

Static Light Scattering of Polystyrene in Good Solvents: Tetrahydrofuran (THF) and Carbontetrachloride (CCl₄)

¹U. KALSOOM, ²A SAEED AND ¹K MUMTAZ*

¹PCSIR Laboratories Complex Jamrud Road,
Peshawar, 25120, Pakistan

²National Center of Excellence in Physical Chemistry,
University of Peshawar, Pakistan

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Summary: Equilibrium and thermodynamic properties of polystyrene of narrow molecular weight distribution in two chemically distinct good solvents i.e. THF and CCl₄ were carried out using static light scattering in dilute solutions at 25 °C. The molecular weight M_w and radius of gyration R_g for all samples in the range $qR_g < 1$ and $qR_g \sim 2$ were obtained using different methods viz Zimm, Berry square root and Fujita. It was observed that the molecular weight obtained for the sample 2×10^6 in given solvent by the three graphical procedures are comparable to each other. However, the R_g estimated by Fujita's method are the highest. Further, it was observed that the R_g estimated by the Fujita's method do not depend on the qR_g limit as similar values of R_g are obtained in the $qR_g < 1$ and $qR_g \sim 2$ (30-80 °C). It was observed that in case of very high molecular weights (20×10^6) sample even the Fujita's method underestimates R_g . This was attributed to the possibility that the chain expansion with increase in molecular weight is not as uniform as predicted by the theory. The second virial coefficients A_2 , estimated by Berry Square root method were in reasonable agreement with the literature values.

Introduction

The theory of light scattering from linear polymer in dilute solutions has been known since the work of Debye and Zimm [1-2]. In the past two decades significant advances have been made in understanding the behaviour of polymer in dilute solutions. New polymerization techniques have made possible the availability of mono disperse samples. Faster computers have enables scientists to apply more powerful mathematical techniques like Renormalization Group Calculation (RG) and Monte Carlo Simulations in modeling the behaviour of polymers in solutions [3-5]. However, all the existing theories are still not able to predict accurate behaviour of polymer in dilute solutions and to account for the experimental results found in different polymer solvent system. In this paper basic concepts (models) in the light of existing experimental data are discussed.

The static properties are not time dependent and include molecular weight M_w , second osmotic virial coefficient (A_2) and radius of gyration (R_g) [6-7]. These properties are defined and discussed with various theoretical models.

Radius of gyration (R_g) [6]

The radius of gyration can be regarded as a statistical average of the configurational distribution of segments around the center of mass.

$$R_g = (R^2)^{1/2} = \left(\frac{\sum m_1 r_1^2}{\sum m_1} \right)^{1/2} \quad (1)$$

where m_1 is mass of the chain segment and r_1 is the distance from the center of mass of the chain. In poor solvents, the polymer chain contracts because segmental interactions are favoured over segment-solvent interactions. It is possible to define a temperature (theta temperature) at which segmental interactions are exactly compensated by the polymer-solvent interactions and the polymer chain configuration is that of a random self-interaction (gaussian) walk. Under these conditions, $R_g^2 = nl^2$ where n is the number of segments and l is the segment length. Under theta condition the coils are compact and smaller in size as compared to good solvents in which

*To whom all correspondence should be addressed.

the coils are expanded confirmation [8]. The following scaling relationship exist between the radius of gyration and molecular weight:

$$R_g = K M^{\nu} \quad (2)$$

where $\nu = 0.5$ (theta solvents) $\nu = 0.6$ (very good solvents). The first result follows for a three dimensional gaussian random walk. The second result has been predicted both by computer simulations of a self-avoiding random walk in three dimensions and RG calculations.

