Title	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
Author(s)	Mays, Jimmy W; Terao, Ken
Citation	European Polymer Journal. 2004, 40(8), p. 1623-1627
Version Type	AM
URL	https://hdl.handle.net/11094/25928
rights	
Note	

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

Ken Terao[a,b,]* and Jimmy W. Mays [a,c,]*

[a] *Department of Chemistry, University of Tennessee, 552 Buehler Hall, Knoxville, TN 37996, USA*

[b] *Department of Biological and Chemical Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu Gunma 376-8515, Japan*

[c] *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

*Corresponding authors. E-mail: terao@bce.gunma-u.ac.jp or jimmymays@utk.edu

Abstract

On-line two-angle (15° and 90°) light scattering measurements with a gel permeation chromatograph 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 $R_g^2k^2$ is less than 1.2 (rod) ~ 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.

Key words: 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 chlomatography 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 degree) which is much 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 co-workers 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

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

$$P(k) = \frac{1}{X_{\mathrm{r}}}\int_0^{2X_{\mathrm{r}}} \frac{\sin z}{z}\,dz - \left(\frac{\sin X_{\mathrm{r}}}{X_{\mathrm{r}}}\right)^2, \quad X_{\mathrm{r}} = Lk/2 \qquad \text{Thin rod (2)}$$

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

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

gives an appropriate linearity at the low k range. Scattering functions calculated from these equations are illustrated in Figure 1. When $R_g^2k^2$ 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 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 2.8×10^5, 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 × 7.5 mm) connected in series were used to fractionate the polymer and the flow rate was set to 1 $\mathrm{cm^3\ min^{-1}}$. For *trans*-decalin solutions the column temperature was set to be 110ºC 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

$$R_g = 0.0118\, M_w^{0.6} \text{ (nm, THF, 25ºC)}$$

$$R_g = 0.0277\, M_w^{0.5} \text{ (nm, \textit{trans}-decalin, 22ºC)} \qquad (4)$$

Polymer solutions with mass concentrations of about 1.7×10^{-3}g cm^{-3} or 2.7×10^{-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.[5]

4. Results and Discussion

Figure 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]

$$A_2^{\mathrm{THF}} = 9.93 \times 10^{-3} M^{-0.247} \qquad (5)$$

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.

Figure 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], Shultz 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 can 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 24ºC, Fukuda et al. [15] at 20.4ºC, and Konishi et al. [16] at 22ºC are shown in Figure 4. Our data have very good agreements with literature values for a theta solvent system.

Figure 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 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]

Acknowledgements

Research sponsored by the Division of Materials Sciences and Engineering, office of Basic Energy Sciences, U. S. Department of Energy, under contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. We thank the National Science Foundation (DMR-0216816) and the Tennessee Advanced Materials Laboratory for the purchase of the GPC and light scattering systems used in this work.

References

[1] Flory PJ. Statistical mechanics of chain molecule, New York: Wiley, 1969.

[2] Yamakawa H. Helical wormlike chains in polymer solutions, Berlin: Springer, 1997.

[3] Wyatt PJ. Light scattering and the absolute characterization of macromolecules. Analytica Chimica Acta 1993; 272: 1-40.

[4] Jackson C, Chen Y-J, Mays JW. Size exclusion chromatography with multiple detectors: solution properties of linear chains of varying flexibility in tetrahydrofuran. J Appl Polym Sci 1996; 61: 865-874.

[5] Jackson C, Frater DJ, Mays JW. Dilute solution properties of asymmetric six-arm star polystyrenes. J Polym Sci, Polym Phys Ed 1995; 33: 2159-2166.

[6] Jackson C, Chen Y-J, Mays JW. Dilute solution properties of randomly branched poly(methylmethacrylate). J Appl Polym Sci 1996; 59: 179-188.

[7] Nakamura Y, Wan Y, Mays JW, Iatrou H, Hadjichristidis N. Radius of gyration of polystyrene combs and centipedes in solution, Macromolecules 2000; 33: 8323-8328.

