



Study on the Concentration Effects in GPC: 6. A New Method for Determination of the Radius of Gyration for Macromolecules

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ABSTRACT

A method for determining the radius of gyration of macromolecules by the combination of GPC and viscosity measurements is presented. The molecular weight and molecular weight distribution of polymers were measured by GPC and the intrinsic viscosity was determined by capillary viscometry; then the radius of gyration for two sets of polystyrene samples (one set with the range of molecular weight, $\bar{M}_w = 7.4 \times 10^4 - 198 \times 10^4$ and molecular weight distribution, $\bar{M}_w/\bar{M}_n = 1.3-4.5$ and the other with $\bar{M}_w = 12.3 \times 10^6 - 40.2 \times 10^6$ and $\bar{M}_w/\bar{M}_n = 1.2-2.0$) were calculated from the relation of effective peak hydrodynamic volumes to the radius of gyration, which was derived from the theory of concentration effects for polydispersed polymers.

The results show that the values of the radius of gyration are in excellent agreement with those obtained from the light-scattering method.

1 INTRODUCTION

The mean square radius of gyration is usually determined from the angular dependence of the scattering intensity of large particles relative to small particles with eqn (1) by light scattering measurement¹ at small observation angles (θ). Increasingly lower observation angles must be used for increasing particle size. Due to the limited accuracy of its measurement, the method has a limited range of molecular weight. Thus it is very difficult to use one method for studying the relationship

between the radius of gyration and the molecular weight over a wide range. Therefore it is necessary to develop a new method for determining the radius of gyration which can be applied to a wide range of molecular weight.

$$P(\theta) = 1 - \frac{1}{3} \left(\frac{4\pi}{\lambda'_0} \right)^2 \langle R_G^2 \rangle \sin^2 \frac{\theta}{2} + \dots \quad (1)$$

where $\lambda'_0 = \lambda_0/n$ is the wavelength of light in the scattering medium, λ_0 is the wavelength of the scattering light in a vacuum and n is the refractive index of the solvent.

In this paper we attempt to develop a new method for determining the radius of gyration of macromolecules by the combination of GPC and viscosity measurements. The molecular weight and its distribution of polymers can be determined by GPC, and the intrinsic viscosity is measured by the capillary viscometer; then the radius of gyration $\langle r_n^2 \rangle^{1/2}$, $\langle r_w^2 \rangle^{1/2}$ and $\langle r_z^2 \rangle^{1/2}$ for macromolecules can be calculated from the relation of effective peak hydrodynamic volumes at infinite dilution to the radius of gyration which was derived from the theory of concentration effects for polydispersed polymer in GPC.² $\langle r_n^2 \rangle^{1/2}$, $\langle r_w^2 \rangle^{1/2}$ and $\langle r_z^2 \rangle^{1/2}$ are defined as

$$\frac{1}{\langle r_n^2 \rangle^{1/2}} = \left(\frac{\sum_i m_i}{\sum_i m_i r_i^2} \right)^{1/2}, \quad (2)$$

$$\langle r_w^2 \rangle^{1/2} = \left(\frac{\sum_i m_i r_i^2}{\sum_i m_i} \right)^{1/2} \quad \text{and} \quad \langle r_z^2 \rangle^{1/2} = \left(\frac{\sum_i m_i (r_i^2)^2}{\sum_i m_i} \right)^{1/2}$$

where m_i is the mass of the i th particle, and r_i is a vector from the mass centre to the i th particle.

2 PRINCIPLE

2.1 Characteristics of chromatograms by hydrodynamic volumes

According to Tung,³ the chromatograms of polymers may be characterized by the equation

$$F(v_e) = \int_0^\infty C(v)G(v - v_e) dv \quad (3)$$

where v is the elution volume; $F(v_e)$ is the response of a detector sensitive to the concentration; $C(v)$ is the distribution of polymer function of elution volume; $G(v - v_e)$ is the axial dispersion function of instrument and $\int_0^\infty F(v_e) dv_e$ is the total amount of polymer injected.

