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# On-line measurement of molecular weight and radius of gyration of polystyrene in a good solvent and in a theta solvent measured with a two-angle light scattering detector

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## Abstract

On-line two-angle (15° and 90°) light scattering measurements with a gel permeation chromatography for linear and branched polystyrene in tetrahydrofuran (a good solvent) and in *trans*-decalin (a theta solvent) were made and compared with data from a multi-angle light scattering detector and literature values. Theoretically, weight-average molecular weight and the radius of gyration $R_g$ can be determined accurately in the range where $R_g^2 k^2$ is less than 1.2 (rod) $\sim$ 1.7 (random coil); here, $k$ is the absolute value of the scattering vector for a right angle detector with the Berry square root method. Molecular weight dependence of the radius of gyration obtained from the two-angle light scattering detector for linear and branched polystyrenes under different thermodynamic conditions were measured and found to be almost the same as values measured with a multi-angle light scattering detector and literature values in the appropriate range of molecular weight.
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*Keywords:* Two-angle light scattering; Multi-angle light scattering; Gel permeation chromatography; Radius of gyration; Theta solvent

## 1. Introduction

In order to investigate the shape of polymer molecules in solution, the combined measurement of radius of gyration $R_g$ and molecular weight yields some of the most useful information [1,2]. These quantities are obtained from static light scattering, small angle X-ray scattering, or small angle neutron scattering. However, narrow molecular weight samples are required for this purpose because $R_g^2$ thus obtained is *z*-average value

whereas molecular weight is a weight-average, $M_w$. Recently, some commercial instruments have been developed to measure $M_w$ and $R_g$ by coupling to a gel permeation chromatography system (GPC). In this way, both the molecular weight and size may be measured at each elution volume, thus making conformational information available for various components that are present in polydisperse macromolecules. The most widely used multi-angle light scattering (MALS) detector is produced by Wyatt Technology [3]. It has been demonstrated that the use of this unit on-line as a GPC detector gives reliable $M_w$ and $R_g$ data for a range of linear [4] and branched [5–7] architectures. However multi-angle detectors are large and expensive. Very recently, Precision Detectors introduced a two-angle light scattering (TALS) detector (15° and 90°) which is much

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smaller and more economical than MALS detectors and it is easy to place in the thermostat. For a limited region of molecular sizes, but one which covers the practical range of interest to most users, accurate molecular weight and radius of gyration can be obtained from this detector. Very recently, Bo and coworkers reported the use of TALS for measuring molecular weight and sizes of a range of linear polymers in trichlorobenzene at 150 °C [8]. In this work, we demonstrate the accuracy of the data from two angle detectors theoretically and experimentally for linear and regularly branched polystyrenes in tetrahydrofuran (THF, a good solvent) and for linear polystyrene in *trans*-decalin (a theta solvent).

## 2. Theoretical background

Scattering functions of various linear polymers in solution have been investigated and they can be explained quantitatively by the wormlike chain model, or more generally the helical wormlike chain model [2]. The theoretical scattering function of the former model is between the theoretical values of the thin rod model and the Gaussian coil model. The scattering functions $P(k)$ of a thin rod and a coil are written with the absolute value $k$ of the scattering vector as

$$P(k) = \frac{2}{X^2}(e^{-X} - 1 + X), \quad X = R_g^2 k^2 \quad \text{Gaussian coil} \tag{1}$$

$$P(k) = \frac{1}{X_r}\int_0^{2X_r}\frac{\sin z}{z}\,\mathrm{d}z - \left(\frac{\sin X_r}{X_r}\right)^2,$$
$$X_r = Lk/2 \quad \text{Thin rod} \tag{2}$$

where $L$ is the length of the rod. It is known that Berry's square root method [9] written as

