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Novel analysis of static light scattering data

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A novel analysis was carried out for static light scattering data to determine the molecular weight, M, and mean square radius of gyration $<s^2>$ of large molecular weight polymers. The analysis is based on the finding that the Debye scattering function $P(x)$ for random flight polymer chains with $x = (4\pi n/\lambda)^2 <s^2> \sin^2(\theta/2)$ can be numerically approximated by the single term $(1 + x/3a)^{-a}$ with the exponent a near 1.5, where λ/n is the wavelength of incident light in medium and θ is the scattering angle. The ratio $(1 + x/3a)/P(x)^{-1/a}$ changes slowly between 0.986 and 1.014 in the range $x < 8.6$ for $a = 1.5$ and between 0.972 and 1.028 in $x < 14.5$ for $a = 1.4$. The plots of $P(\theta)^{-1/a}$ vs $\sin^2(\theta/2)$ with $a = 1.4$ and 1.5 were applied successfully to various light scattering data on polymers of large molecular weight more than several million yielding the intercept of unity and correct values of $<s^2>$. Copyright © 1996 Elsevier Science Ltd.

(Keywords: static light scattering; radius of gyration; large molecular weight)

INTRODUCTION

Static light scattering measurements is a familiar technique for the study of dilute polymer solutions[1,2]. Lasers of various wavelengths are available as a light source and an electric device is readily available to pick up the low signal from scattered light. The optical purification of solutions can be achieved by membrane filters of various pore sizes and suitable materials. Thus, intensity measurements can be carried out with high precision. Nevertheless, scattered intensities are usually determined in the angular range from 30° to 150° by light scattering apparatus. Below 30° light scattering measurements are disturbed by stray light due to the slit system and reflection of the incident beam at air–glass and liquid–glass interfaces. Slight distortion in optical alignment may affect measurements of angular dependence of scattered light at low angles.

For polymers of large molecular weight it is difficult to determine the molecular weight, M, and the mean-square radius of gyration $<s^2>$ with light scattering data obtained in the angular range from 30° to 150°, because scattering data below 30° are crucial for the linear extrapolation of scattered intensity to zero angle and for the determination of the initial slope. For particles of known shape observed intensities of scattered light can be analysed with the aid of the theoretical scattering function.

On the basis of the Debye scattering function for random flight polymer chains[3], Berry[4] proposed the square-root analysis of scattering data for determination of M and $<s^2>$. Experimental and theoretical studies suggest that the Debye function is also applicable to polymer chains perturbed by the excluded volume effect between chain segments, unless polymers dissolved in a good solvent have very large M and broad molecular weight distribution[5-8]. The square-root plot has been used as a standard method for light scattering data analysis of dilute polymer solutions with M up to a few million. It was attempted to estimate $<s^2>$ by direct comparison of the Debye scattering function with measured ones[9,10]. In this analysis by curve fitting, scattering data at higher angles may be taken into account. Based on the Debye equation, Fujita proposed a plot to determine M and $<s^2>$ by using scattering data in the whole angular range of measurement[11]. Although this plot deduced reasonable values of M and $<s^2>$ for polymers with M more than 10 million, the procedure of the plot was time-consuming and used only in limited cases. It is required to establish a practical method of light-scattering data analysis, which makes it feasible to determine M and $<s^2>$ of polymers with large M from light scattering data obtained at angles above 30°. In this paper we propose a novel method of data analysis which satisfies the above requirement. The present method was applied to various light scattering data in the literature with successful results.