We assume that $G(v - v_e)$ is a Gaussian distribution function and the relation between the hydrodynamic volumes V_h and elution volumes v follows the relation

$$(v - v_e) = A \ln (V_h/V_{he}) \quad (4)$$

So it is possible to change the variables of elution volumes v to hydrodynamic volumes V_h and the concentration of polymers with elution volumes $C(v) dv$ is transformed to $C(V_h) dV_h$. Then we have

$$F(V_h) = \frac{1}{\sqrt{2\pi}} \frac{A}{\sigma} \int_0^\infty \frac{1}{V_h} C(V_h) \exp \{-A^2/2\sigma^2 \ln^2 (V_h/V_{he})\} dV_h \quad (5)$$

where $C(V_h)$ represents the true chromatograms of the sample. Thus the chromatograms are characterized by the hydrodynamic volumes.

2.2 Average effective hydrodynamic volumes of true polymers

We assume that the polymers have a Wesslau-type distribution function; then the distribution function $C(V_h)$ has the following form.

$$C(V_h) = \frac{1}{\sqrt{2\pi r^*}} \frac{1}{V_h} \exp \left\{ -\frac{1}{2r^*} \ln^2 (V_h/V_{he}) \right\} \quad (6)$$

where $r^* = (\sigma/A)^2$. Thus the three kinds of average effective hydrodynamic volumes may be obtained with the definition from eqn (6):

$$\langle V_{hnc} \rangle = \int_0^\infty \frac{V_h}{C(V_h)} dV_h \quad (7)$$

$$\langle V_{hwc} \rangle = \int_0^\infty V_h C(V_h) dV_h \quad (8)$$

$$\langle V_{hzc} \rangle = \int_0^\infty V_h^2 C(V_h) dV_h \quad (9)$$

2.3 Relation of effective hydrodynamic volumes of peak at infinite dilution to the radius of gyration

2.3.1 Effective hydrodynamic volumes of peak at infinite dilution

It is known that the effective average hydrodynamic volume is not a unique function of peak elution volumes for polydispersed polymers.

After introducing the correction for the polydispersity of molecular weight distribution and for hydrodynamic volume distribution, by our proposed method,² then the effective hydrodynamic volumes of peak at infinitive dilution for polydispersed polymers may be expressed by the three types of average values:

$$V_{\text{hnop}} = \langle V_{\text{hno}} \rangle / Q_{2n} = [\eta] \bar{M}_w Q_{1n} / Q_{2n}$$

$$V_{\text{hwop}} = \langle V_{\text{hwo}} \rangle / Q_{2w} = [\eta] \bar{M}_w Q_{1w} / Q_{2w}$$

and

$$V_{\text{hzop}} = \langle V_{\text{hzo}} \rangle / Q_{2z} = [\eta] \bar{M}_w Q_{1z} / Q_{2z}$$

2.3.2 Relation of hydrodynamic volumes of peak at infinite dilution to the radius of gyration

These relations were obtained from the Flory-Fox relationship.⁴ They are given below.

For monodispersed polymers

$$V_{\text{ho}} = V_{\text{hz}} = \langle r_z^2 \rangle^{1/2} \cdot \Phi \quad (10)$$

