

# Dilute Solution Properties of Flexible Polymers in Toluene: A Comparison of Commercially Available Photometers

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## SYNOPSIS

Dilute solution properties of polystyrene and poly( $\alpha$ -methylstyrene) in toluene have been measured using several of the commercially available instruments for intensity light scattering. Results are compared among the instruments used and with literature values. Relative advantages and disadvantages of the instruments are discussed.

## INTRODUCTION

Recently several new light scattering photometers have become commercially available. These instruments differ in various ways from the classical photogoniometers and have in some cases additional capabilities such as suitability for photon correlation studies, or direct measurement of the effluent from a liquid chromatography column.

We report dilute solution parameters for two flexible polymers [polystyrene and poly( $\alpha$ -methylstyrene)] in a good solvent (toluene) using several light scattering instruments: a Chromatix KMX-6 low angle light scattering photometer (LDC-Milton-Roy), a DAWN-F multiangle light scattering detector (Wyatt Technology), size exclusion chromatography (SEC) coupled with a DAWN-F, and a BI200SM photogoniometer (Brookhaven Instruments). The low angle light scattering photometer (LALS) gives information of the weight average molecular weight ( $M_w$ ) and the effect of solute-solute interactions from the second virial coefficient ( $A_2$ ). A reflectance accessory in the LALS photometer permits measurement of the root mean square radius of gyration ( $R_g$ ) as well. In the DAWN-F light scattering instrument, the scattering intensity at the 15 scattering angles viewed by the permanently mounted detectors is measured, and  $M_w$ ,  $A_2$ , and  $R_g$

may be obtained using a Zimm plot.<sup>1</sup> Both the KMX-6 and the DAWN-F may be coupled with a size exclusion chromatography (SEC) instrument to obtain the absolute molecular weight distribution as well with only one SEC injection. With the SEC-LS technique the scattered intensity is measured continuously as the polymer elutes from the column, eliminating the need for calibration of the column. In principle,  $M_w$  and  $R_g$  (with the DAWN-F) may be obtained for each slice across the distribution, eliminating the need for tedious fractionation procedures and large samples of polymer. The BI200SM may be used to measure the scattered intensity as well as the autocorrelation of the scattered light with the BI30AT correlator.

Scattered intensities of seven polystyrene samples with the molecular weight range of 380,000 to 80,000,000 in toluene and of nine poly( $\alpha$ -methylstyrene) samples with the molecular weight range of 8000 to 4,000,000 in toluene were measured. Values of  $M_w$ ,  $A_2$ , and  $R_g$  are compared among the instruments used and with literature values.

## EXPERIMENTAL

### Materials

The polymers used were polystyrene (PS) and poly( $\alpha$ -methylstyrene) (PAMS). All PS and PAMS samples were synthesized by anionic polymerization. All PS samples were purchased from the Polymer Laboratories and PAMS samples were purchased from the Pressure Chemical Company. Toluene was

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used as the solvent. Toluene is a good solvent for PS and PAMS at room temperature. All solutions were clarified by direct filtration into the cell except solutions for SEC. Millipore FGLP (0.2  $\mu\text{m}$ ) filters were used for polymers with  $M_w < 3 \times 10^6$  and Millipore HVHP (0.45  $\mu\text{m}$ ) for polymers with  $M_w > 3 \times 10^6$ . Differential refractive index increment  $dn/dc$  were measured using a Chromatix KMX-16 laser differential refractometer at 25°C with 632.8 nm light; 0.1226 and 0.110 mL/g are the values obtained for PAMS in toluene and PS in toluene, respectively.

### Instruments

The Chromatix low angle light scattering photometer (LALS) used has a He-Ne laser operating at a wavelength of  $\lambda = 632.8$  nm as a light source. For these measurements the 15 mm Teflon spacer with the 6–7° annulus and 0.2 mm field stop were used. The weight average molecular weight  $M_w$  and the second virial coefficient  $A_2$  may be obtained from LALS by extrapolation of the Rayleigh ratio  $R_\theta$  at scattering angle  $\theta = 0$  to infinite dilution:

$$(Kc/R_0)^{1/2} = M_w^{-1/2} + A_2 c M_w^{1/2} \quad (1)$$

where  $K = (4\pi^2/N_A\lambda^4)n^2(dn/dc)^2$ ,  $c$  is the concentration in grams per milliliter,  $N_A$  is Avogadro's number, and  $n$  is the refractive index of the solvent. Here, we have assumed that the measured  $R_\theta$  at  $\theta = 4.4^\circ$  is same as  $R_0$  at zero scattering angle.

