

MEASUREMENT OF UNPERTUBED DIMENSION OF POLYMER*

TIAN Bingshou (田炳寿)

(Department of Chemistry, Wuhan University, Wuhan)

ABSTRACT

The unperturbed dimension of polymer is measured by a gel permeation chromatography (GPC) coupling with viscometer. The intrinsic viscosities of the fractions are measured with an automatic viscometer, and the molecular weight of the fractions are calculated based on the universal calibration. Using a theoretical expression with linearized Mark-Houwink's equation an unperturbed dimension is obtained by extrapolating to the unperturbed state. The results agree with the values measured by conventional method comparisons with various theoretical expressions are made.

INTRODUCTION

An unperturbed mean-square end to end distance ($\bar{h}_0^2$) of a polymer is a characteristic parameter which directly reflects the conformation of the chain. The conformation will influence many properties of polymer both in the bulk state and in solution.

The measuring methods may be divided into two kinds^[1-3]. First, it may be determined directly in θ solvent. This seems very simple, but it is not easy to find θ solvent for some polymer. Second, it may be measured in thermodynamically good solvent. Several samples of narrow molecular weight distribution and different molecular weight (generally being fractionated) with the same chemical component have been used to measure the molecular weight and the intrinsic viscosity simultaneously, then the unperturbed dimension is obtained from the intercept of the appropriate plot^[4, 5]. But considerable time and labour are needed in such measurement. Recently, using GPC coupling with a Low-Angle Laser Light Scattering Photometer have been reported^[6, 7]. Some authors have used it to measure the molecular weight of each fraction^[8]. The intrinsic viscosity of corresponding fraction can be calculated in accordance with the universal calibration, and the linear section of the curve may be extrapolated to unperturbed state, then the parameter K_0 is obtained.

EXPERIMENTAL

In the previous work we have reported upon GPC combined with automatic viscometer^[9].

The chromatogram column was composed of three stainless steel tubes (length: 1 m; inside diameter: 1 cm). It was filled with silica gel NDG-1,2,3,4,5,6 L. The logarithmic values of molecular weight from 2×10^3 to 1×10^6 was plotted against the elution volume and a straight line obtained.

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The theoretical number of plates is about 1843 per meter. Other experimental conditions are: the column and differential refractometer have been reflowed with constant temperature (25°C) water, temperature in the viscometer tube during flowing can be measured within ± 0.005 s, flow rate: 1 ml/min, solvent: THF, sample injected is from 2 to 6 mg.

The experimental chromatogram was obtained with the GPC- $[\eta]$ apparatus. Each intermediate compartment was divided into four equal parts. The height of each part was read with a magnifying glass then calculated the mean-height, $\bar{h}_i$. The values was made smoothly, in the case of narrow distributed sample, using the method of five dots three times^[10], for broad sample, using the seven dots three times^[11]. After this, the correction of the spreading was made through Ishige's numerical method^[12]. The relationship between h and elution volume V is

$$h(V) = 9.8744 - 0.8601V + 0.01597V^2 - 0.000121V^3 \quad (1)$$

The flow time of each fraction in the viscometer was measured automatically. The corresponding $[\eta]_i$ was calculated with the following equation

$$[\eta]_i = \frac{1}{C} \left(\frac{\eta_p - \ln \eta_r}{0.5} \right)^{\frac{1}{2}} \quad (2)$$

Before calculating the value of $[\eta]_i$, two corrections must be made. Since the syphon is behind the refractometer, a correction for the volume of the connecting tube should be made. If we ignored the diffusion of solution in the tube, this volume between the syphon and refractometer can be measured by injecting the fluid from the end connecting to refractometer.

The residual correction of a syphon is given by the following equation (see Appendix).

$$\bar{h}_{i,c} = \bar{h}_i - \frac{1}{2} (\bar{h}_{i+1} + \bar{h}_i - 2\bar{h}_{i-1}) \Delta H - \frac{1}{2} (\bar{h}_i + \bar{h}_{i-1} - 2\bar{h}_{i-2}) \Delta H^2 - \dots \quad (3)$$

ΔH is generally small. The term after ΔH^2 may be neglected. For our system, ΔH is about 0.04.

After correction, the results are listed in Table 1 for several samples of polymer. For

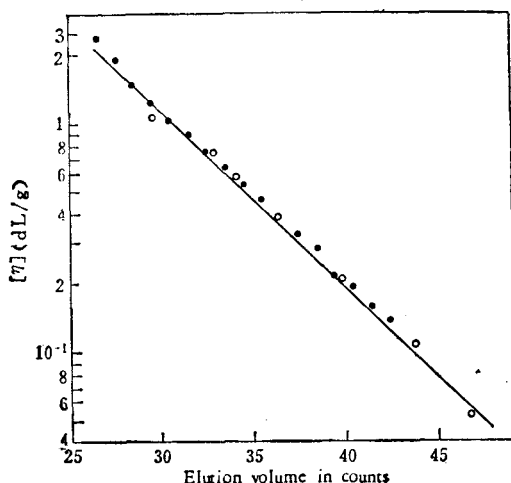


Fig. 1 The relation between the intrinsic viscosity and the mean elution volume of PS
○ The standard sample; ● The broad sample.