For polydispersed polymers

$$V_{\text{hnop}} = \langle V_{\text{hno}} \rangle / Q_{2n} = \langle r_n^2 \rangle^{1/2} / Q_{2n} \cdot \Phi = \langle r_n^2 \rangle_p^{1/2} \cdot \Phi \quad (11)$$

$$V_{\text{hwop}} = \langle V_{\text{hwo}} \rangle / Q_{2w} = \langle r_w^2 \rangle^{1/2} / Q_{2w} \cdot \Phi = \langle r_w^2 \rangle_p^{1/2} \cdot \Phi \quad (12)$$

and

$$V_{\text{hzop}} = \langle V_{\text{hzo}} \rangle / Q_{2z} = \langle r_z^2 \rangle^{1/2} / Q_{2z} \cdot \Phi = \langle r_z^2 \rangle_p^{1/2} \cdot \Phi \quad (13)$$

where V_{hnop} , V_{hwop} and V_{hzop} are the effective peak hydrodynamic volumes obtained by the number-, weight- and z-average method; $\langle r_n^2 \rangle_p^{1/2}$, $\langle r_w^2 \rangle_p^{1/2}$ and $\langle r_z^2 \rangle_p^{1/2}$ are the most probable radius of gyration obtained the number-, weight- and z-average hydrodynamic volume methods; \bar{M}_w is the weight-average molecular weight; $[\eta]$ is the intrinsic viscosity; Q_{1n} , Q_{1w} and Q_{1z} represent corrected factors for molecular weight distribution obtained by the method of the number-, weight- and z-average hydrodynamic volumes; Q_{2n} , Q_{2w} and Q_{2z} represent corrected factors for hydrodynamic volumes distribution obtained by the number, weight and z-average method; Φ is constant between radius of gyration and hydrodynamic volumes for macromolecules.

3 EXPERIMENTAL

Samples of polydispersed polymers were prepared by polymerization in our laboratory. Their molecular weights are in the range 7.4×10^4 – 195×10^4 and 12.3×10^6 – 40.2×10^6 .⁵

The dilute-solution viscosities in THF solvent were measured in an Ubbelohde viscometer at 25 °C. The intrinsic viscosities were obtained from extrapolation to zero concentration of the plot of η_{sp}/C vs C by least-squares computation (PS-THF; 25 °C; $[\eta] = 1.17 \times 10^{-2} M^{0.717}$).

The GPC measurements were made using a Waters 150 °C type chromatograph. The porosity range of this column set was ranged from 10^4 to 10^6 Å.

Purified THF was used as the carrier solvent at a flow rate of 1 ml/min; the injected quantity was 200 μ l. The temperature of measurement was 25 °C.

\bar{M}_w and $\langle r_z^2 \rangle^{1/2}$ were measured using the LS601 wide-angle photometer (Japan) in THF solvent at 25 °C.

4 RESULTS

The molecular characteristics of polydispersed PS, \bar{M}_w , \bar{M}_w/\bar{M}_n , Q_{1n} , Q_{2n} , Q_{1w} , Q_{2w} , Q_{1z} and Q_{2z} are given in Tables 1 and 2.

5 TREATMENT OF DATA

The experimental data in Tables 1 and 2 and Φ^\dagger were used to calculate $\langle r_z^2 \rangle_p^{1/2}$, $\langle r_w^2 \rangle_p^{1/2}$ and $\langle r_n^2 \rangle_p^{1/2}$ with eqns (11), (12) and (13). These values are listed in the Tables 1 and 2. It shows that

$$\langle r_n^2 \rangle_p^{1/2} = \langle r_w^2 \rangle_p^{1/2} = \langle r_z^2 \rangle_p^{1/2}$$

and these values are in agreement with the those obtained by the (light scattering) LS method. These plots are given in Figs 1 and 2 and a straight line passing through the origin was obtained. The results show that the eqns (11), (12) and (13) are rational; and the radii of gyration obtained by the method are the most probable values. The dependence of $\ln \langle r_w^2 \rangle_p^{1/2}$ on $\ln \bar{M}_w$ is given in Fig. 3. It shows that the radius of gyration increases with increasing molecular weight.

$\dagger \Phi_0 = 6.3 \times 10^{22}$ in Table 1; $\Phi_0 = 13.57 \times 10^{22}$ in Table 2;⁶ $\Phi = \Phi_0(1 - 2.63\varepsilon + 2.86\varepsilon^2)$; $\varepsilon = (2\alpha - 1)$; $\alpha = \text{Mark-Houwink constant}$.