For polymer molecules with dimensions larger than about  $\lambda/20$ , light scattering yields information on the size of the molecule in solution, specifically the root mean square radius of gyration  $R_g$ . In the limit of infinite dilution,

$$\left(\frac{Kc}{R_\theta}\right) = \frac{1}{M_w} + \frac{R_g^2 q^2}{3M_w} + \frac{R_g^4 q^4}{36M_w} + O(q^6) \quad (2)$$

where  $q = (4\pi n/\lambda) \sin \theta/2$ . Normally, terms above  $q^2$  in eq. (2) are ignored to determine the values of  $R_g$ . However, for a high molecular weight polymer in a good solvent the  $q^4$  term cannot be ignored in eq. (2). Thus, eq. (2) can be written as<sup>2</sup>

$$(Kc/R_\theta)^{1/2} = M_w^{-1/2} + R_g^2 q^2 M_w^{-1/2}/6 \quad (3)$$

The values of  $R_g$  can be determined using either eq. (2) truncated above  $q^2$  or eq. (3).

The Chromatix LS instrument may be used to obtain  $R_g$  with a reflectance accessory. Scattered in-

intensities at two scattering angles, at  $\theta = 175.6^\circ$  and  $\theta = 4.4^\circ$ , were measured using a Chromatix KMX-6 photometer with and without a reflectance accessory, respectively. Thus, in the KMX-6 only two scattering angles are used to determine  $R_g$  using eq. (3). We will compare these values of  $R_g$  with literature values.

The DAWN-F light scattering instrument from Wyatt Technology consists of 15 permanently mounted detectors, a flow cell, and a He-Ne laser at  $\lambda = 632.8$  nm. The range of scattering angles  $\theta$  is 14.3–132.6° after correction for the refractive index of the solvent. The individual gain of each of the 15 permanently mounted detectors is different, so that normalization of the intensities is required. Thirty milligrams per milliliter of polystyrene ( $M_w = 9000$ ) in toluene was used to determine normalization coefficients. The  $R_g$  of PS of 9000 molecular weight is less than 100 Å in toluene, and the scattered intensity is independent of scattering angle. The values of output measured at various scattering angles from DAWN-F are normalized to be the same as that at  $\theta = 90^\circ$  for the PS solution. These values of output were multiplied by a calibration constant to determine Rayleigh ratios at all scattering angles. The calibration constant was obtained using as standards a group of solvents with known values of the Rayleigh ratio at 90° scattering angle with 632.8 nm light, such as toluene with  $R_{90^\circ} = 14.1 \times 10^{-6} \text{ cm}^{-1}$ . Thus,  $R_\theta$  was determined at every scattering angle and yielded information on  $M_w$ ,  $A_2$ , and  $R_g$  using eqs. (1) and (3).

SEC measurements were carried out in toluene at ambient temperature using a modular system composed of a Waters 590 pump, a Waters R401 differential refractive index detector (RI), the DAWN-F LS instrument, and a set of crosslinked polystyrene columns. The column set consisted of four PL gel columns (Polymer Laboratories) of  $10^6$ ,  $10^6$ ,  $10^5$ , and  $10^4$  Å porosity. Sample injections of 50  $\mu\text{L}$  to 200  $\mu\text{L}$  were made using a WISP Model 710B autoinjector. Flow rate was 1.0 mL/min and the run time was 40 min. The eluent was directed through the DAWN-F LS detector and then through the R401 differential refractometer to protect the fragile RI cell from high pressure. Concentrations for each eluent are calculated from the mass injected using the integrated RI peak. The values of concentration and the scattered intensities obtained using the DAWN-F LS detector can be used to calculate  $M_w$  with eq. (1). The data were acquired with the aid of a IBM PCAT, and  $M_w$  and  $R_g$  across the distribution were calculated using software from Wyatt Technology.