$$[P(k)]^{-1/2} = 1 + \frac{1}{6}R_g^2 k^2 \tag{3}$$

gives an appropriate linearity at the low $k$ range. Scattering functions calculated from these equations are illustrated in Fig. 1. When $R_g^2 k^2$ is less than 1.73 for a Gaussian coil or 1.22 for a thin rod, the ratio of $R_{g,app}$ (the radius of gyration determined from this equation with $P(k)$ for higher angle) to the true $R_g$ is more than 0.98, i.e. the error of $R_{g,app}$ is less than 2%. These range are equivalent to $R_g < 72$ nm for a Gaussian coil and 60 nm for a thin rod when the wavelength of the incident beam and the refractive index are assumed to be 680 nm and 1.4, respectively. This corresponds to $M_w = 2 \times 10^6$ for linear polystyrene in THF. Furthermore, $R_g$ for branched polymer is smaller than that for the linear polymer with the same molecular weight. Therefore, it is expected that accurate molecular weight and radius of
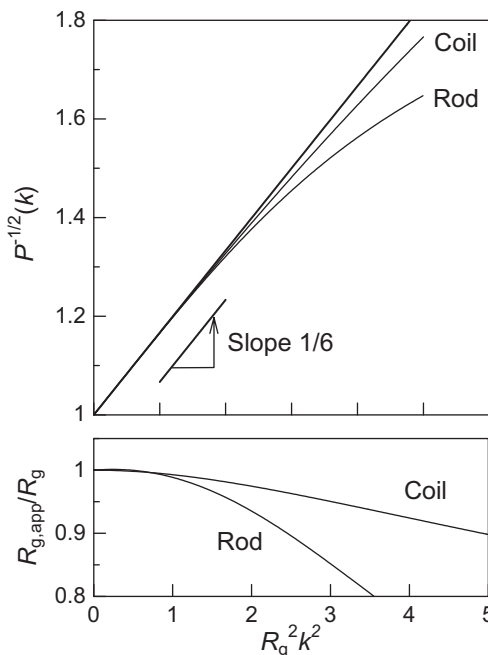


Fig. 1. Plots of $P^{-1/2}(k)$ and $R_{g,app}/R_g$ vs $R_g^2 k^2$ for the Gaussian coil model and the thin rod model.

gyration for branched polymers will be obtained from TALS detectors for a considerable region of molecular weight.

## 3. Experimental

A linear polydisperse polystyrene, sample PS-1 purchased from Aldrich with the nominal molecular weight being $2.8 \times 10^5$, and previously investigated multi-branched polystyrenes (comb polystyrenes CS25-35, GS60-15, GS40-25, and GS15-35) were chosen in this study. Weight average molecular weight and $R_g$ in THF at 25 °C and in *trans*-decalin at 22 °C were determined using a Polymer Laboratories PL-GPC-120 GPC system with a Precision Detector two-angle (15° and 90°) light scattering photometer with a 680 nm laser and a refractive index detector. Two PLgel 10 μm MIXED-B columns ($300 \times 7.5$ mm) connected in series were used to fractionate the polymer and the flow rate was set to 1 cm$^3$ min$^{-1}$. For *trans*-decalin solutions the column temperature was set to be 110 °C to avoid adsorption of the polymer to the column. To calibrate the TALS detector, two standard polystyrene samples whose $M_w$ were determined using the Wyatt Technology DAWN EOS to be 50,000 and 65,000 were used for this study, and we used $R_g$ value for these two polystyrene samples estimated by the relations

$$R_g = 0.0118 M_w^{0.6} \quad \text{(nm, THF, 25 °C)}$$
$$R_g = 0.0277 M_w^{0.5} \quad \text{(nm, } trans\text{-decalin, 22 °C)} \tag{4}$$

Polymer solutions with mass concentrations of about $1.7 \times 10^{-3}$ or $2.7 \times 10^{-3}$ g cm$^{-3}$ for THF or *trans*-decalin solutions, respectively, were injected using a sample loop of 0.1 cm$^3$ capacity. For comparison with the data from multi-angle light scattering detection, light scattering measurements with a Wyatt DAWN EOS multi-angle photometer and a refractive index detector (Wyatt OPTILAB DSP) were made for THF solutions of PS-1 at the wavelength being 690 nm. Toluene and a narrow distributed polystyrene sample with the molecular weight being 50,000 were used to calibrate the right angle detector and to normalize the other scattering detectors, respectively. The specific refractive index increment for polystyrene in THF at 25 °C was taken to be 0.184 cm$^3$ g$^{-1}$ to determine molecular weight with the DAWN EOS [10].