TABLE I
Molecular Characteristics of Polydispersed PS

Sample	$\bar{M} \times 10^{-4}$	$[\eta]$ (ml/g)	\bar{M}_w/\bar{M}_n	$\langle r_z^2 \rangle^{1/2, a}$ (Å)	$\langle r_z^2 \rangle^{1/2, b}$ (Å)	Q_{1z}	Q_{2z}	$\langle r_w^2 \rangle^{1/2, c}$	Q_{1w}	Q_{2w}	$\langle r_n^2 \rangle^{1/2, d}$ (Å)	Q_{1n}	Q_{2n}
PS-1	7.30	34.05	1.80	140	159	3.133	4.544	159	1.1419	1.6563	159	0.4162	0.6038
PS-2	8.40	42.12	1.95	110	176	3.659	5.584	176	1.1627	1.7741	176	0.3694	0.5636
PS-3	8.90	43.00	2.13	187	177	4.344	7.010	177	1.1861	1.9138	177	0.3238	0.5225
PS-4	9.60	44.02	1.84	161	189	3.269	4.808	189	1.1475	1.6879	189	0.4028	0.5925
PS-5	18.80	60.95	3.47	216	231	11.212	24.638	231	1.3242	2.9098	231	0.1564	0.3436
PS-6	22.70	82.60	2.48	260	286	5.838	10.373	286	1.2275	2.1809	286	0.2581	0.4585
PS-7	47.20	109.54	4.52	445	360	18.739	48.670	360	1.4056	3.6514	360	0.1054	0.2737
PS-13	105.48	209.00	3.71	642	608	12.768	29.270	608	1.3443	3.0818	608	0.1415	0.3244
PS-8	143.00	268.01	3.82	767	727	13.514	31.558	727	1.3530	3.1600	727	0.1355	0.3164
PS-9	195.00	385.70	3.12	949	950	9.120	18.736	950	1.2928	2.6560	950	0.1833	0.3765

^a Value of $\langle r_z^2 \rangle^{1/2}$ obtained by LS methods.

^{b, c, d} Values of $\langle r_z^2 \rangle^{1/2}$ obtained from eqns (11), (12), (13) respectively.

TABLE 2
Molecular Characteristics of Polystyrenes

Sample ^a	$\bar{M}_w \times 10^{-6}$	\bar{M}_w/\bar{M}_n	$\langle S_z^2 \rangle^{1/2 b}$ (Å)	$\langle S_z^2 \rangle^{1/2 c}$ (Å)	Q_{1z}	Q_{2z}	$\langle S_w^2 \rangle^{1/2 d}$ (Å)	Q_{1w}	Q_{2w}	$\langle S_n^2 \rangle^{1/2 e}$ (Å)	Q_{1n}	Q_{2n}
TH ₂ -181F1	35.6	1.5	4940	4550	2.208	2.853	4550	1.097	1.418	4550	0.545	0.705
TH ₂ -181F2	40.2	1.2	5150	5132	1.427	1.602	5132	1.043	1.170	5132	0.761	0.855
TH ₂ -181F4	29.7	1.2	3920	3490	1.427	1.602	3490	1.043	1.170	3490	0.761	0.855
TH ₂ -181F6	23.4	1.2	3490	3760	1.427	1.602	3760	1.043	1.170	3760	0.761	0.855
TH ₂ -181F9	12.3	1.2	2490	2590	1.425	1.602	2590	1.043	1.170	2590	0.761	0.855
TH ₂ -181F	24.4	2.0	3700	3452	3.870	6.004	3452	1.172	1.818	3452	0.355	0.550

^a TH₂-181F denotes the first fraction of the second thermal polymerization at -18 °C. This notation is followed by the fraction number.

^b Value of $\langle S_z^2 \rangle^{1/2}$ obtained by LS method in toluene at 20 °C.