LIGHT SCATTERING EQUATIONS

For dilute polymer solutions the Rayleigh ratio R_θ for excess scattered intensity at a scattering angle θ can be written as[2]

$$Kc/R_\theta = 1/MP(\theta) + 2A_2c + 3A_3c^2 + \ldots \quad (1)$$

with

$$k = (2\pi^2 n^2 N_A \lambda^4)(dn/dc)^2$$

where c is the polymer mass concentration, n is the refractive index of the solution, λ is the wavelength of incident light *in vacuo*, N_A is Avogadro's number, and A_2 and A_3 are the second and third virial coefficients, respectively. In general the scattering function $P(\theta)$ may

be expanded in terms of the scattering vector $q = (4\pi n/\lambda)\sin(\theta/2)$ as

$$P(\theta) = 1 - <s^2>q^2/3 + \ldots \tag{2}$$

Equations (1) and (2) imply that the mean-square radius of gyration $<s^2>$ can be evaluated by plotting Kc/R_θ extrapolated to $c = 0$ against $\sin^2(\theta/2)$ provided that the higher order terms in the reciprocal of $P(\theta)$ are neglected. This condition is not satisfied in usual dilute polymer solutions. Thus, for reliable estimation of $<s^2>$ the contribution from the higher order terms should be taken into account in the data analysis.

For random flight polymer chains Debye derived the scattering function as[3]

$$P(\theta) = (2/x^2)(e^{-x} - 1 + x) \tag{3}$$

where $x = <s^2>q^2$. In light scattering data analysis the plot for the estimation of M and $<s^2>$ should be simple and straightforward such as the linear plot due to equations (1) and (2). Accordingly, we assumed that equation (2) may be replaced by the form

$$P(x) = (1 + x/3a)^{-a} \tag{4}$$

In *Figure 1*, $P(x)^{-1/a}$ is plotted against x. The straight lines and the accompanying open circles are given, respectively, by equations (4) and (3) for the indicated values of a. The plots with $a = 1$ and 1.4 are shifted along the ordinate by unity. The straight lines due to equation (4) have a slope $1/3a$ equal to the initial slope for the plots by equation (3). Berry compared the plots for $a = 1$ and 2 and recommended the square-root plot in light-scattering data analysis[4]. For $a = 1.4$ the open circles given by equation (3) deviate slightly along the straight line due to equation (4). For $a = 1.5$ the plot made by eq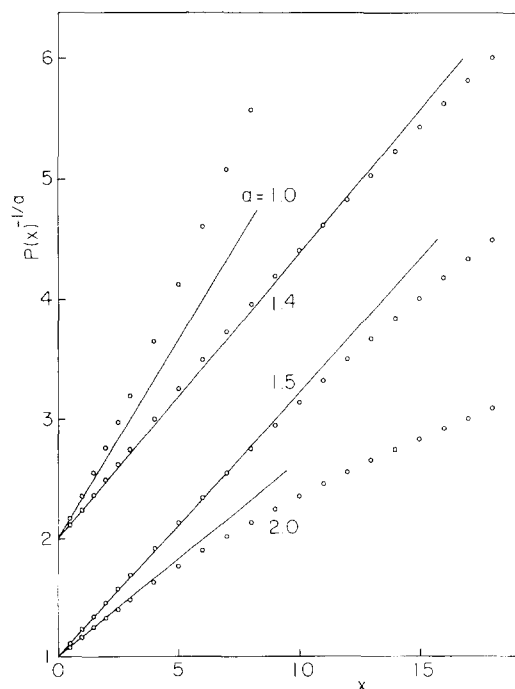uation (3) appears to have a broad region for the initial slope compared to that for $a = 2$. In *Figure 2* a more stringent comparison between equations (3) and (4) is made by plotting the ratio $Q(x) = (1 + x/3a)/P(x)^{-1/a}$ against x for the indicated values of a. At $x = 0$ the slope of the curves vanishes. For $a = 1.3, 1.4, 1.5,$ and 1.6 a minimum is located at the point $(x = 7.0, Q = 0.947),$ $(5.0, 0.972), (3.6, 0.986),$ and $(2.6, 0.994),$ respectively. Thus, the deviation of Q from unity is less than 0.053 in the range $x < 30$ for $a = 1.3,$ 0.028 in $x < 14.5$ for $a = 1.4, 0.014$ in $x < 8.6$ for $a = 1.5,$ and 0.006 in $x < 5.4$ for $a = 1.6.$ For $x = 2$ the minimum coincides with the maximum at $x = 0$ extending the flat region to higher x and a rapid deviation from $Q = 1$ occurs with increasing x. In light of the plots in *Figure 2* the relationship between the straight lines and the open circles in *Figure 1* is obvious. For $a = 2$ the initial slope of the plot by equation (3) may be evaluated only near $x = 0,$ while for $a = 1.4$ and 1.5 the initial slope can be estimated reliably from a straight line fitted to the open circles in a broad range of x. Moreover, the initial slope may be predicted safely without the points in the asymptotic range near $x = 0$ for $a = 1.4$ and $1.5.$ This may also be the case for $a = 1.6.$ Thus, the scattering function in the form of equation (4) is just what is required for light scattering data analysis. In actual data analysis a relevant value of a should be used in consideration of the experimental range of x.