Second osmotic virial coefficient (A_2) [6]

This is defined from the virial expansion of the osmotic pressure

$$\pi = \frac{CRT}{M} + A_2 C^2 + A_3 C^3 + \dots \quad (3)$$

where C is the concentration of the polymer solution, T is the temperature and M is the molecular weight of the polymer, A_2 is the second virial coefficient. If we consider polymer molecule as a hard sphere of Radius R , then A_2 is related to the intermolecular excluded volume, U as:

$$A_2 = N_A U / 2M^2 \quad (4)$$

$$\text{where } U = 32 / \pi R^3 = 8 / N_A M_2 v_2 \quad (5)$$

where v_2 is the partial specific volume and N_A is the avagadros constant

Like R_g , the thermodynamic interaction between the polymer segments and the solvent molecules essentially determine A_2 . In theta solvents polymer-polymer contacts are compensated by polymer-solvent interaction, $U = 0$, where $A_2 = 0$. In good solvents, however, polymer-solvents contacts are favored and therefore, the value of A_2 increases with quality of solvent. Since in good solvents we may approximate $U \propto R_g^3$, it follows from equation (3) and (4) that the second virial coefficient decreases with increase in the molecular weight and the molecular weight dependence of A_2 can be described by the following relationship.

$$A_2 = K M^{-\nu} \quad (6)$$

where $\nu = 0.2$ for a good solvent and

K is an optical constant and is equal to $2\pi^2 n_0^2 [dn/dc]^2 / \lambda^4 N_A$

Results and Discussion

Figures (1) and (2) show Zimm plots of different molecular weights of Polystyrene in THF and CCl_4 in $qR_g \sim 2$ limit. It can be noted that for the high molecular weight sample ($M_w = 8.42 \times 10^6$) only three points are available in the $qR_g < 1$ limit. Similar plots were also obtained by the methods of Berry square root and Fujita's. In Figures (3) and (4), Fujita plots were shown over the angular range $30-80^\circ$ ($0 \sim qR_g \sim 3.5$) for all samples in the two solvents. Values of the weight average molecular weight (M_w) and R_g obtained from various plots corresponding to $qR_g < 1$ and $qR_g \sim 2$ limit are listed in tables 1 to 3 and for the Fujita plots over extended angular range, in table 4.

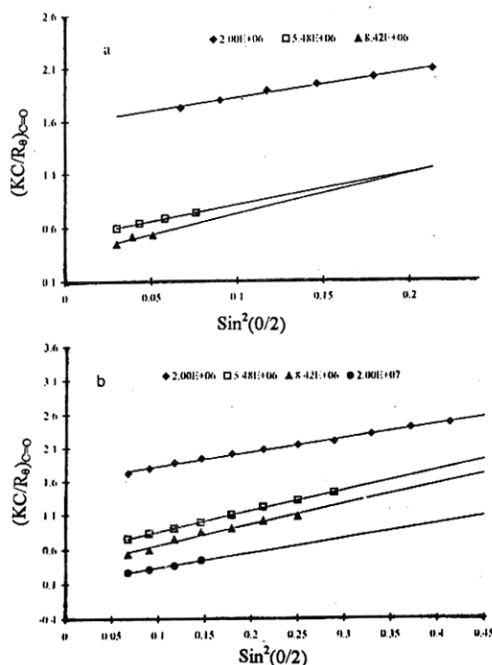


Fig. 1: Zimm plots of all Polystyrene samples in THF over region a. $qR_g < 1$ and b. $qR_g \sim 2$ at $25^\circ C$.

The values of M_w and R_g were compared with the three graphical procedures. For the lowest molecular weight sample was studied in this work, ($\sim 2.0 \times 10^6$), as sufficient number of data points are available for this sample which satisfy Zimm's

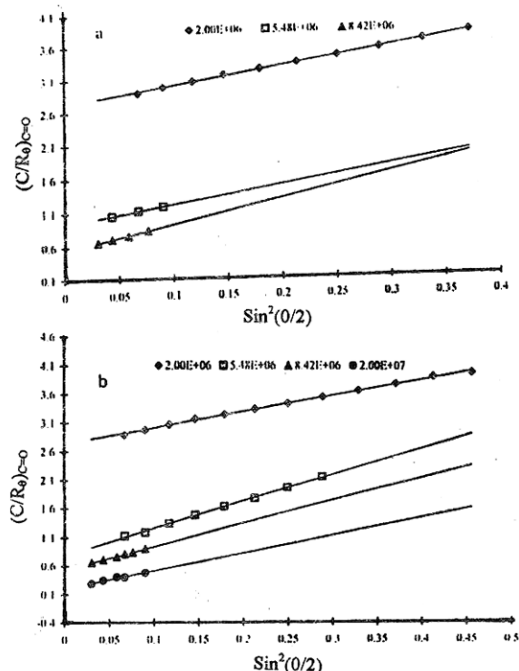


Fig. 2: Zimm plots of all Polystyrene samples in CCl_4 over region a. $qR_g < 1$ and b, $qR_g 0 \sim 2$ at 25°C .

