

Characterization of Randomly Branched Polymers by Svedberg Equation

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Abstract

A new characterization method, which allows us to obtain molecular weight distribution curves of the branched polymers, is proposed by using the Svedberg equation. The validity of the method was tested for three samples of randomly branched polydisperse polystyrene.

It was experimentally ascertained that the distribution curve of the molecular weight was well established and the average molecular weights derived from the distribution curve were in good agreement with those observed within experimental error.

1 Introduction

Branching effect on dilute solution properties of branched polymer is often overlapped with the effect of molecular weight distribution, and it is very difficult to estimate the mutual effects separately from each other. One of the reasons is the fact that the preparation of branched polymer sample with narrow molecular weight distribution is considerably difficult.

Since gel-permeation chromatography (GPC) has been used in many fields of polymer characterization, studies of branched polymer also have been developed experimentally and theoretically by many workers¹⁻⁵).

In the previous papers⁶⁻⁷), a new method for characterizing randomly branched polydisperse polymers has been proposed, which is based on sedimentation velocity and diffusion measurements. According to the method, the distribution curve of the molecular weight is well established, and the sedimentation and diffusion constants vs. molecular weights relationships are obtained without any effect of molecular weight distribution.

In the present paper, an another method which enables us to obtain the molecular weight distribution of the branched polymer is proposed, whose experimental procedures required are not laborious compared with those required in the previous method.

2 Theoretical

2.1 Outline of Previous Method

From measurements of sedimentation velocity and diffusion on branched polymer sample at the theta temperature, integral weight distribution curves of sedimentation constant and diffusion constant, S and D , are obtained by the ordinary methods⁸⁻⁹) proposed for linear polymers. (See Fig. 1.)

These curves can be readily converted into the integral distribution curves of the apparent molecular weights, M_S and M_D , by the following equations, which are empirical relations

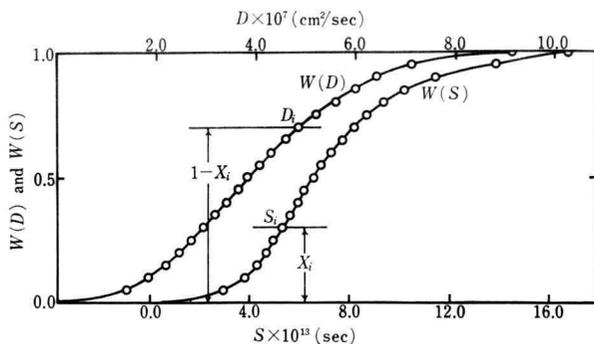


Fig. 1. Integral weight distribution curves of diffusion constant D and sedimentation constant S for **PSB-3**. Sedimentation constant S_i at the integral value X_i on $W(S)$ and diffusion constant D_i at the integral value $1-X_i$ on $W(D)$ belong to the same molecular species i .

valid only for linear polymers,

$$S = K_{S\theta} M_S^{0.5} \quad (1)$$

$$D = K_{D\theta} M_D^{-0.5} \quad (2)$$

where $K_{S\theta}$ and $K_{D\theta}$ are constants depend upon the polymer-theta solvent system employed.

The real molecular weight M for each set of points with the same integral values on the integral distribution curves of the apparent molecular weights, $W(M_S)$ and $W(M_D)$, is calculated by the equation

$$M = (M_S \cdot M_D)^{0.5}. \quad (3)$$

Thus, integral distribution curve of the real molecular weight, $W(M)$, is obtained as shown in Fig. 2.

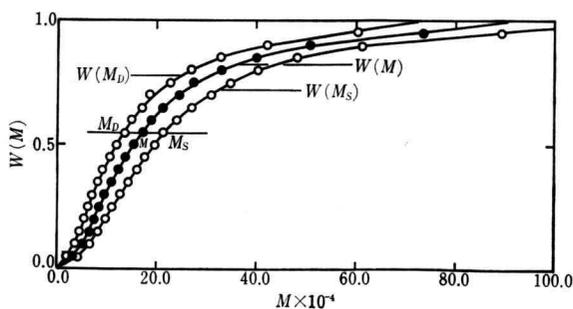


Fig. 2. Molecular weight distribution curve (**MWDC**) for **PSB-3** obtained from the previous method. $W(M_D)$, apparent **MWDC** obtained from diffusion method; $W(M_S)$, apparent **MWDC** obtained from sedimentation velocity method; $W(M)$, real **MWDC** calculated by $M = (M_S \cdot M_D)^{0.5}$.