From equations (1) and (4) a practical equation for light scattering data analysis may be written as

$$(Kc/R_\theta)^{1/a} = (1/M^{1/a})\{1 + (1/3a)x + (2/a)MA_2c\}$$

$$= 1/M^{1/a} + (16\pi^2n^2/3a\lambda^2)<s^2>M^{-1/a}$$

$$\times \sin^2(\theta/2) + (2/a)M^{1-1/a}A_2c \tag{5}$$

In this equation the third virial coefficient A_3 is incorporated through the relation

$$A_3 = gMA_2^2 \tag{6}$$

with $g = (2/3)(1 - 1/a)$. g takes $1/3$ and $2/9$ for $a = 2$ and $1.5,$ respectively. These values of g can be compared

Figure 1 Scattering functions by the plot of $P(x)^{-1/a}$ vs x for the indicated vales of a. The open circles stand for the Debye equation (3) and the straight lines for equation (4). The plots for $a = 1$ and 1.4 are shifted along the ordinate by unity
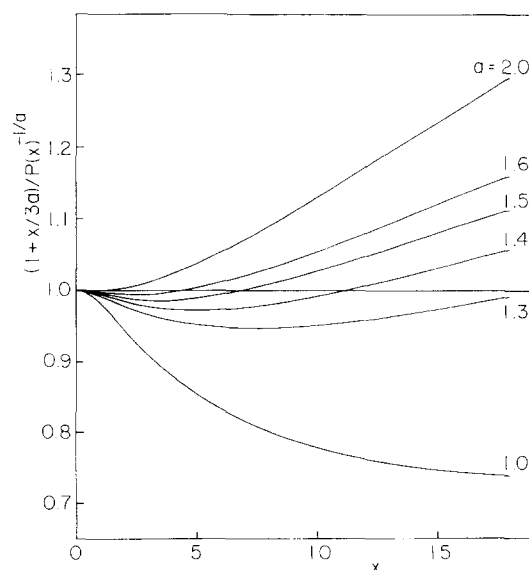

Figure 2 Ratio $(1 - x/3a)/P(x)^{-1/a}$ against x for the indicated values of a, where $P(x)$ represents the Debye equation (3)

with $g = 1/4$ used for osmotic pressure data analysis[12]. Since the plot due to equation (5) with a value of a near 1.5 is based on the Debye equation (3), the plot is applicable to data obtained for polymers of narrow molecular weight distribution. Although equation (5) can be used beyond the asymptotic range near $x = 0$, the analysis with equation (5) gives the weight average molecular weight, M_w, and z-average mean-square radius of gyration, $< s^2 >_z$. In the following we will analyse literature data of scattered light intensities extrapolated to $c = 0$ and will not be concerned with the second virial coefficient A_2.