[8] Liu Y, Bo S, Zhu Y, Zhang W. Determination of molecular weight and molecular sizes of polymers by high temperature gel permeation chromatography with a static and dynamic light scattering detector. Polymer 2003; 44: 7209-7220.

[9] Berry GC. Thermodynamic and conformational properties of polystyrene. I. Light-scattering studies on dilute solutions of linear polystyrenes. Jnl Chem Phys 1966; 44(12): 4550-4564.

[10] Huglin MB. In Polymer Handbook, 3rd ed.; Brandrup J, Immergut EH. Eds.; Wiley-Interscience: New York, 1989.

[11] Fetters LJ, Hadjichristidis N, Lindner JS, Mays JW. Molecular weight dependence of hydrodynamic and thermodynamic properties for well-defined linear polymers in solution. J. Phys. Chem. Ref. Data 1994; 23: 619-640.

[12] Schultz GB, Baumann H. Static and hydrodynamic size of polystyrene coils in various solvents. Macromol Chem 1968; 114: 122-138.

[13] Park S, Chang T, Park IH. Thermodynamic behavior, expansion coefficient, and viscosity number of polystyrene in tetrahydrofuran. Macromolecules 1991; 24: 5729-5731.

[14] Inagaki H, Suzuki H, Fujii M, Matsuo T. Note on experimental tests of theories for the excluded volume effect in polymer coils. J Phys Chem 1966; 70: 1718-1726.

[15] Fukuda M, Fukutomi M, Kato Y, Hashimoto T. Solution properties of high molecular weight polystyrene. J Polym Sci: Polym Phys Ed 1974; 12: 871-890.

[16] Konishi T, Yoshizaki T, Yamakawa H. On the "Universal constants" ρ and Φ of frexible polymers. Macromolecules 1991; 24: 5614-5622.

[17] Baskaran D, Terao K, Mays JW. in preparation.

Figure Captions

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

Figure 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 (b) data from the two-angle light scattering detector.

Figure 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: Schulz and Baumann [12], filled squares: Park et al. [13]).

Figure 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 22ºC, filled squares: Inagaki et al. [14] at 24ºC, filled triangles: Fukuda et al. [15] at 20.4ºC, filled circles: Konishi et al. [16] at 21ºC.

Figure 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).