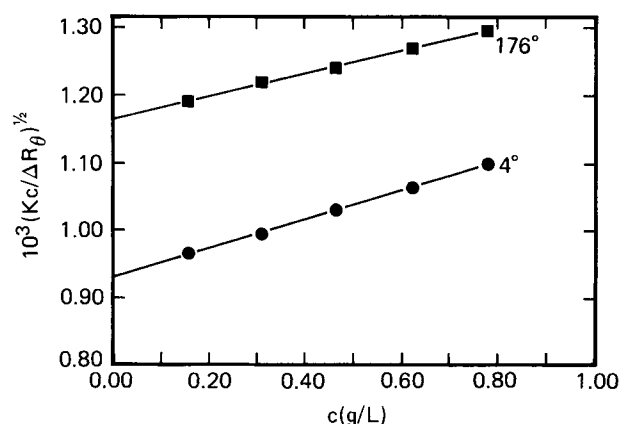
The BI200-SM is a photogoniometer with a photomultiplier detector mounted on an arm which rotates about the cylindrical sample cell held in the thermostatted bath of index matching fluid, in this case a blended silicone oil with refractive index of 1.45. When the instrument is aligned properly, the scattering volume at each scattering angle  $\theta$  is proportional to  $\sin \theta$ . Software from Brookhaven instruments was used to determine scattered intensities at eight angles  $\theta$  where  $30^\circ < \theta < 135^\circ$  for six concentrations of PAMS-9. Values of  $M_w$ ,  $A_2$ , and  $R_g$  obtained with the BI200SM are compared with those obtained using the LALS with the reflectance accessory as discussed above.

## RESULTS

### KMX-6

The weight average molecular weight and the second virial coefficient were calculated from the intercept and the slope of a plot of  $(Kc/\Delta R_\theta)^{1/2}$  at  $\theta = 4.4^\circ$  versus  $c$  as explained above. A representative plot to obtain  $A_2$  and  $M_w$  for PAMS-8 is shown in Figure 1. The root mean square radius of gyration is obtained from the two values of the intercepts at  $\theta = 4.4^\circ$  and  $\theta = 175.6^\circ$  in Figure 1 using eq. (3). The parameters obtained for PS in toluene and for PAMS in toluene are listed in Tables I and II, respectively.

The experimental values of  $A_2$  and  $R_g$  are plotted as a function of molecular weight in Figures 2–5. For PS in toluene  $A_2 = 6.12 \times 10^{-3} M_w^{-0.22}$  is obtained from the slope of Figure 2. It agrees well with the result of Appelt and Meyerhoff<sup>3</sup> as shown in Figure



**Figure 1**  $[Kc/\Delta R_\theta]^{1/2}$  as a function of concentration for PAMS-8 at low ( $\theta = 4^\circ$ ) and high ( $\theta = 176^\circ$ ) scattering angles obtained with the KMX-6.

**Table I** Summary of Results for Polystyrene in Toluene

Sample	$M_w$	$A_2$ ( $10^{-4}$ mL mol/g <sup>2</sup> )	$R_g$ (nm)
PS-1	383,000	3.56	25.8
PS-2	653,000	3.04	37.3
PS-3	1,097,000	2.79	48.7
PS-4	2,140,000	2.43	68.2
PS-5	3,252,000	2.19	87.6
PS-6	4,053,000	2.00	94.8
PS-7	7,909,000	1.82	122.5

2. The values for  $R_g$  correspond well with Appelt and Meyerhoff's values<sup>3</sup> for PS with  $M_w < 2 \times 10^6$ , but deviate from their values for very high molecular weight samples.  $R_g = 1.08 \times 10^{-9} M_w^{0.606}$  is obtained with the first three values.