## 4. Results and discussion

Fig. 2 illustrates the curves of the polymer mass concentration $c$, $M_w$ and $R_g$ against elution volume $V_e$ for PS-1. The molecular weight and $R_g$ at each $V_e$ were calculated when each light scattering intensity and concentration are more than 10% of the peak value. It is seen that the maximum $R_g$ value is obviously less than 60 nm, that is the upper limit to determine $R_g$ correctly
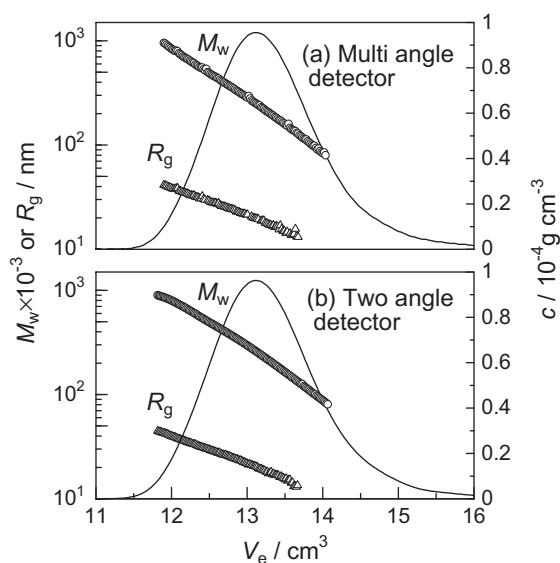
from the Berry's square root plot. The value of $c$, $M_w$ and $R_g$ at the same $V_e$ from the two kinds of light scattering detectors are almost the same. Generally, the molecular weight determined from finite concentrated solutions in a good solvent is estimated to be smaller than the true value due to the effect of the second viral coefficient $A_2$. For the current system, the value of $A_2$ is known as a function of the molecular weight as [11]

$$A_2^{\text{THF}} = 9.93 \times 10^{-3} M^{-0.247} \tag{5}$$

In this case, the true $M_w$ value was at most 2.5% larger than the obtained value. In fact, this underestimation does not affect the plot of $R_g$ vs $M_w$ because this difference is essentially offset by the very slight underestimation of the $R_g$.

Fig. 3 shows the comparison of the measured molecular weight dependence of $R_g$ with literature values. The present data are showed as open symbols along with literature values of Nakamura et al. [7], Schultz and Baumann [12], and Park et al. [13]. It is seen that $R_g$ for the same molecular weight are almost the same irrespective of the detector used. Furthermore, these values are very close to literature values but slightly smaller than them. This difference in $R_g$ might be explained due to the molecular weight distribution of the samples used in the previous works. Also, the comparisons between the data for linear polystyrene in *trans*-decalin and literature values of Inagaki et al. [14] at 24 °C, Fukuda et al. [15] at 20.4 °C, and Konishi et al. [16] at 22 °C are shown in Fig. 4. Our data have very good agreements with literature values for a theta solvent system.



Fig. 2. Plots of $M_w$, $R_g$ and $c$ vs $V_e$ for linear polystyrene PS-1 in THF at 25 °C: (a) data from the multi-angle light scattering detector and (b) data from the two-angle light scattering detector.
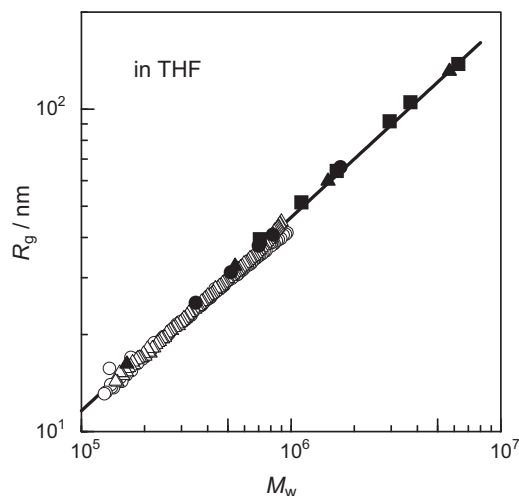