^{c,d,e} Values of $\langle S_z^2 \rangle^{1/2}$ obtained from eqns (11), (12), (13) respectively.

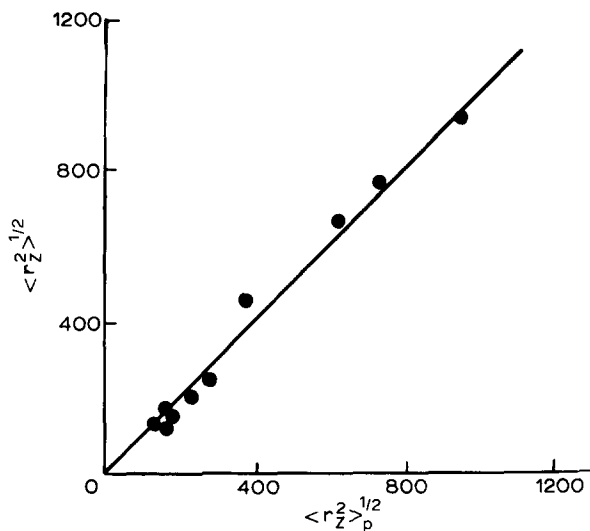


Fig. 1. Comparison of $\langle r_z^2 \rangle^{1/2}$ (Å) by LS method with $\langle r_z^2 \rangle_p^{1/2}$ (Å) from eqn (11) for polydispersed PS.

6 CONCLUSION

A new method for determination of radius of gyration for macromolecules is proposed.

It is shown that the radii of gyration obtained by this method are the most probable radii of gyration for macromolecules, and are in excellent agreement with those obtained from the LS method.

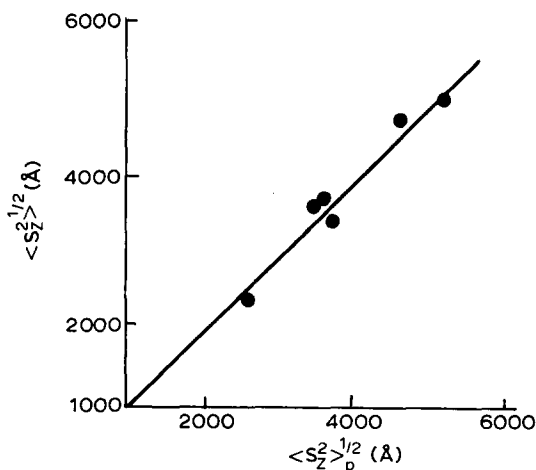


Fig. 2. Comparison of $\langle S_z^2 \rangle^{1/2}$ by LS method with $\langle S_z^2 \rangle_p^{1/2}$ from eqn (11) for polydispersed PS.

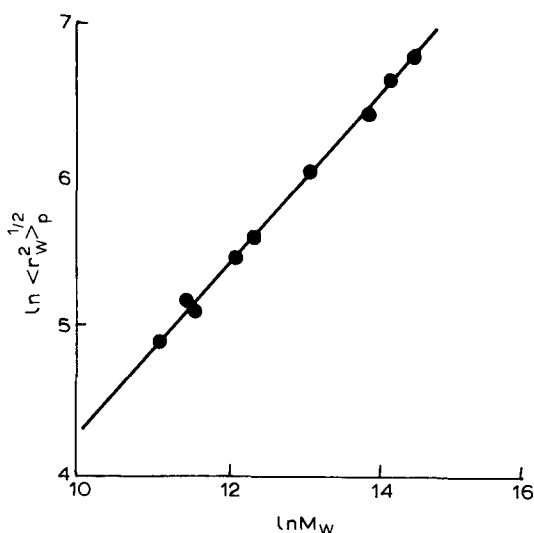


Fig. 3. Logarithmic plot of $\langle r_w^2 \rangle_p^{1/2}$ (Å) against molecular weight for polydispersed PS.

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