ANALYSIS OF LIGHT-SCATTERING DATA

The analysis by equation (4) was applied to light scattering data for polystyrene (PS) in cyclohexane at $34.5°C$[13] and in benzene[14,15], poly-α-methylstyrene (PMS) in *trans*-decalin at $9.6°C$ and in benzene[16], poly(methyl methacrylate) (PMMA) in methyl ethyl ketone (MEK)[17], and poly(hexyl isocayanate) (PHIC) in hexane[18]. The above data were obtained for polymer samples with a very narrow molecular weight distribution with the exception of PMMA and PS of extremely large molecular weight. For the systems of PS in cyclohexane and PMS in *trans*-decalin, the measurements were carried out at the θ-temperature, while for the other systems a good solvent was employed in the measurements. For the PMS system light-scattering data extrapolated to zero concentration were taken from tables in the literature and for the other systems data were read from figures in which the square root of inverse scattered intensities was plotted against $\sin^2(\theta/2)$. The present data analysis was made by the plot of $P(\theta)^{-1/a}$ vs $\sin^2(\theta/2)$ for $a = 1.4$, 1.5 and 2. *Table 1* gives the systems with the original sample code and literature values of M and $< s^2 >^{1/2}$ in the first three columns. $\Delta\theta$ in the fourth column denotes the angular range of scattering data used in the present analysis and Δx in the fifth indicates the corresponding range of x. Values of $< s^2 >^{1/2}$ determined by the present plots with $a = 1.4$ and 1.5 are given in the last two columns.

Figure 3 shows the data obtained for PS(C1) in cyclohexane (●) and for PMS (BB-15) in *trans*-decalin (○) at the θ-temperature by the plots with $a = 1.4$, 1.5 and 2. The plot with $a = 1.4$ is shifted by unity along the ordinate. PS(C1) was prepared from Toyo Soda's
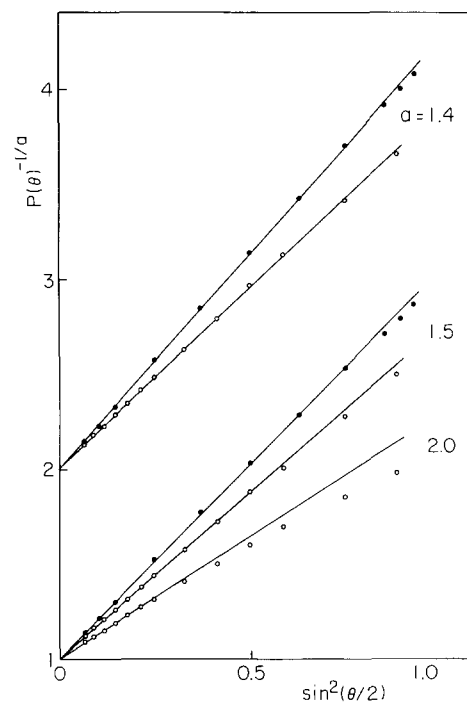

Figure 3 Plots of $P(\theta)^{-1/a}$ vs $\sin^2(\theta/2)$ with the indicated values of a for polystyrene (C1) in cyclohexane (●) and poly-α-methylstyrene (BB-15) in trans-decalin (○) at the θ-tempereature. The plots with $a = 1.4$ are shifted along the ordinate by unity

standard polystyrene by column fractionation and had a narrow molecular weight distribution. PMS(BB-15) was obtained by column fractionation of anionically polymerized PMS and had a sharp molecular weight distribution as $M_w/M_n < 1.01$. For the plot with $a = 1.5$ the straight lines are determined with a small uncertainty by the data points and have an intercept of unity. In view of the range of x given in *Table 1*, the agreement between the straight lines and the data points is in good accord with the corresponding plots in *Figure 1*. For the plot with $a = 1.4$ the data points are well represented by the straight lines with an intercept of unity, though straight lines with the correct initial slope should run slightly below the data point as shown in *Figure 1*. The values of $< s^2 >^{1/2}$ estimated from the straight lines in *Figure 3* are given in the last two columns in *Table 1*. The literature values of $< s^2 >^{1/2}$ in the third column were estimated by