criteria of $qR_g < 1$. It can be seen from the tables that the molecular weights obtained for this sample in a given solvent by the three graphical procedures are comparable to each other within the experimental error. However, some variation can be observed in the R_g values estimated by the Zimm and Berry square root method (BSM). Values of R_g estimated by BSM are slightly lower than those estimated by other two methods viz Zimm and Fujita. Of these two methods R_g values estimated by the Fujita's method are the highest while those by Zimm and Berry Square root methods are comparable to each other. Further it can be seen from the tables that in case of Fujita's method the values of R_g obtained are not dependent on the qR_g limit as similar values of R_g are obtained in the $qR_g < 1$ and $qR_g \sim 0 \sim 4$ limit ($30 \sim 90^\circ$ angular range) (tables 3 & 4) [9-11]. If the values of R_g estimated by the Zimm and Berry Square root method are compared in the $R_g = 0 \sim 2$ limit, it can be observed that R_g values estimated by both the methods are lower than those in the $qR_g < 1$ limit. However, R_g values estimated by the Zimm method are slightly higher than those estimated by Berry Square method, although the difference is not very significant [12]. In case of higher molecular weights, differences between M_w and R_g estimated by different methods become more significant. It may be

Table-1: Static light scattering results for various PS-Solvent system obtained from Zimm plots at $qR_g < 1$ and $qR_g 0 \sim 2$.

	$qR_g < 1$				$qR_g 0 \sim 2$			
	THF $M_w \times 10^{-6}$	R_g (nm)	CCl_4 $M_w \times 10^{-6}$	R_g (nm)	THF $M_w \times 10^{-6}$	R_g (nm)	CCl_4 $M_w \times 10^{-6}$	R_g (nm)
1.	2.125	76.82	1.974	60.52	2.085	71.96	1.969	61.28
2.	6.574	149.43	5.716	101.37	6.120	147.30	6.862	146.49
3.	9.484	200.75	9.883	157.83	10.052	180.72	10.052	163.80
4.	-	-	-	-	29.377	272.135	26.158	231.08

Table 2. Static light scattering results for various PS-solvent system obtained from Berry square-root plots at $qR_g < 1$ and $qR_g 0 \sim 2$.

	$qR_g < 1$				$qR_g 0 \sim 2$			
	THF $M_w \times 10^{-6}$	R_g (nm)	CCl_4 $M_w \times 10^{-6}$	R_g (nm)	THF $M_w \times 10^{-6}$	R_g (nm)	CCl_4 $M_w \times 10^{-6}$	R_g (nm)
1.	2.048	71.98	1.957	60.52	2.054	66.99	1.948	57.60
2.	6.338	131.89	5.656	96.03	5.556	121.60	6.171	119.56
3.	8.771	170.03	9.658	145.03	8.761	153.76	9.491	145.34
4.	-	-	-	-	22.137	191.66	26.158	231.08

Table 3. Static light scattering results for various PS-solvent system obtained from Fujita plots at $qR_g < 1$ and $qR_g 0 \sim 2$.

	$qR_g < 1$				$qR_g 0 \sim 2$			
	THF $M_w \times 10^{-6}$	R_g (nm)	CCl_4 $M_w \times 10^{-6}$	R_g (nm)	THF $M_w \times 10^{-6}$	R_g (nm)	CCl_4 $M_w \times 10^{-6}$	R_g (nm)
1.	2.092	95.475	1.977	89.48	2.058	95.184	1.951	84.75
2.	5.794	187.62	6.099	172.10	5.866	191.55	6.208	178.77
3.	9.133	251.40	9.465	203.08	8.721	219.80	9.892	220.58
4.	-	-	-	-	22.137	280.42	24.57	303.14