Fig. 3. Molecular weight dependence of $R_g$ for linear polystyrenes in THF. Open circles: data for PS-1 from the two-angle detector, open triangles: data for PS-1 from the multi-angle detector, filled circles: Nakamura et al. [7], filled triangles: Schultz and Baumann [12], filled squares: Park et al. [13].
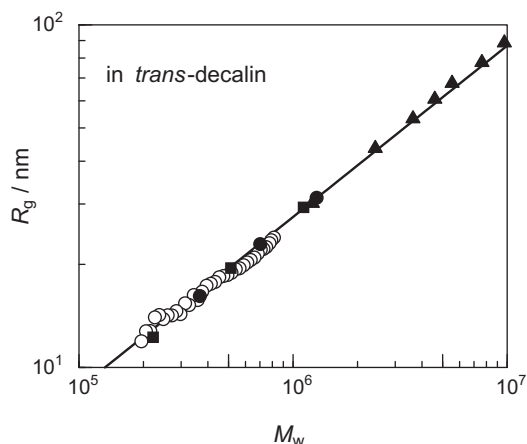
Fig. 4. Molecular weight dependence of $R_g$ for linear polystyrenes in *trans*-decalin. Open circles: data for PS-1 from the two-angle detector at 22 °C, filled squares: Inagaki et al. [14] at 24 °C, filled triangles: Fukuda et al. [15] at 20.4 °C, filled circles: Konishi et al. [16] at 21 °C.

Fig. 5 shows the comparison between $R_g$ data from MALS and TALS in the plot of $R_g$ vs $M_w$ for regular comb polystyrenes (multiple, regularly spaced trifunctional branch points) and regular centipede polystyrenes (multiple, regularly spaced tetrafunctional branch points) [7]. It is clearly seen that data from two-angle
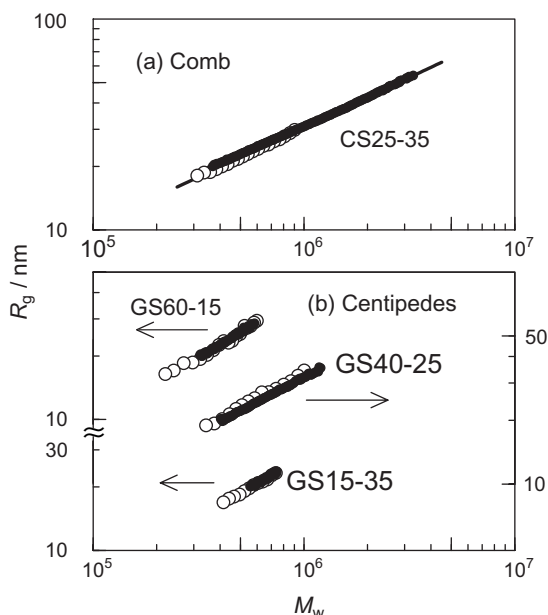


Fig. 5. Molecular weight dependence of $R_g$ for regularly branched polystyrenes in THF (open circles: this work from the two-angle detector, filled circles: Nakamura et al. [7] from a multi-angle detector).

light scattering detector are essentially the same as those from the multi-angle light scattering detector.

## 5. Conclusions

In this paper, we report and compare light scattering data from multi-angle light scattering and two-angle light scattering detectors. The data from the TALS detector are almost the same as those from the MALS detector for both linear and branched polystyrene solutions in good and theta solvents over a very broad range of molecular weights. This result shows that molecular weight dependence of radius of gyration can be obtained using the compact and lower cost TALS detector for polymers having an appropriate radius of gyration. Another certification of two-angle light scattering will be published for multi-branched polybutadiene solutions [17].

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