Table 1 Analysis of light scattering data in literatures

Sample + solvent	$M_w \times 10^{-6}$ (g mol^{-1})	$< s^2 >^{1/2, a}$ (nm)	$\Delta\theta$ (deg)	Δx	$< s^2 >^{1/2, b}$ (nm)	$< s^2 >^{1/2, c}$ (nm)
PS(C1) + cyclohexane[13]	6.48	74.1	30–150	0.6–8.7	74.7	73.5
PMS(BB-15) + *trans*-decalin[16]	6.85	65.1	30–140	0.5–6.9	66.2	65.7
PMS(BB-15) + benzene[16]	6.85	127.3	9–100	0.2–18.2	129.1	128.2
PS(FF-34) + benzene[14]	4.59	111.8	30–110	1.6–16.0	114.8	114.1
PS(FF-36) + benzene[14]	9.70	173.5	11–60	0.5–14.4	178.4	176.9
PS(IK1500-1) + benzene[15]	56.8	506	7–29	0.8–14.1	498	493
PMMA(178) + MEK[17]	16.1	199	17–45	0.9–5.8	206	204
PHIC(F-7) + hexane[18]	0.311	68.3	30–150	0.5–6.9	69.6	70.1

[a] From the literature
[b] Estimated from the plot of $P(\theta)^{-1/1.4}$ vs $\sin^2(\theta/2)$
[c] Estimated from the plot of $P(\theta)^{-1/1.5}$ vs $\sin^2(\theta/2)$

the Berry plot with the aid of data points at scattering angles below 30°. For PMS(BB-15) the Berry plot with $a = 2$ is made in *Figure 3*. It is difficult to determine the initial slope by the data points at angles above 30°. The straight line is given with the literature value of $< s^2 >^{1/2}$ in *Table 1*.

On the basis of the Debye scattering function Miyaki *et al.* evaluated the number average molecular weight, M_n, and characteristic ratio $< s^2 >_o /M$ for PS(C1). It should be noticed that their analysis was made with the data points which were used in the present analysis to estimate M_w and $< s^2 >_z$.

Figure 4 shows plots for PMS(BB-15) in the good solvent benzene at 30°C[16]. The plot with $a = 1.4$ is shifted by unity along the ordinate. Data points below 30° are omitted for the plots with $a = 1.4$ and 2. For the plot with $a = 1.4$ the straight line fitted to the data points at lower angles gives an intercept of 1.03. Since the plot is made in the range of x from 2.1 to 18.2, this slight overestimation of the intercept may be ascribed to the lack of data points below 30° as inferred from the plot in *Figure 1*. For the plot with $a = 1.5$ the straight line is accurately determined by the data points at lower angles. The values of $< s^2 >^{1/2}$ estimated from the straight lines for $a = 1.4$ and 1.5 are given in *Table 1*. The straight line for the Berry plot is described with the literature value of $< s^2 >^{1/2}$, which was determined by the Fujita plot.

In *Figure 5* plots similar to those in *Figure 4* are shown for PS(FF-34) in benzene at 30°C[14]. PS(FF 34) was prepared by anionic polymerization followed by repeated precipitation in benzene + methanol and was found to have the molecular weight distribution $M_w/M_n = 1.05$. The plots are made with data points in the angular range from 30° to 110°. The straight lines for plots with $a = 1.4$ and 1.5 have an intercept of unity and values of $< s^2 >^{1/2}$, shown in *Table 1*. The literature value of $< s^2 >^{1/2}$ was evaluated by the Berry plot with resort to data at angles down to 12°, and yields the straight line for the plot with $a = 2$ in *Figure 5*.

In *Figure 1* the straight line deviates from the Debye function near $P(\theta)^{1/a} = 3$ and 4 for $a = 1.5$ and 1.4, respectively. The same trend is also observed in *Figures 4* and *5*, though the deviation of the data point from the Debye function is more noticeable for PMS(BB-15) than for PS(FF34). This difference in departure from the Debye function at large angles is also observed in the plot of $xP(x)$ vs x given in the original literature.