noted here that in case of these samples only few angles are available in order to meet the criteria of $qR_g < 1$. Thus the Zimm method in the $qR_g < 1$ and $qR_g = 0-2$ region the yielded molecular weights are significantly higher than those specified by the supplier who estimated them by the Berry square root method. Fujita's method seems to yield reasonable good estimates of R_g and M_w . The R_g values estimated by this method are about 30% higher than those estimated by the BSR method while the M_w s are not significantly different. In the light of these facts, Fujita's graphical procedure has been selected for the estimation of M_w and R_g of polystyrene samples used in these studies. Since these results for the 2.0×10^6 molecular weight sample show that in Fujita method the selection of angular range has negligible effect on the estimated values of M_w and R_g . These parameters were estimated by Fujita's method for an angular range where the qR_g values lies between 0-2.

Fujita plots for all samples in different solvents (THF and CCl_4) in the qR_g 0-2 regions are shown in figures (3) and (4). Values of R_g estimated from these graphs are listed in Table 4. Double logarithm plot of R_g vs molecular weight for the two systems are shown in figures 5 & 6. For estimation of the scaling parameters "k" and "a" we have omitted values of R_g for the 20×10^6 samples, as its inclusion results in an unrealistic exponent "a". A linear least square fit results in the following scaling relationships for each system is given.

$$\text{PS-THF} \quad R_g = 1.93 \times 10^{-2} M_w^{0.586 \pm 0.01} \text{ (nm)}$$

$$\text{PS-CCl}_4 \quad R_g = 1.53 \times 10^{-2} M_w^{0.590 \pm 0.01} \text{ (nm)}$$

In figures 5 & 6, available literature data for each system has been included. It should be noted that the solid line is a linear least square fit to present data only. A comparison with literature shows that for each system the R_g values are comparable to those of Wolinski *et al* [13] and are much higher than the rest

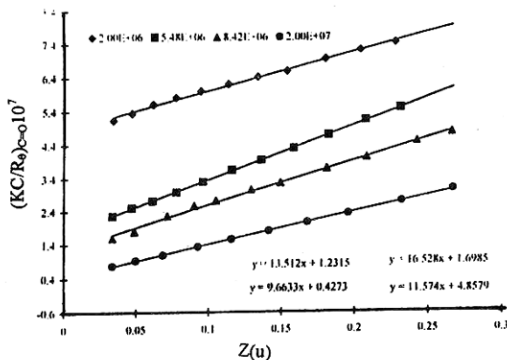


Fig. 3: Fujita's plots of all Polystyrene samples in the entire range (30° to 80°) in THF.

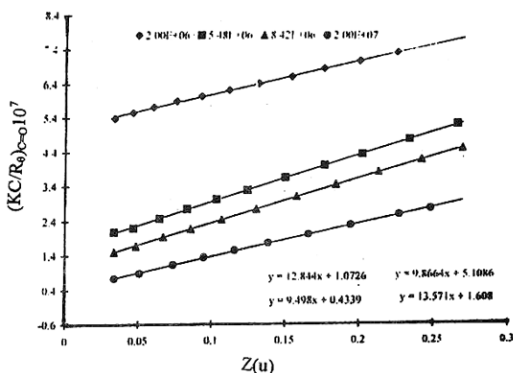


Fig. 4: Fujita's plots of all Polystyrene samples in the entire range (30° to 80°) in CCl_4 .

of the literature values [14-15]. This difference obviously is due to the use of Fujita method as compared to the Berry square root method reported in literature [16-19]. The results show that even the Fujita's method under estimates the R_g for higher molecular weight samples like 20×10^6 . To estimate the accurate values of R_g for high molecular weight samples, collection of data at very small angles would be required to fulfill the Zimm criteria of

Table 4. Static light scattering results for PS-THF and PS- CCl_4 system obtained from Fujita plots ($30^\circ - 90^\circ$) at $25^\circ C$.