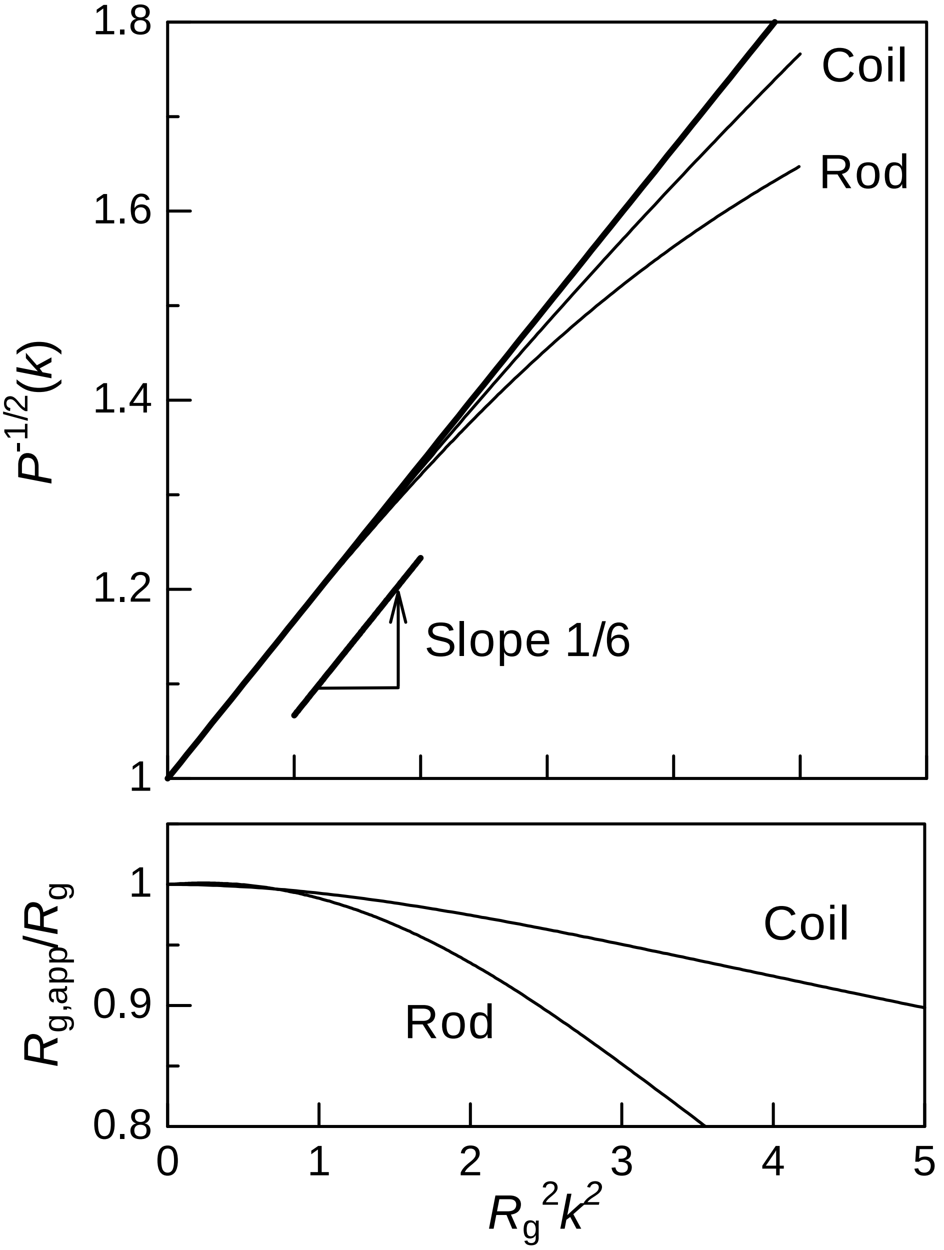

1.8
1.6
1.4
1.2
1
Coil
Rod
Slope 1/6
$P^{-1/2}(k)$
1
0.9
0.8
Coil
Rod
$R_{g,app}/R_g$
0
1
2
3
4
5
$R_g^2k^2$

Figure 1.