On the other hand, the branching parameter h is estimated at each given integral point

of molecular weight distribution curve by the following equation

$$h^2 = (R_b / R_l)^2 = (M_D / M_S)^{0.5} \quad (4)$$

Here R_b and R_l are the hydrodynamic radii of branched polymer and linear polymer, respectively, having the same molecular weight. The branching parameter h vs. molecular weight M relationship provides a useful information on the type of branching.

In the method described above, we must have the relationships of Eqs. (1) and (2), and it is essential that the constant values $K_{S\theta}$ and $K_{D\theta}$ are sufficiently accurate. It is, however, very laborious to obtain those values about monodisperse system at the theta point.

2.2 Description of Present Method

An another method which remedies the above mentioned difficulty is now proposed. If the partial specific volume of the polymer in the solution is not affected by chain branching, then Eq. (3) leads to the well-known Svedberg equation¹⁰

$$M = SRT / D (1 - \bar{v} \rho_0) \quad (5)$$

where R is the gas constant, T the absolute temperature, \bar{v} the partial specific volume of the solute and ρ_0 the density of the solvent. In order to obtain the molecular weight distribution by Eq. (5), the following procedure was applied.

The value of sedimentation constant S_i at the integral value X_i on $W(S)$ corresponds to that of diffusion constant D_i at the integral value $1 - X_i$ on $W(D)$. (See Fig. 1.) S_i and D_i belong to the same molecular species i . Therefore, molecular weight M_i at the integral value X_i on $W(M)$, calculated by substitution of values of S_i and D_i into Eq. (5), also belongs to the same molecular species i . Then, the molecular weight distribution is obtained by joining a series of M_i .

3 Experimental

Three samples of copolymer of styrene and divinylbenzene, *PSB-3*, *PSB-4* and *PSB-5*, were used in the present study. These samples were prepared by the radical mechanism, and are randomly branched polydisperse polymers with long-chain branching. The polymerization conditions employed are shown in Table 1. Measurements of sedimentation velocity and diffusion were carried out in cyclohexane at 35°C, which is the theta temperature of this polymer-solvent system.

Table 1. Polymerization conditions of branched polymers.

Sample	Styrene (ml)	Divinylbenzene (ml)	AIBN* (g)	Temp. (°C)	Time (hours)	Conv. (%)
PSB-3	30	0.027	0.033	70	7.0	26
PSB-4	30	0.028	0.038	70	6.0	25
PSB-5	60	0.028	0.024	70	7.5	21

* AIBN = azobisisobutyronitrile.

3.1 Sedimentation Velocity Measurements

Sedimentation velocity measurements were carried out by using a Hitachi Ultracentrifuge.

A Schlieren optical system was employed and the rotor speed was 43,700 rpm for each polymer sample. Weight distribution curves of sedimentation constants were obtained by the standard method⁸⁾ proposed for linear polymers with the corrections¹¹⁾ due to pressure, diffusion and concentration effects.

3.2 Diffusion Measurements

Diffusion measurements were carried out by using a Hitachi *HTB*-type electrophoresis apparatus with Schlieren optics. A new type of diffusion cell¹²⁻¹³⁾, equipped with an apparatus for boundary formation, was used. Diffusion constants, extrapolated to infinite dilution, were calculated by the area-method and moment-method, and weight distribution curves of diffusion constants were obtained according to Gralén method¹⁴⁾.

3.3 Light-Scattering Measurements

Light-scattering measurements were carried out in methylethylketone (*MEK*) at 35°C for the light of 436 nm wavelength by using a Shimadzu *PG-21* type light-scattering photometer with a cylindrical cell. The refractive index increment was 0.240 ml/g in *MEK* at 35°C for randomly branched polystyrene. The value of refractive index of *MEK* was 1.388 at 436 nm¹⁵⁾. The weight-average molecular weights obtained, M_w , are shown in Table 2.