In *Figure 6* the plot with $a = 1.5$ is made for low angle scattering data obtained for large molecular weight samples in good solvents, i.e. PS(IK1500-1) in benzene at 25°C (plot a)[15], PS(FF-36) in benzene at 30°C (b)[14], and PMMA(178) in MEK at 25°C (c)[17]. PS(FF-36) was prepared by the same method as PS(FF-34) and has $M_w/M_n = 1.03$. PS(IK1500-1) was a sample fractionated from JSR polystyrene (IK1500). PMMA(178) was prepared by the plasma-initiated polymerization technique and purified by the precipitation method. The molecular weight distribution of these samples is not
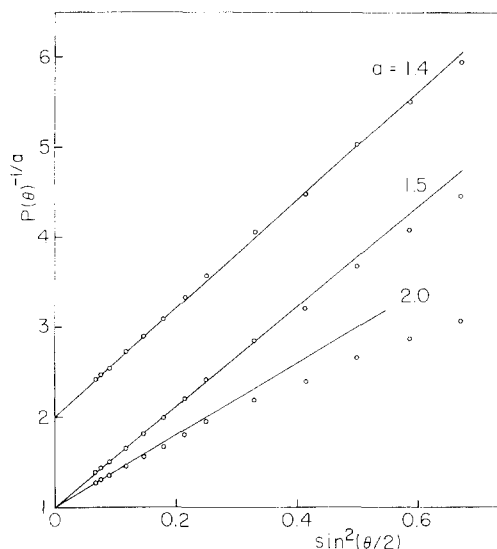

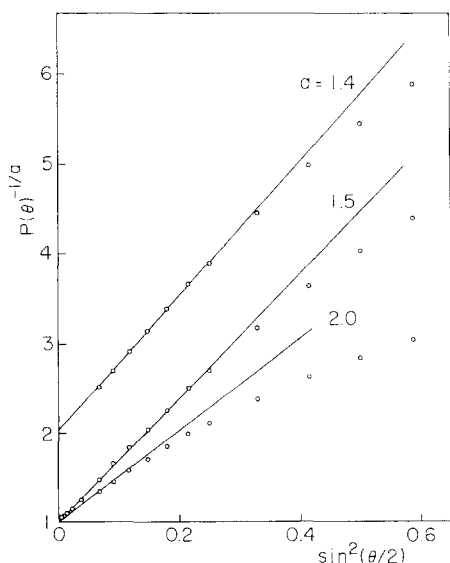**Figure 5** Plots for polystyrene (FF-34) in benzene as for *Figure 4*

Figure 4 Plots of $P(\theta)^{-1/a}$ vs $\sin^2(\theta/2)$ with the indicated values of a for poly-α-methylstyrene (BB-15) in benzene. The plot with $a = 1.4$ is shifted along the ordinate by unity
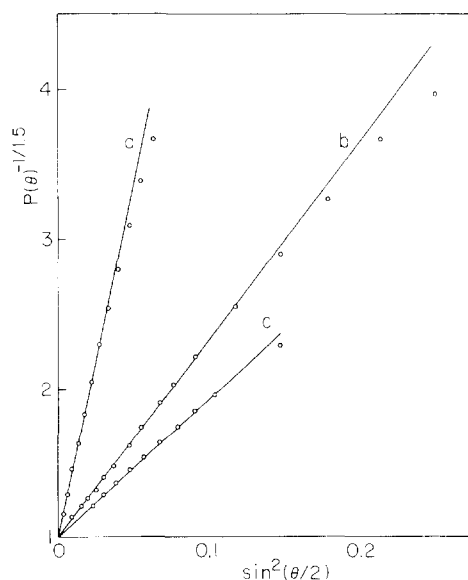