	THF			CCl_4		
	$M_w \times 10^{-6}$	R_g (nm)	$A_2 \times 10^{-4} \text{ Cm}^3 \text{ mol}^{-1} \text{ g}^{-2}$	$M_w \times 10^{-6}$	R_g (nm)	$A_2 \times 10^{-4} \text{ Cm}^3 \text{ mol}^{-1} \text{ g}^{-2}$
1.	2.058	95.184	2.795	1.957	85.697	2.494
2.	5.887	192.36	2.202	6.219	179.146	1.837
3.	8.120	204.26	1.760	9.323	213.39	1.698
4.	23.402	293.25	1.451	22.507	283.56	1.571

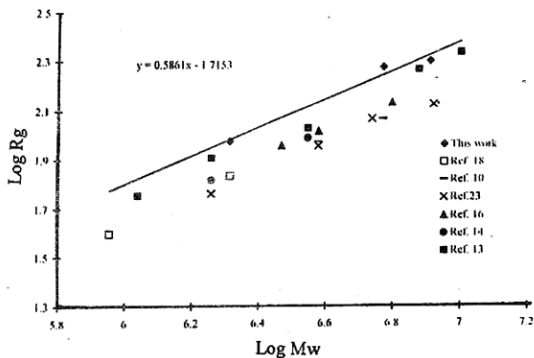


Fig. 5: Logarithmic plot of radius of gyration against molecular weight for all Polystyrene samples in THF at 25°C (including literature values).

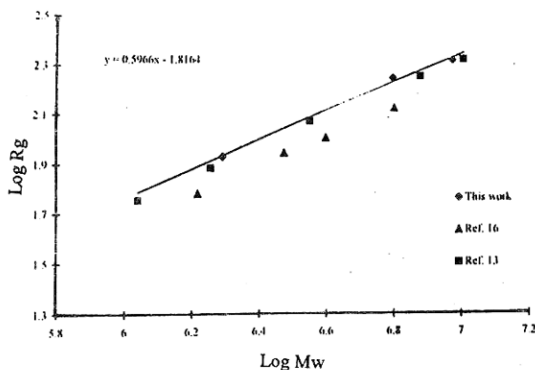


Fig. 6: Logarithmic plot of radius of gyration against molecular weight for all Polystyrene samples in CCl₄ at 25°C (including literature values).

$qR_g < 1$. But since Fujita's method is not very sensitive to the qR_g range as shown for 2×10^6 sample, it may be possible that with increase in molecular weight, the chain expansion is not as uniform as predicted by the theory even when the polymer is dissolved in a good solvent [20-22]. Thus at very high molecular weights ($\sim 20 \times 10^6$) the quality of good solvents decreases relatively lower values of Rg. If this is true, then both A_2 and R_g should depend on temperature for such systems. Such data is not available in literature to support this argument, it was therefore planned to carry out further experiments to test this possibility.

Berry Square root method was applied for the estimation of virial coefficients (A_2) values indicated in Table 4. The trend in figure 7 & 8 regarding linear relationship of $\log A_2$ vs $\log M$ has not been indicated in the present study due to few samples with high molecular weight range.

$$\text{PS-THF} \quad R_g = 1.28 \times 10^{-2} M_w^{0.267 \pm 0.02} \text{ (nm)}$$

$$\text{PS-CCl}_4 \quad R_g = 1.17 \times 10^{-2} M_w^{0.268 \pm 0.01} \text{ (nm)}$$

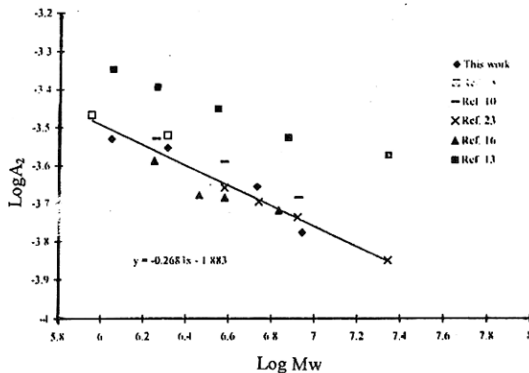


Fig. 7: Logarithmic plot of second coefficient against molecular weight for all Polystyrene samples in THF at 25°C (including literature values).