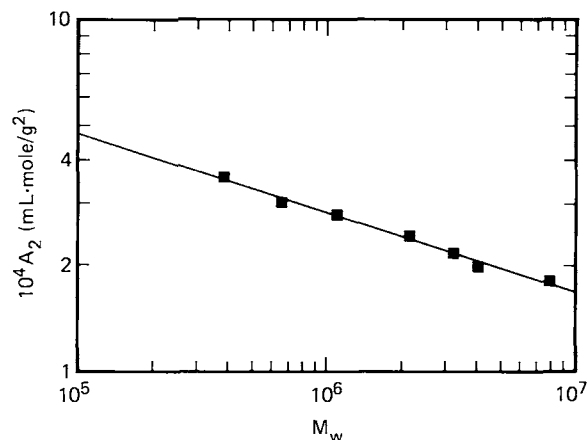
For PAMS in toluene the values for  $A_2$  are consistent with results of Kato et al.,<sup>4</sup> as well as those of Kim et al.<sup>5</sup> and Lindner et al.<sup>6</sup> for the whole experimental range of molecule weight.  $A_2 = 7 \times 10^{-3} M_w^{-0.25}$  is obtained from the slope of Figure 4. The plot  $R_g$  versus  $M_w$  for PAMS is also in agreement with data reported by Kato et al.,<sup>4</sup> as well as those of Kim et al.<sup>5</sup>  $R_g = 1.2 \times 10^{-9} M_w^{0.583}$  is obtained from the slope of Figure 5.

### DAWN-F

The scattered intensities for three samples of PAMS in toluene were measured using a DAWN-F LS instrument. The values of  $R_g$  are obtained from the slope and intercept of a Zimm plot using eq. (2) truncated above  $q^2$ . A representative Zimm plot for PAMS-6 in toluene is shown in Figure 6, where  $k$  is

**Table II** Summary of Results for Poly( $\alpha$ -Methylstyrene) in Toluene

Sample	$M_w$	$A_2$ ( $10^{-4}$ mL mol/g <sup>2</sup> )	$R_g$ (nm)
PAMS-1	6700	9.63	—
PAMS-2	24,800	5.38	—
PAMS-3	69,000	4.07	—
PAMS-4	114,500	3.55	—
PAMS-5	297,000	2.71	—
PAMS-6	611,000	2.29	30.2
PAMS-7	779,000	2.18	35.9
PAMS-8	1,050,000	2.00	42.4
PAMS-9	3,000,000	1.56	82.7

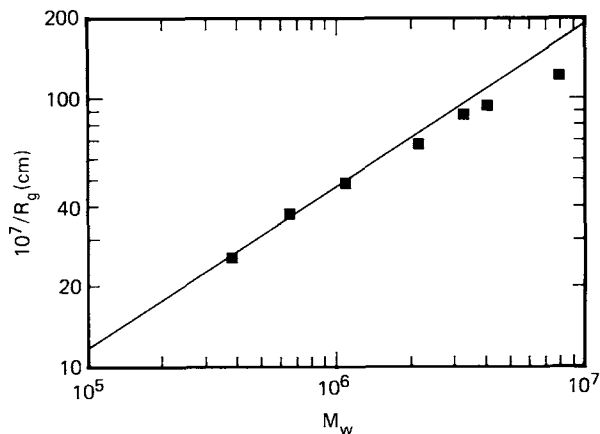


**Figure 2**  $A_2$  as a function of  $M_w$  for PS in toluene (see Table I). The line through the data is the equation given by Appelt and Meyerhoff.<sup>3</sup>

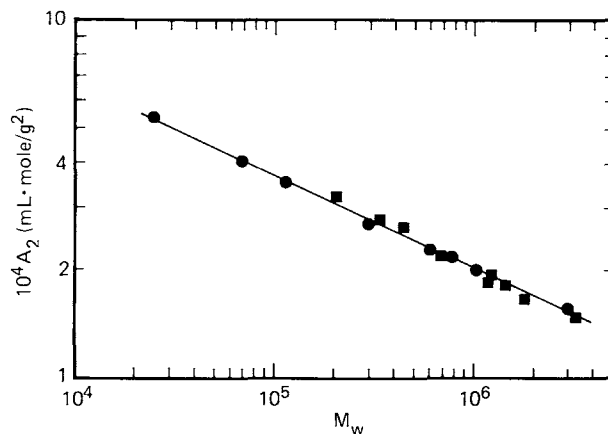
a constant value. The values of square root of Rayleigh ratio at  $\theta = 0$  were calculated for five concentrations from Figure 6 and plotted as a function of concentration  $c$  in Figure 7. The molecular weight and the second virial coefficient were calculated from the slope and the intercept of Figure 7 using eq. (1). The values obtained for three samples of PAMS are listed in Table I and compared to those obtained with the KMX-6.

