsic viscosities as a function of molecular weight of the four fractions of the PES.

$^2M^{0.686}$ . The exponent value of  $-0.686$  shows that the polymer chain possesses a random coil chain conformation at 25 °C. According to Flory's result for a polymer coil [11],  $\alpha_D = (1 + \alpha_\eta)/3$ , where  $\alpha_D$  is the scaling constant in  $\langle D \rangle = k_D M^{-\alpha_D}$  with  $\langle D \rangle$ , is the average translational diffusion coefficient distribution. Our previous LLS results [10] showed that  $\alpha_D \sim 0.555$ . This leads to  $\alpha_\eta = 0.68$ , which shows that our results from viscosity are in consistency with the previous laser light scattering results where  $\alpha_\eta$  is  $\sim 0.686$ .

To determine the unperturbed chain dimension of polymer, the results obtained for  $M_w$  and  $[\eta]$  are plotted in Figure 4 by using Stockmayer Fixman equation [12]. The required parameter  $K_o$  was calculated directly from the intercept, which is 0.30 only. Since we know that  $K_o = \phi_o A$ , where  $\phi_o$  is the

universal constant having the value of  $2.80 \times 10^{21} \text{ mol}^{-1}$  and  $A$  is given as  $A = (\langle R_o^2 \rangle / M)^{1/2}$ , where  $\langle R_o^2 \rangle$  is the mean square end to end distance of the polymer chain in the unperturbed state. The values of  $\langle R_o^2 \rangle^{1/2}$  calculated from these equations are given in Table 1. The values of  $\langle R_o^2 \rangle^{1/2}$  are slightly greater than the  $\langle R_g^2 \rangle_z^{1/2}$  values as obtained from static LLS results. This is due to the fact that Stockmayer Fixman equation overestimates the chain dimensions in good solvent [13]. The values of  $(\langle R_o^2 \rangle / M)^{1/2}$  are listed in Table 1. We see that these values increase with the decrease in molecular weight for a particular polymer and hence it will be stretched more.

Figure 5 shows the typical plot of intrinsic viscosity as a function of the inverse of temperature. The activation energy was calculated from the data of intrinsic viscosity obtained at different temperature

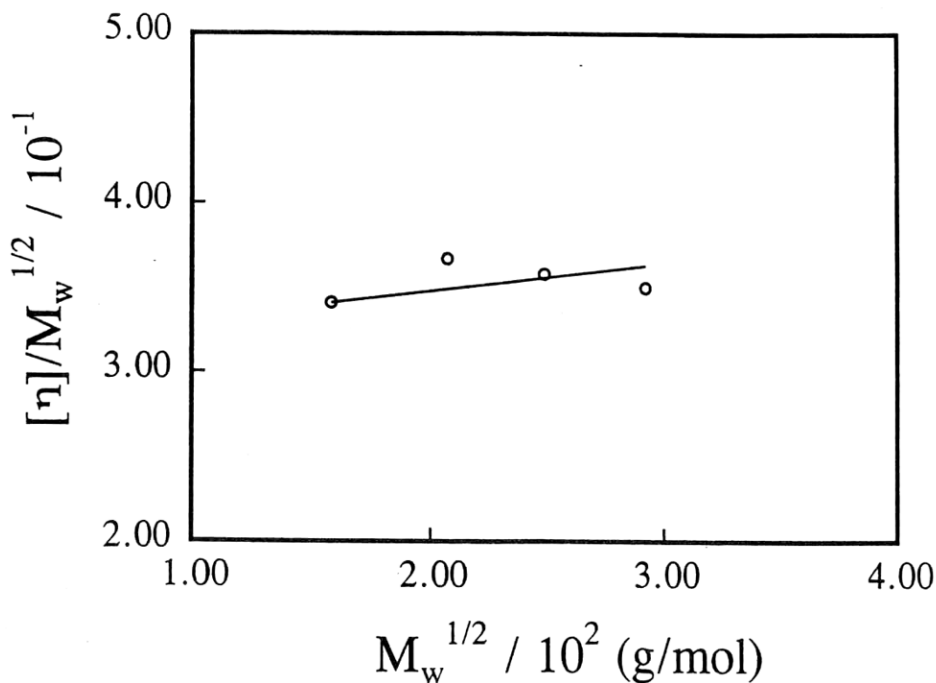


Fig. 4: Stockmayer-Fixman plot of  $[\eta]M_w^{1/2}$  as function of  $M_w^{1/2}$  (eq.8) of the PES.