Table 1

Samples	$M \times 10^{-3}$	M_w/M_n	GPC - $[\eta]$				Conventional method $[\eta]$	Error (%)
			$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	$[\eta](\text{dl/g})$		
PS*	434	—	456	383	1.19			
	305	—	278	208	1.34			
	200	1.14	187	161	1.13			
	100	1.07	88.2	79.9	1.10			
	30	1.09	31.5	28.6	1.10			
	10	—	10	9.3	1.08			
	5	1.14	5.34	4.55	1.17			
PS (unfractionated)	—	—	220.5	93.2	2.37	0.63	0.65	-3.1
PMMA (atactic)	—	—	529.1	303.7	1.74	4.66	4.54	2.6

* Standard samples.

samples of PS (standard and broad), the relation between their intrinsic viscosities and the mean elution volumes are represented in Fig. 1.

The calibration and the universal calibration of PS are all straight lines from the values in Table 1. The equation as follows:

$$\log M = 9.3572 - 0.1217V \quad (4)$$

$$\log M[\eta] = 13.4827 - 0.1819V \quad (5)$$

RESULTS AND DISCUSSION

This method belongs to the second kind as stated above. Of each fraction was given by an automatic viscometer. The relevant molecular weight was calculated from the calibration or the universal calibration. The linear section is extended to the unperturbed state from the curve plotted with the theoretical expression. The unperturbed parameter K_θ is obtained. Then $\bar{h}_0^2$ is given by

$$K_\theta = \Phi(\bar{h}_0^2/M)^{3/2} \quad (6)$$

where $\bar{h}_0^2$ is an unperturbed mean-square end to end distance; Φ is an universal constant. From their model Fox and Flory^[14] derived an equation (7)

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + K_\theta^{5/3}C_T(M/[\eta]) \quad (7)$$

where

$$C_T = 2\psi_1 C_M \left(1 - \frac{\theta}{T} \right) = (\alpha_r^5 - \alpha_r^3) M^{1/2}$$

$$\alpha_r = (\bar{h}^2/\bar{h}_0^2)^{1/2} \text{ or } (\bar{r}^2/\bar{r}_0^2)^{1/2}$$

here α_r is the ratio of rms end to end distance for the chain in a good solvent and in the unperturbed state.

Stockmayer and Fixman's equation is

$$[\eta]/M^{1/2} = K_\theta + 0.51\Phi BM^{1/2} \quad (8)$$

where $B = \beta/M_s^2$, here CM is the molecular weight of a chain segment; β is the binary cluster integral.

The experimental results deviate from the lines of the preceding expressions in the high molecular weight range. Several authors have, therefore, presented various corrections for making the relation of the viscosity and molecular weight to become a straight line. For example, Bondos and Benoit^[15] have modified eq. (8) into

$$[\eta]/M^{1/2} = K_\theta + 0.51\Phi BM^{1/2}(1 - DM^{1/2}) \quad (9)$$

If D is known, the relation between $[\eta]/M^{1/2}$ and $M^{1/2}(1 - DM^{1/2})$ should give a straight line. They have given D values of six different systems.

Berry's equation is^[16]

$$([\eta]/M^{1/2})^{1/2} = K_\theta^{1/2} + 0.42K_\theta^{3/2}B(\bar{r}_0^2/M)^{-3/2}(M/[\eta]) \quad (10)$$

Inagaki, Buzuki and Kurata's eq. (11)

$$[\eta]^{4/5}/M^{2/5} = 0.786K_\theta^{4/5} + 0.950K_\theta^{4/5}K^{2/5}M^{1/5} \quad (11)$$

and Cowie eq. is^[17]

$$[\eta]/M^{1/2} = (\varphi^{(*)}/\varphi_0)K_\theta + 0.9166(\varphi^{(*)}/\varphi_0)K_\theta K^{7/10}M^{7/10} \quad (12)$$

where

$$K = 0.33 B (M/\bar{r}_0^2)^{3/2}$$

$$s = (2\alpha - 1)/3$$

$$\varphi(s) = (1 - 2.63s + 2.86s^2)$$

here α is the Mark-Houwink exponent.

The values of K_θ are listed in Table 2, for the standard samples PS and a broad distributed PS, obtained by the above expressions.

Table 2 The unperturbed parameter K_θ of PS (standard and broad) and PMMA (atactic)

Samples	eq. (7)	eq. (8)	eq. (9)	eq. (10)	Ref.
PS (standard)	—	9.40×10^{-4}	—	—	7.8×10^{-4} 8.0×10^{-4}
PS (broad)	8.14×10^{-4}	8.43×10^{-4}	9.20×10^{-4}	8.90×10^{-4}	
PMMA (atactic)		5.60×10^{-4}			5.6×10^{-4}

Using the parameters in Table 2, $(\bar{h}_0^2/M)$ calculated from eq. (6), are from 4.29 to 4.76 $\times 10^{-17}$, and the reference values are 4—5 $\times 10^{-17}$. This shows that the unperturbed dimension of polymer obtained with the GPC- $[\eta]$ apparatus are agreed with other methods, and this

method does not need polymer fractionated with precipitating method, and will save both time and labour.