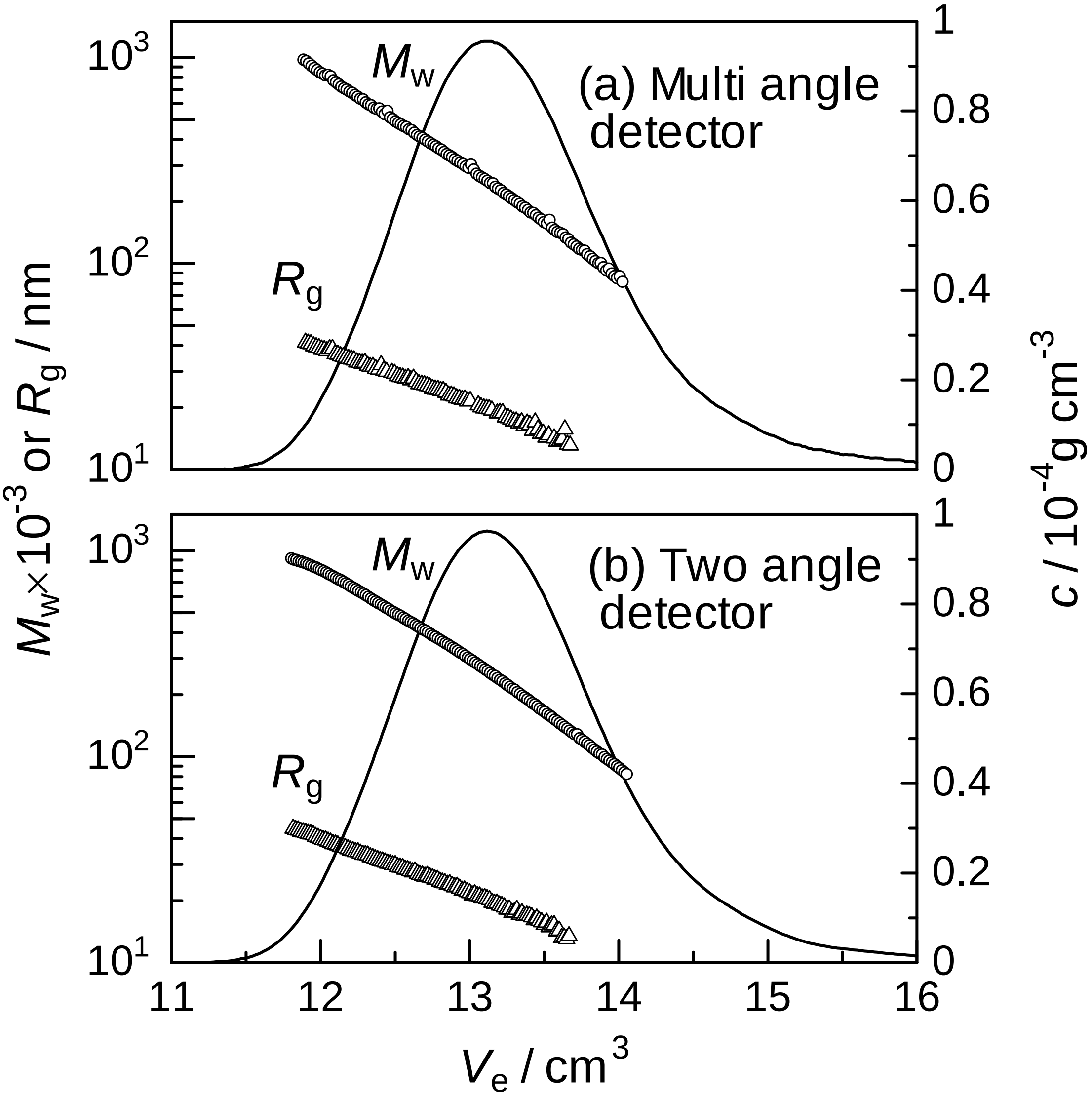

(a) Multi angle detector
(b) Two angle detector
M_w
R_g
$M_w \times 10^{-3}$ or R_g / nm
c / 10^{-4} g cm^{-3}
V_e / cm^3
10^1
10^2
10^3
0
0.2
0.4
0.6
0.8
1
11
12
13
14
15
16

Figure 2.