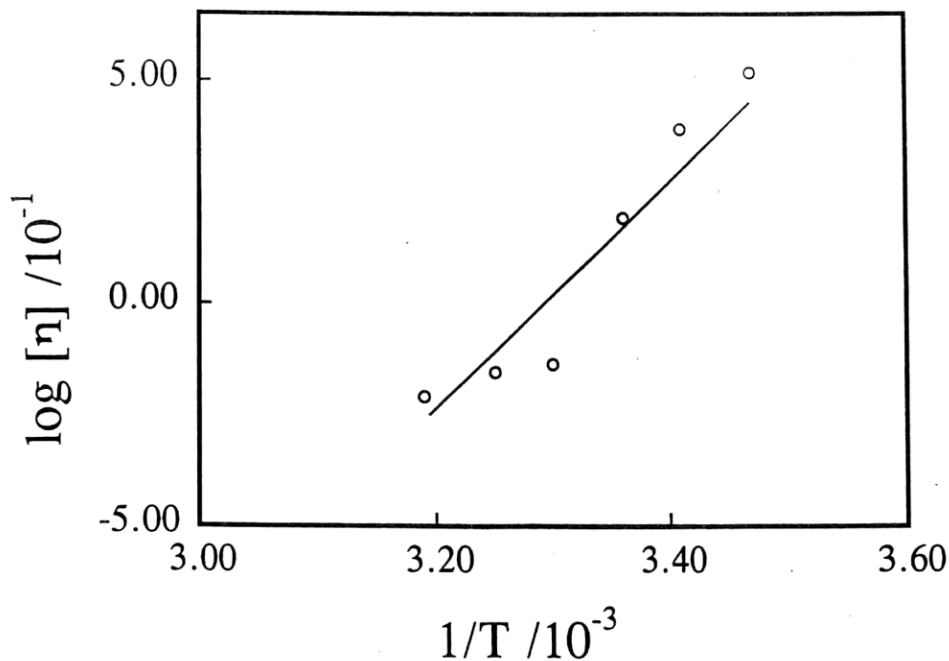


Fig. 5: Typical plots of intrinsic viscosity as a function of the inverse temperature of the four fractions of PES in  $\text{CHCl}_3$ .

by using Arrhenius equations given in equation 9. The results so obtained are given also listed in Table-1. The activation energy was found to decrease with the decrease in molecular weight of the polymer. This is according to the expectation. With the increase in molecular weight the interaction will increase and hence it will be difficult for the polymer to flow, resulting in higher activation energy.

## Experimental

### Preparation of PES fractions

The synthesis of PES samples can be found elsewhere [10]. A 2 % solution of PES in DMF was fractionally precipitated with ethanol at room temperature. The precipitate were washed with ethanol and then dried in vacuo at 60 °C for 48h. The fractionated samples were labeled as PES-1 → PES-4, hereafter. Analytical grade chloroform (Merck) was used as a solvent without further purification. For each fraction five concentrations ranged from  $2.0 \times 10^{-3}$  to  $5.00 \times 10^{-3}$  g/mL were prepared by dilution. All polymer solutions were clarified by using a 0.22- $\mu$ m Whatman filter in order to remove dust completely.

### Laser light scattering (LLS)

A commercial light-scattering spectrometer (ALV/SP-150 equipped with an ALV-5000 multi- $\tau$  digital time correlator) was used with a solid-state laser (ADLAS DPY 425II, output power  $\approx$  400 mW at  $\lambda = 532$  nm) as 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 has no angular dependence in the scattering angle of 20°-150° from toluene. The detail of the LLS instrumentation and theory can be found elsewhere [14,15]. All the measurements were carried out at  $25 \pm 0.1$  °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 a dilute polymer solution at a relatively low angle  $\theta$ ,  $R_{vv}(q)$  can be expressed as [16]

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

Where  $K=4\pi^2 n^2 (dn/dC)^2 / (N_A \lambda_0^4)$  and  $q = (4n/\lambda_0) \sin(\theta/2)$  with  $N_A, dn/dC$ ,  $n$  and  $\lambda_0$  being

Avogadro's number, the specific refractive index increment, the solvent refractive index, and the wavelength of the light in vacuo, respectively.  $M_w$  is the weight average molar mass;  $A_2$  is the second virial coefficient; and  $\langle R_g^2 \rangle_z^{1/2}$  is the root-mean square z-average radius of gyration of the polymer chain. Refractive index increment of (0.204 mL/g) for PES was measured by a high-precision differential refractometer [17], which enables us to measure  $dn/dC$  and the scattered wavelength under identical experimental condition, so that the wavelength correction was eliminated. 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  $(dn/dC)^2$ .