We have compared the results with various theories (see Table 2). From Fig. 2—3, it is apparent that the experimental values are deviated from a straight line in the high molecular weight range. The relative percentage error is about 6%.

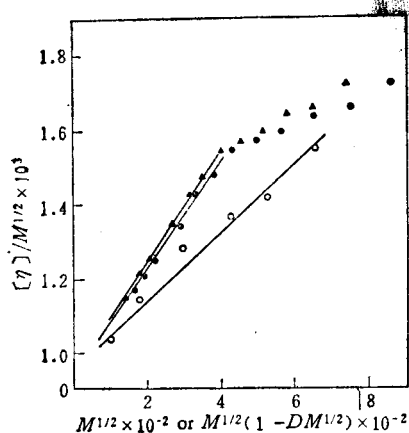


Fig. 2 Estimation of the unperturbed dimension for PS

- The method of Stockmayer and Fixman;
- ▲ The method of Bondos and Benoit;
- The standard sample.

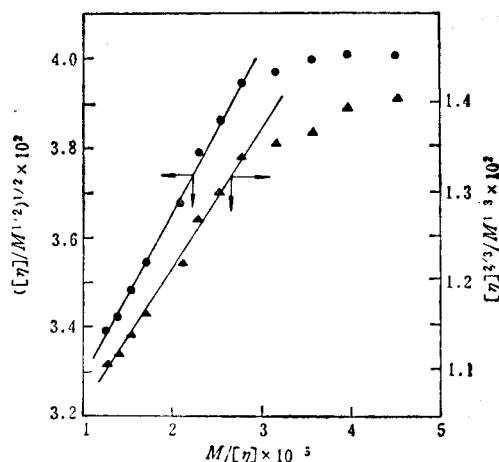


Fig. 3 Estimation of the unperturbed dimension for PS

- The method of Berry;
- ▲ The method of Flory and Fox.

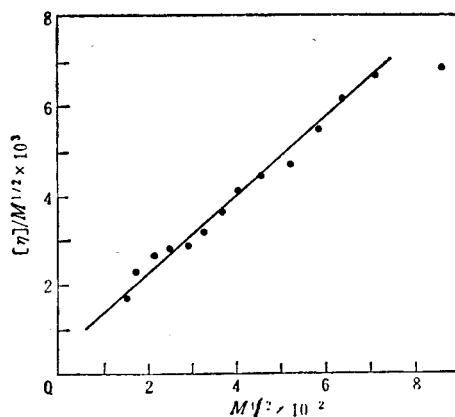


Fig. 4 Estimation of the unperturbed dimension for PMMA (atactic) using the method of Stockmayer and Fixman

APPENDIX

The correction of the residual volume in the syphon. Assume that: m is injected weight of polymer;

V_s is the volume of the syphon;

ΔV is residual volume in the syphon;

h_i is the chromatogram height of count i th;

$\bar{h}_i$ is a mean-height from $i-1$ th to i th;

$m_i, m_{i,c}$ is content of polymer correcting before and after in i th, respectively.

We have approximately

$$m_{i,c} = m_i + m_{i-1,c} \frac{\Delta V}{V_s} - \frac{\bar{h}_{i+1}}{\sum h_i} m \frac{\Delta V}{V_s} \quad (1')$$

$$m_i = \frac{\bar{h}_i}{\sum h_i} m = G \bar{h}_i, \quad \text{lets } \Delta V/V_s = \Delta H$$

$$m_{i,c}/G = \bar{h}_{i,c} = \bar{h}_i - (\bar{h}_{i+1} - h_{i-1,c}) \Delta H \quad (2')$$

It is known from the above expression which corrected the concentration in a syphon to become height in the chromatogram. h_{i+1} is a chromatogram height for $i+1$ th syphon. $\bar{h}_{i+1}$, moreover, is the mean value of $i+1$ th.

The approximation

$$\bar{h}_{i+1} = (\bar{h}_{i+2} + \bar{h}_{i+1})/2 \quad \text{holds}$$

for $\bar{h}_{i+1,c}$, that is

$$\bar{h}_{i+1,c} = \bar{h}_{i+1} - \left(\frac{\bar{h}_{i+2} + \bar{h}_{i+1}}{2} - \bar{h}_{i,c} \right) \Delta H \quad (3')$$

Substituting (2') into (3'), we got the equation (4')

$$\bar{h}_{i+1,c} = \bar{h}_{i+1} - \frac{1}{2} (\bar{h}_{i+2} + \bar{h}_{i+1} - 2\bar{h}_i) \Delta H - \frac{1}{2} (\bar{h}_{i+1} + \bar{h}_i - 2\bar{h}_{i-1}) \Delta H^2 - \dots \quad (4')$$

This is equation (3) in this paper.

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