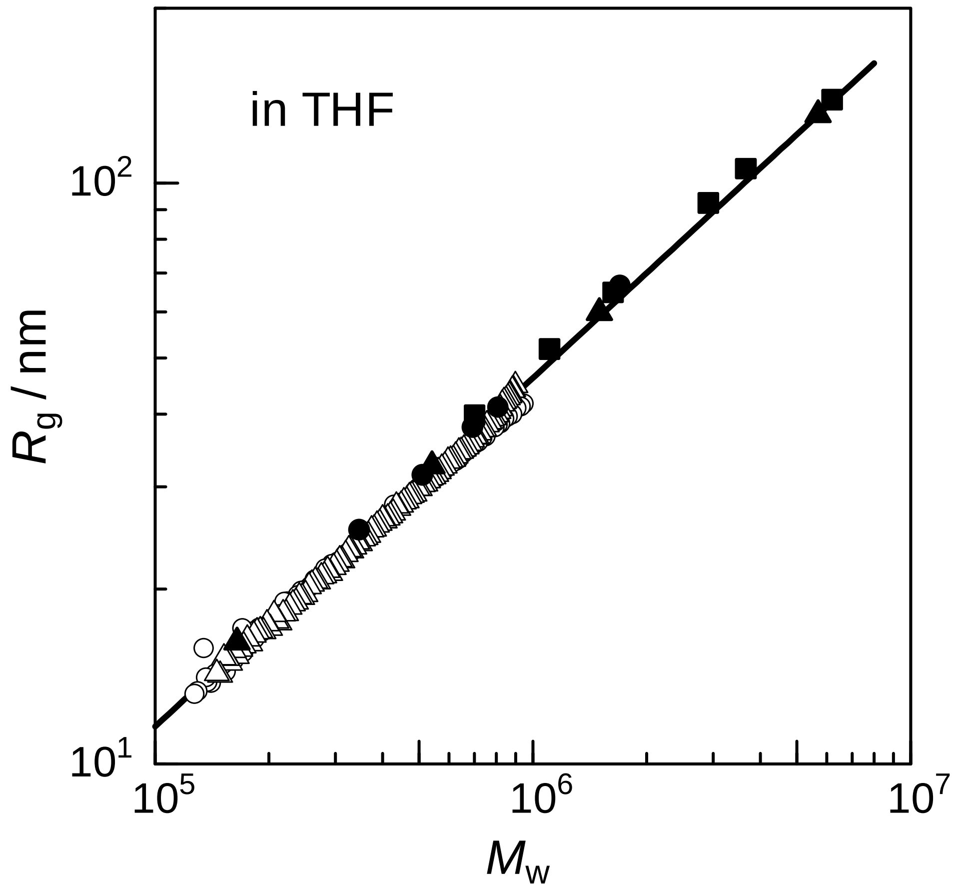


Figure 3.