#### SEC/LS (DAWN-F)

Three samples of PAMS in toluene were investigated using a SEC with LS and RI detectors. A representative chromatogram for PAMS-8 obtained with LS detector at  $\theta = 90^\circ$  is shown in Figure 8. Scattered intensities at the peak of Figure 8 are



**Figure 3**  $R_g$  as a function of  $M_w$  for PS in toluene (see Table I). The line through the data is the equation given by Appelt and Meyerhoff.<sup>3</sup>

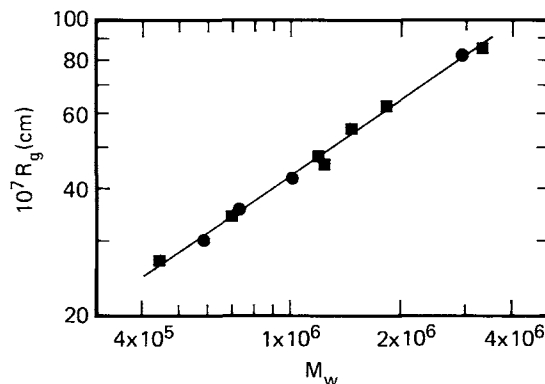


**Figure 4**  $A_2$  as a function of  $M_w$  for PAMS in toluene ( $\bullet$ ) (see Table II). The line through the data is the equation in the text. Also shown are data of Kato et al. ( $\blacksquare$ ).<sup>4</sup>

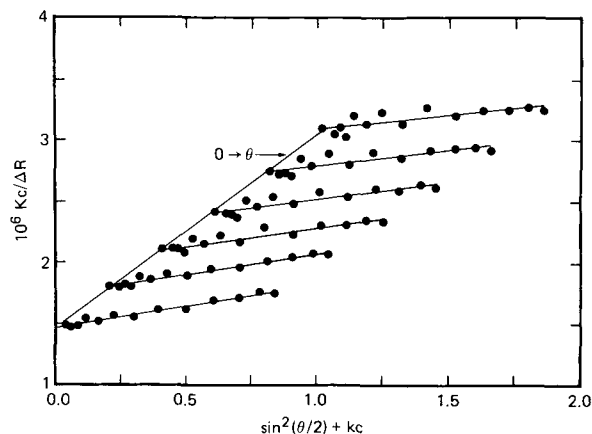
plotted as a function of scattering angle in Figure 9. The values of  $M_w$  and  $R_g$  were calculated using software from Wyatt Technology as explained above. The values are listed in Table III. The mass of polymer injected in SEC was 0.1–0.2 mg for these PAMS samples. Therefore, solutions coming from columns in SEC are so dilute that  $A_2 c M_w \ll 1$  in eq. (1) and scattered intensities are independent of concentration. Thus, the second virial coefficient  $A_2$  cannot be obtained using SEC with a LS detector. Table III indicates that the values obtained using SEC with the DAWN-F are consistent with those obtained using the DAWN-F alone and with a KMX-6.

#### BI200SM

PAMS-9 was measured using the KMX-6 and the BI200SM, with the results displayed in Figures 10



**Figure 5**  $R_g$  as a function of  $M_w$  for PAMS in toluene ( $\bullet$ ) (see Table II). Also shown are data of Kato et al. ( $\blacksquare$ ).<sup>4</sup> The line through the data is the equation in the text.