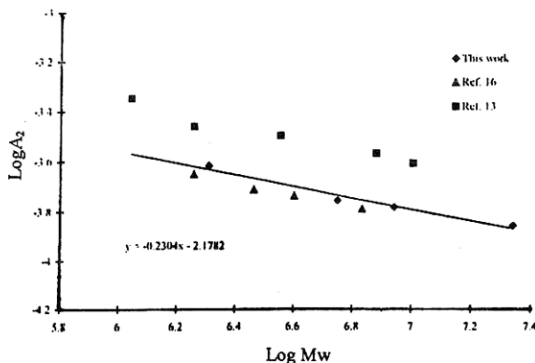


Fig. 8: Logarithmic plot of second coefficient against molecular weight for all Polystyrene samples in CCl₄ at 25°C (including literature values).

Comparing the values of A_2 in samples with relatively lower molecular weight (2.0×10^6 , 5.48×10^6), it has been observed that there is decrease in the

quality of solvent and the order of THF > CCl₄. similar values of A₂ for all the solvents have been indicated using samples with higher molecular weights (8.42 x 10⁶, 20 x 10⁶). Therefore A₂ has attained asymptotic values in these solvents as shown in Table 4.

In figures 7 & 8 the values obtained were compared with the available literature in all solvents studied [23]. It can be seen that in each solvent, the values obtained are in close agreement with the literature values except those of Wolinski et al which are significantly higher than those studied and those reported in literature. This difference mainly arises from the fact that Wolinski et al has utilized Zimm plots for the estimation of A₂ as compared to Berry Square root plots in the rest of literature [10,16,19,23].

Experimental

Materials

Polystyrene (PS) samples of narrow molecular weight distribution were obtained from Pressure Chemicals and Toyo Soda (Japan). The weight average molecular weight ranged from 2 x 10⁶ to 2 x 10⁶. The samples were used as such and were not further purified. The solvents, tetrahydrofuran (THF) and CCl₄ were obtained from E.merck of Germany and Aldrich Chemical Co. Due to its hygroscopic nature THF was further distilled because the presence of significant amounts of water can markedly alter the thermodynamic properties of PS in THF. CCl₄ was used as such without any further purification. The physical constants of PS in THF at 25 °C are refractive index n₂₅ = 1.407, viscosity η = 0.460 cP and with PS solute (dn/dc)₂₅ = 0.192ml/g. For CCl₄ at 25 °C n₂₅ = 1.495, η = 0.793cp and with PS solute (dn/dc)₂₅ = 0.146 ml/g. Estimation of static parameters require the use of dilute solutions. A dilute solution is one in which the concentration of the solute is such that solute molecules are sufficiently apart and no overlapping of molecules occur. For a polymer solution, an overlap concentration is defined as

$$C^* = \frac{M_w}{(N_A R_g^3)} \quad (7)$$

where R_g is the radius of gyration of the polymer coil. In the present study the highest

concentration was approximately ten times less than the overlap concentration. Dilute solution of PS in given solvent were made by weighing PS sample on balance (Model Sartorius) with accuracy of ± 0.001 mg. For stock solution, the purified distilled solvent was directly transferred into dust free volumetric flask containing pre weighed polystyrene. Solutions of sample of molecular weight 2x 10⁶, 5.48x10⁶ and 8.42 x 10⁶ were prepared directly by dissolution method, and then shaken for several hours to promote complete dissolution. While solutions of the sample with molecular weight 20 x 10⁶ were placed in dark without shaking for 2 to 3 days so that the polymer completely dissolves in the given solvents. Solutions of the desired concentration were prepared by dilution from stock solution in clean light scattering cells. The entire cells containing the solutions were then sealed. Cells containing solution of samples 2 x 10⁶, 5.48 x 10⁶ and 8.42 x 10⁶ were centrifuged at 5000 rpm, for at least 24 hours, while cells containing the solution of sample 20 x 10⁶ were centrifuged slowly for one week to make the solutions further dust free. All the solutions were checked for optical clarity and only those solutions were used in which the fluctuation in the scattered intensity were less than 2%.