Figure 6 Plots of $P(\theta)^{-1/a}$ vs $\sin^2(\theta/2)$ with $a = 1.5$ for PS(IK1500-1) in benzene (a), PS(FF-36) in benzene (b) and PMMA(178) in MEK (c)
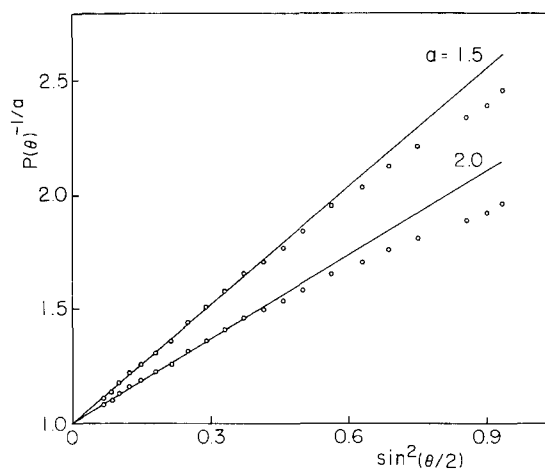
Figure 7 Plots of $P(\theta)^{-1/a}$ vs $\sin^2(\theta/2)$ for poly(hexyl isocyanate) (F-7) in hexane with the indicated values of a

clear. In *Figure 6* the straight lines are described to meet the data points at lower angles with the range of x taken into account and give the values of $< s^2 >^{1/2}$ in *Table 1*. The literature values of $< s^2 >^{1/2}$ were estimated with the Fujita plot for the polystyrene samples and with the Berry plot for PMMA(178).

In *Figure 7* plots with $a = 1.5$ and 2 are made for the data obtained in the angular range from $30°$ to $150°$ for PHIC(F-7) in hexane at $25°C^{18}$. PHIC(F-7) has the molecular weight $M_w = 3.11 \times 10^5$ and a narrow molecular weight distribution. The straight lines were given to determine the initial slope. For both the plots with $a = 1.5$ and 2 the data points start to deviate from the straight lines near $\sin^2(\theta/2) = 0.4$, though the data points are located in the range of x from 0.5 to 6.9. For $a = 1.5$ this deviation occurs near $P(\theta)^{1/1.5} = 1.7$. This behaviour of $P(\theta)$ for PHIC is very different from that of the Debye scattering function in *Figure 1*. In fact, PHIC in hexane was shown to be well described by the unperturbed wormlike chain.

DISCUSSION AND CONCLUSIONS

In *Table 1* the values of $< s^2 >^{1/2}$ determined by the plot with $a = 1.4$ is roughly 1% larger than the values obtained with $a = 1.5$ with the exception of PHIC. This small difference can be explained by the plots in *Figure 1*. For the plot with $a = 1.4$, a straight line fitted to the points in the range $x < 8$ will have a slope slightly larger than the initial one, while for $a = 1.5$ a straight line fitted to the points in the same range of x may have a slope close to the initial one.

The present values of $< s^2 >^{1/2}$ appear to be larger than the values estimated by the Berry plot. In the Berry plot, the tangent of $P(\theta)^{1/2}$ at $x = 0$ is necessary for the determination of $< s^2 >$ and points at higher x underestimate the initial slope in data analyses. The Berry plot gives a reliable estimation of $< s^2 >$ in the range $P(\theta)^{-1/2} < 1.25$ or $x < 1.5^{16}$. In the present analysis, data in the asymptotic range near $x = 0$ have minor importance and $< s^2 >$ is determined with data in the range where the ratio $(1 + x/3a)/P(\theta)^{-1/a}$ is close to unity. In *Figures 3–7* the plots with $a = 1.4$ and 1.5 give an intercept of unity in most cases. This means that the present plots can also be used for the determination of the molecular weight. For PS(IK1500-1), PS(FF-36) and PMS(BB-15) in benzene, the values of $< s^2 >^{1/2}$ determined by the present plots agree with the literature values obtained by the Fujita plot. In view of a rapid data treatment the present plots are much more practical than the Fujita plot.

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