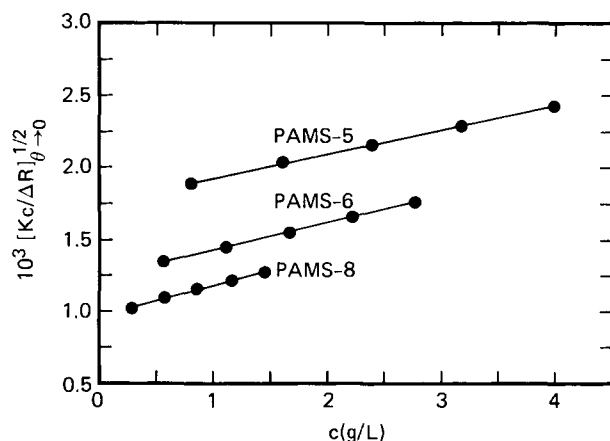


**Figure 6** Zimm plot of  $Kc/\Delta R$  vs.  $\sin^2(\theta/2) + kc$  for PAMS-6 in toluene obtained using the DAWN-F.

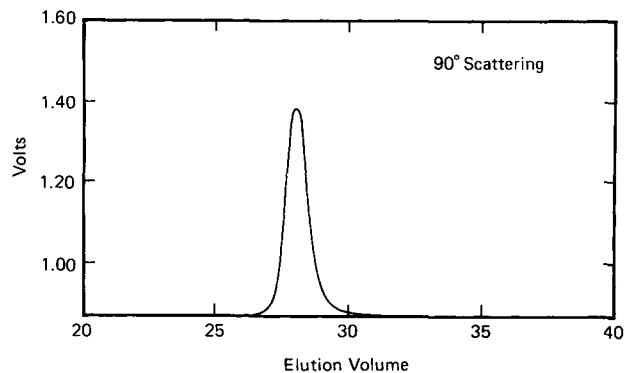
and 11, respectively. Figure 10 shows the results obtained at scattering angles  $\theta$  of 4 and 176° with the KMX-6, and Figure 11 shows the Zimm plot obtained with the BI200SM photogoniometer. Table IV lists the values of  $M_w$ ,  $A_2$ , and  $R_g$  obtained with both instruments using eqs. (1) and (3).

## DISCUSSION

From statistical theory the second virial coefficient  $A_2$  for a highly expanded polymer in dilute solution becomes a function of only  $M_w$  and  $R_g$ .<sup>7</sup> Thus,  $A_2 \propto R_g^3/M_w^2$  for a highly expanded polymer. If  $R_g \propto M_w^\nu$ , the molecular weight dependence of  $A_2$  can



**Figure 7**  $[Kc/\Delta R]^{1/2}$  at the limit of zero scattering angle versus concentration for PAMS-5, PAMS-6, and PAMS-8 in toluene. Data obtained with the DAWN-F; results are compared with those obtained with the KMX-6 in Table III.

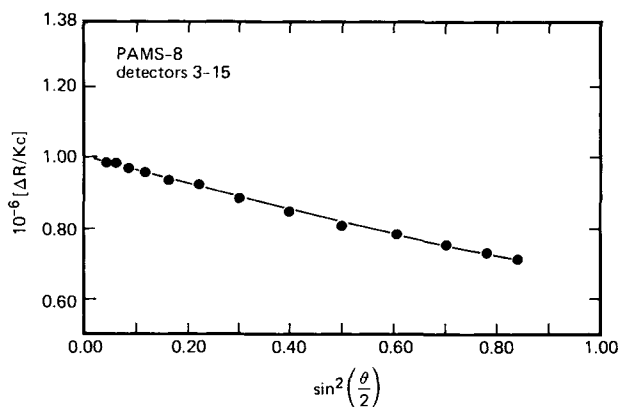


**Figure 8** A chromatogram obtained for PAMS-8 at 90° scattering angle using the DAWN-F as a detector for size exclusion chromatography. Results are shown in Table III.

be expressed as  $A_2 \propto M^{3\nu-2}$ . The exponent  $\nu$  for PS in toluene is calculated from the molecular weight dependence of  $A_2$  obtained experimentally,  $A_2 \propto M^{-0.22}$ , and  $\nu = 0.593$  is obtained. It is in good agreement, within the error limit, with  $\nu = 0.606$  obtained from the slope of plot of  $R_g$  vs.  $M_w$ .