Method

The instrument used to carry out light scattering experiments was from Brookhaven Instrument Corp. Spectrophotometer comprising a B1-200SM goniometer and B1-9000AT correlator with spectra Physics 60nW He/Ne laser, Model 127-35, Serial no. 35211, integrated scattering intensity was measured with our laboratory-made computer operated goniometer at angle 25° to 120° at wavelength of 633nm and temperature of 25 °C. Molecular weights M_w and mean square radius of gyration (R_g) of the samples were usually estimated by different standard methods in the range qR_g < 1 and qR_g 0~2.

Calculations

Static Light Scattering

Measured scattered intensities of the solvent and the solutions were converted into Rayleigh ratios using the following equations. Rayleigh ratio of toluene was (R₀ = 1.4 x 10⁻⁵)

$$I_{0,polymer} = I_{0,solution} - I_{0,solvent} \quad (8)$$

$$R_0 = \frac{I_{0,p}}{I_{0,std}} \cdot R_0 \text{ 90 (toluene)} \frac{n_0^2 \text{ solvent}}{n_0^2 \text{ toluene}} \quad (9)$$

For the estimation of M_w , R_g and A_2 , data was plotted according to Zimm, Berry and Fujita equation.

Zimm Equation [2]

This is illustrated by the following equation

$$\lim_{\Delta R_0} \frac{KC}{\Delta R_0} = \frac{1}{M_w} \left(1 + \frac{16\pi^2 n^2 \langle R_g^2 \rangle}{3\lambda_0^2} \text{Sin}^2 (0/2) \right) \quad (10)$$

$$\lim_{\Delta R_0} \frac{KC}{\Delta R_0} = \frac{1}{M_w} + 2A_2 C \quad (11)$$

where

$$q = \left(\frac{4\pi n}{\lambda} \right) \text{Sin} (0/2)$$

$$k = \left(\frac{4\pi^2 n_0^2}{N_A \lambda_0^4} \right) \left(\frac{\partial n}{\partial c} \right)^2$$

The quantity $KC/\Delta R_0$ is plotted against $\text{Sin}^2 (0/2)$ and also against concentration. Each line has a common intercept, inversely proportional to the weight average molecular weight M_w . The slope of the line representing the angular dependence of the data extrapolated to zero concentration is proportional to $\langle R_g^2 \rangle$, while the slope of line representing concentration dependence of the data extrapolated to zero angle is equal to $2A_2$. the Zimm plot works well for polymer of $M_w \sim 10^6$ under the condition $qR_g < 1$. however, for polymer of $M_w \sim 10^7$, dissolved in good solvent, this plot shows curvature and accurate extrapolation to zero angle and zero concentration becomes difficult due to contributions from third virial coefficient.

Berry Equation [24]

Berry suggested the square root plots to correct contribution from the third virial coefficient. The equation are illustrated as follows

$$\left(\frac{KC}{\Delta R_0} \right)^{1/2} = \left(\frac{1}{M_w} \right)^{1/2} (1 + 2A_2 M_w C)^{1/2} \quad (12)$$

and

$$\left(\frac{KC}{\Delta R_0} \right)_{c \rightarrow 0}^{1/2} = \left(\frac{1}{M_w} \right)^{1/2} \left(1 + \frac{16\pi^2 n^2 (R_g)^2}{3\lambda^2} \text{Sin}^2 (0/2) \right) \quad (13)$$

Fujita Equation [25]

For extremely high molecular weight, curvature appears in the square root plots. Fujita derived the following equations

$$\frac{1}{y(U)} = \frac{1}{M} + bz(U) \quad (14)$$

where

$$y = \lim_{c \rightarrow 0} \frac{R_0}{KC}$$

$$b = \frac{32\pi^2 (R_g)^2}{3\lambda^2 M}$$

and

$$z(U) = [y(U)U^{4/3}]^{-1} \int_0^U y(U)U dU \quad (15)$$

where

$$U = \text{Sin}^3 (0/2)$$

where U is the rate of flow in cm^3/sec , $y(U)$ is the y component of the flow rate and $Z(U)$ is the z component of the flow rate, b represents the free draining case and b_z is the z component of the draining case.

By plotting of $1/y(U)$ Vs $z(U)$ from intercept, the values of M_w were calculated and from the slope, R_g values were obtained.

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