### Viscometric Study

Dilute polymer solutions for viscosity measurement were prepared in chloroform. The efflux time of the dilute polymer solutions were measured using Ubbelohde capillary viscometer at the temperature of  $25 \pm 0.1$  °C maintained with the thermostat bath. The efflux times were converted to reduce viscosities according to the formula given below.

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

And

$$\frac{\ln \eta_r}{C} = \frac{\ln \eta / \eta_s}{C} = \frac{\ln(t/t_0)}{C} \quad (3)$$

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  $t_0$  is the efflux time of solvent.

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

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

The intrinsic viscosities of the four fractions were obtained by extrapolation of the reduced and inherent viscosity to zero polymer concentration

using either the Huggin's [18] or the Kraemer's [19] equation, respectively:

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

and

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

Where  $K_H$  is the Huggins coefficient, and  $K_k$  the kraemer coefficient. The intrinsic viscosity data can be scaled to the molecular weight by using the Mark-Houwink equation:

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

The constants  $K_\eta$  and  $\alpha_\eta$  in equation 7 are dependent on the polymer and solvent type and also on the temperature.

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

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

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

To calculate the activation energy, the Arrhenius equation was used which has the following form.

$$[\eta] = A e^{\frac{AE}{RT}} \quad (9)$$

Where E is the activation energy and A is a constant or exponential factor.

## Conclusions

In summary the solution properties of four fractions of PES were characterized by both static

LLS and viscosity methods in  $CHCl_3$  at 25 °C. The calibration between intrinsic viscosity ( $\eta$ ) and molecular weight ( $M_w$ ), namely,  $[\eta] = 4.42 \times 10^{-2} M_w^{0.686}$ , has been established. The established method and the calibration between ( $\eta$ ) and ( $M$ ) can be used in future to characterize PES as long as the  $CHCl_3$  is used as a solvent and temperature is 25 °C.

## References

1. J.B. Rose and P. A. Stained, *US Patent* 4, 320, 244 (1982).
2. J. Mijovic, *Polymer. News*, **14**, 177,(1989).
3. J. P. Critchley, G. J. Knight and W.W. Wright *Heat Resistant Polymers*, Pleum Press: NY, (1983).
4. M. J. Mullan and E.P. Woo, *J. Macromol. Science, Macromol Chem. Phys.*, **5**, C27, 313 (1987).
5. M. Day, T Suprunphuk, T.D. Cooney and D. M. Wiles, *J. Appl Polymer Science*, **36**, 1097 (1988).
6. T.B.Mathew, E.K. Frank and H.L. Kenneth *Macromolecules*, **18**, 86 (1985).
7. J. Roovers T.D. Cooney and M. Toporowski *Macromolecules*, **23**, 1161 (1990).
8. B. Shuqin, H. Yang and T. Chen, *Functional Polymers*, **4**, 147 (1991).
9. C. Wu, M. Siddiq and K.F. Woo *Macromolecules*, **28**, 4914 (1995).
10. M. Siddiq, C. Wu, B. Shuqin and T. Chen, *Macromolecules*, **29**, 3157 (1996).
11. P.J. Flory *Principal of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953).
12. W.H. Stockmayer and M.J. Fixman, *J. Polymer Science Part C*, **1**, 137 (1963).
13. N. Ahmad and M.K. Baloch, *J. Macro. Sci. Chem. A24*, **10**, 1241-1261 (1987).
14. R. Pecora J. Berne, *Dynamic light Scattering*, Plenum Press, NY (1976).
15. B. Chu, *Laser Light Scattering*, 2nd ed., Academic Press, NY (1991).
16. B.H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
17. C. Wu, K.Q. Xia *Review Science instruments*, **65**(3), 587 (1994).
18. M.L. Huggin, *J. Am. Chem. Soc.*, **64**, 2716 (1942).
19. E.O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).