The exponent  $\nu$  for PAMS in toluene is also calculated from  $A_2 \propto M_w^{-0.255}$  obtained from the slope of Figure 4 and  $\nu = 0.582$  is obtained. It agrees well with  $\nu = 0.583$  obtained from the slope of Figure 5. These results indicate that PS and PAMS are highly expanded in toluene. The exponents  $\nu$  obtained for PS and PAMS in toluene correspond with  $\nu = 0.589$  predicted by renormalization group theory.<sup>8</sup>

In the KMX-6,  $M_w$ ,  $A_2$ , and  $R_g$  could be obtained with a reflectance accessory. Although this dissymmetry method can yield erroneous values for  $R_g$  for narrow distribution polymers of very high molecular



**Figure 9**  $\Delta R/Kc$  vs.  $\sin^2(\theta/2)$  (detectors 3-15) at the peak of the chromatogram obtained for PAMS-8 (see Fig. 8).

**Table III Comparison of Results for PAMS-5, PAMS-6, and PAMS-8**

Sample	KMX-6			DAWN-F			SEC/DAWN-F	
	$M_w$	$10^{-4} A_2$ (mL mol/g <sup>2</sup> )	$R_g$ (nm)	$M_w$	$10^{-4} A_2$ (mL mol/g <sup>2</sup> )	$R_g$ (nm)	$M_w$	$R_g$ (nm)
PAMS-5	297,000	2.71	—	323,000	2.96	—	314,000	—
PAMS-6	611,000	2.29	30.2	651,000	2.34	29.1	673,000	29.6
PAMS-8	1,050,000	2.00	42.4	1,080,000	2.11	41.4	1,079,000	39.8

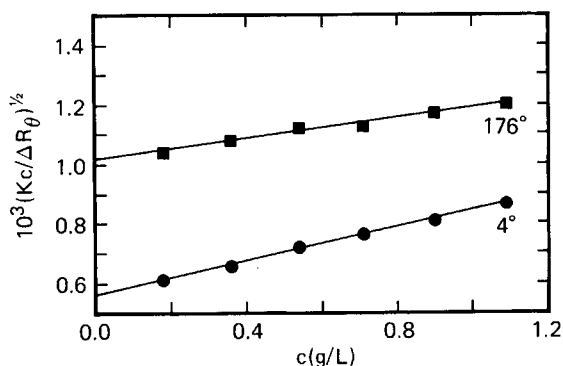
weight (more than several million), it can be very useful for a wide variety of synthetic polymers, and provides a very rapid assessment of  $R_g$ . Values of  $R_g$  obtained for polymers with  $300,000 < M_w < 3,000,000$  using this dissymmetry technique are in good agreement with those obtained with the Zimm plot of eight or more angles from the DAWN-F or BI200SM. The values of  $M_w$ ,  $A_2$ , and  $R_g$  are compared and agree well with literature values for PS and PAMS solutions. In the DAWN-F, scattered intensities at 15 different scattering angles may be measured simultaneously.  $M_w$ ,  $A_2$ , and  $R_g$  were obtained using DAWN-F and correspond well with those obtained with the KMX-6. For SEC with light scattering detectors (in this study a DAWN-F),  $M_w$  and  $R_g$  may be obtained from less than 1 mg of sample. The values agree well with those obtained with the DAWN-F alone and with the KMX-6. Although the average values of  $R_g$  obtained using SEC with the DAWN-F are reasonable, the values of  $R_g$  across the distribution are not consistent with the values of  $M_w$  and yield erroneously small values for the exponent  $\nu$  in the molecular weight dependence of  $R_g$ ,  $R_g \propto M_w^\nu$ .

The three light scattering instruments used for this study have advantages and disadvantages which

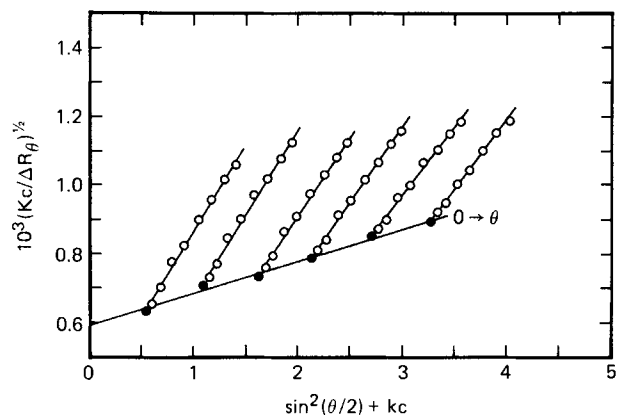
can be significant for specific applications. As an example, the ease of use of the KMX-6 (no calibration, no normalization, flow-through cell design) is obtained at the expense of flexibility in the scattering angles. Use of the reflectance accessory can mitigate this disadvantage, but care must be taken to ensure that eq. (3) may be used with confidence for the range of scattering angles  $4^\circ < \theta < 176^\circ$ . The angular dependence of  $R_\theta$  at infinite dilution in eq. (2) may be expressed as