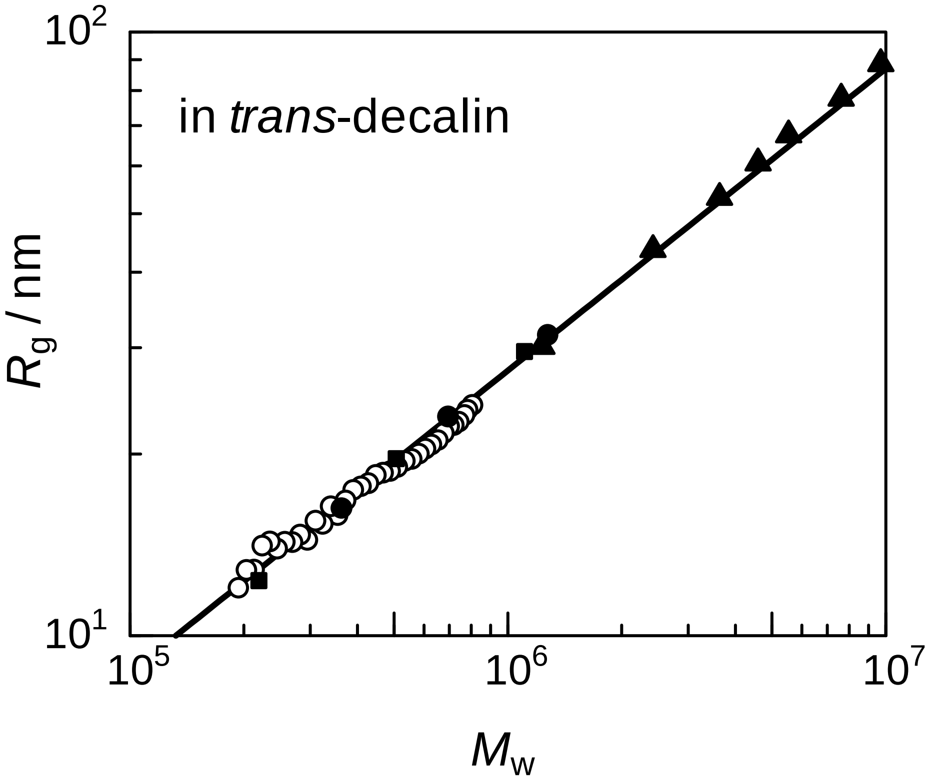
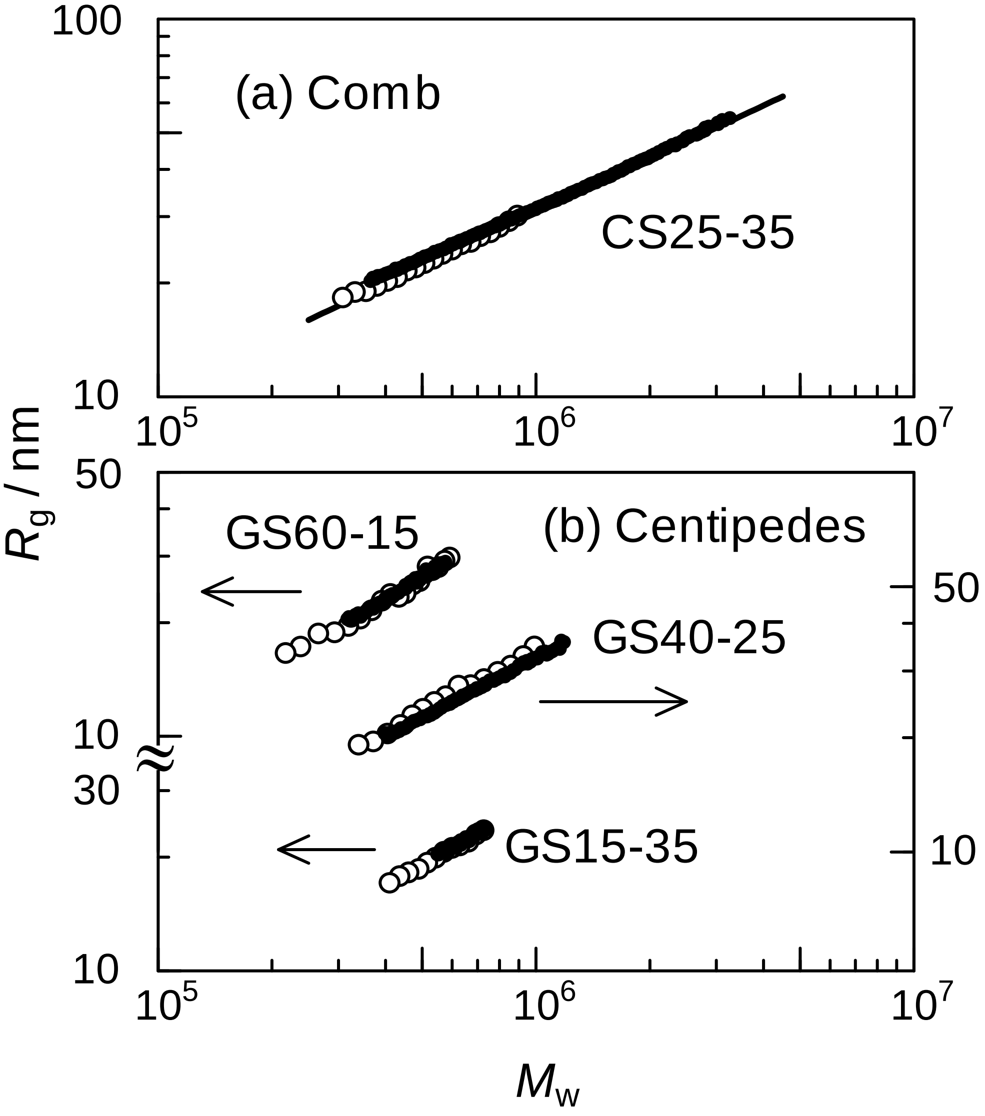


Figure 4.



100
10
(a) Comb
CS25-35
10^5
10^6
10^7
R_g / nm
50
10
30
10
GS60-15
(b) Centipedes
GS40-25
GS15-35
50
10
10^5
10^6
10^7
M_w

Figure 5.