$$S^0(q) \equiv \frac{R_0}{R_\theta} = \frac{2}{u^2} [\exp(-u) - 1 + u] \quad (4)$$

where  $u = q^2 R_g^2$ , the superscript 0 indicates infinite dilution, and the subscript 0 indicates scattering angle  $\theta = 0$ . A plot of  $[S^0(q)]^{1/2}$  versus  $u$  [analogous to eq. (3)] begins to deviate from linearity above about  $u = 2$ .<sup>9</sup> This suggests that use of eq. (3) with the reflectance accessory of the KMX-6 should be limited to polymers with an  $R_g \lesssim 700 \text{ \AA}$ , corresponding to molecular weights below about  $2 \times 10^6$  for polystyrene in toluene.



**Figure 10**  $[Kc/\Delta R_\theta]^{1/2}$  as a function of concentration for PAMS-9 at low ( $\theta = 4^\circ$ ) and high ( $\theta = 176^\circ$ ) scattering angles obtained with the KMX-6.



**Figure 11** Zimm plot of  $[Kc/\Delta R_\theta]^{1/2}$  vs.  $\sin^2(\theta/2) + kc$  for PAMS-9 obtained with the BI200SM. Results are in Table III.

**Table IV Comparison of Results for PAMS-9 in Toluene**

Instrument	$M_w$	$A_2$ ( $10^{-4}$ mL mol/g <sup>2</sup> )	$R_g$ (nm)
KMX-6	3,000,000	1.56	82.7
BI200SM	2,800,000	1.80	88.7

The DAWN-F has more flexibility than the KMX-6 in terms of angular range, with 15 permanently mounted detectors, and retains the flow-through cell design which is necessary for SEC/LS measurements and advantageous for sample clarification. However, both calibration and normalization measurements are necessary to obtain experimental results, and the quality of the results directly reflects the care and precision in these procedures. The DAWN-F is the only commercially available instrument which can provide the scattered intensity at 15 angles continuously as the polymer elutes from a chromatography column. In principle, these results could permit investigation of the molecular weight dependence of  $R_g$  with as little as one injection of a few milligrams of polymer. As discussed above, we have not been able to observe this for the narrow distribution polymers studied here, but promising results have been obtained for some broad distribution sample.<sup>10</sup>

The BI200SM retains the most flexibility for light scattering measurements, with the rotating photomultiplier detector permitting continuously selectable scattering angles. The light source may also be varied easily, allowing measurements at various wavelengths. The sample cell is immersed in an index matching fluid which is temperature controlled, so that measurements where temperature control is crucial (for measurements at the  $\theta$  temperature, for example) are more easily accomplished than with the KMX-6 or DAWN-F. The goniometer design is also excellent for measurements of the autocorrelation of the scattered light (dynamic light scattering or photon correlation spectroscopy) so that measurement of both  $R_g$  and the hydrodynamic radius

$R_h$  may be done simultaneously. Intensity measurements require more time than is required with either the KMX-6 or the DAWN-F, and the BI200SM cannot be used as a detector for the eluent from a chromatography column. When used without modification, the BI200SM requires more sample and does not have the flow-through sample cell which facilitates sample clarification significantly. The results from the angular dependence of the scattered intensity depend critically on the alignment of the BI200SM.

Commercially available instruments have been used to obtain dilute solution properties of PS and PAMS in toluene. The results for  $M_w$ ,  $R_g$ , and  $A_2$  are in agreement among the instruments used and with literature data for these polymers. In most cases, these parameters may be obtained more rapidly than with the more classical photogoniometers, and often results may be obtained on very small quantities of polymer (a few milligrams). Use of these instruments as absolute molecular weight (and in some cases size) detectors for SEC can eliminate many of the problems with column calibration.

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