3.4 Osmotic Pressure Measurements

Osmotic pressure measurements were carried out in *MEK* at 35±0.001°C by using a modified Zimm-Myerson type osmometer with a gel cellophane membrane. The dynamic-osmotic method was employed in the measurements. The number-average molecular weights obtained, M_n , are shown in Table 2.

4 Results and Discussions

As stated above, the method is based upon the assumption that the partial specific volume \bar{v} of branched polymer must be equal to that of linear polymer. The validity of this assumption was experimentally ascertained in the previous paper⁷⁾, and it was found that the observed values of \bar{v} were 0.934 cm³/g for both linear and branched polystyrenes in cyclohexane at 35°C. Therefore, use of the method is justified for determination of the molecular weight distribution of branched polymer.

Examples of weight distribution curves of sedimentation constant as well as of diffusion constant are shown in Fig. 1. The molecular weight distribution curve $W(M)$, determined by the procedure described in the theoretical section, was obtained as shown in Fig. 3.

A diffusion curve does not directly represent the molecular weight distribution. Therefore, suitable distribution function should be assumed analytically. In the present study, Gralén function¹⁴⁾, which is well expressible to linear polystyrenes¹⁶⁾ polymerized by radical mechanism, was utilized for branched polystyrenes. Although the present samples were also polymerized by radical mechanism, if the distribution function of the molecular weight may be fairly affected by chain branching, experimental results may not be valid. This will be a weak point and applicable limitation of the present method. The values of constants used in Eq. (5) are as follows: $R=8.314 \times 10^7$ erg.mol⁻¹.deg⁻¹, $T=308.15$ deg, $\rho_0=0.7634$ g/cm³

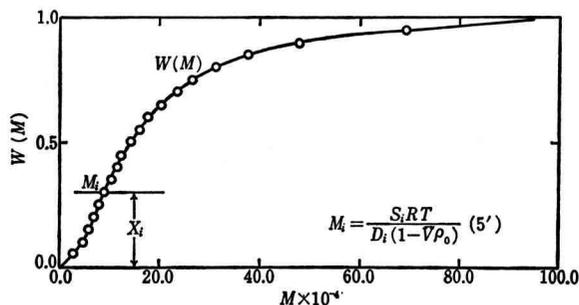


Fig. 3. Integral weight distribution curve of molecular weight for **PSB-3** according to Eq. (5). Molecular weight M_i at the integral value X_i on $W(M)$ is calculated by substitution of S_i and D_i in Fig. 1 into Eq. (5').

and $\bar{v}=0.934 \text{ cm}^3/\text{g}$.

Number-average and weight-average molecular weights, calculated from the distribution curves, are shown in Table 2 with the results of osmotic pressure and light-scattering measurements. The calculated values are in good agreement with those obtained by the experiment. The same table also lists the average molecular weights derived from the previous method (by Eq. (3)).

It may be seen that the values of M_w and M_n calculated by Svedberg equation are smaller about 8% than those obtained by Eq. (3) on each polymer sample. The slight difference in the molecular weights can be considered the following reason. The substitution of Eqs. (1) and (2) into Eq. (5) yields

$$RT (K_{S\theta} / K_{D\theta}) / (1 - \bar{v} \rho_0) = 1. \quad (6)$$

Eq. (6) is an alternative expression of Svedberg equation. Using the numerical values of $K_{S\theta}=1.48 \times 10^{-15} \text{ sec (mol/g)}^{0.5}$ and $K_{D\theta}=1.43 \times 10^{-4} \text{ (cm}^2/\text{sec) (g/mol)}^{0.5}$, which were used in the previous method, the left-hand side of Eq. (6) is then calculated at 0.924. It makes a

Table 2. Values of molecular weights.

Sample	$M_w \times 10^{-4}$		$M_n \times 10^{-4}$	
	This method	Observed*	This method	Observed**
PSB-3	24.2 (26.2)	28.0	11.1 (12.0)	14.2
PSB-4	20.0 (21.7)	22.4	9.0 (9.7)	8.4
PSB-5	35.8 (38.8)	39.5	24.6 (26.6)	27.4

The values in parentheses were calculated from the previous method.

* Light-scattering measurement

** Osmotic pressure measurement

difference about 8%. Thus, the deviation of this value from unity causes the difference between the molecular weights calculated by Eq. (3) and those calculated by Svedberg equation. In any case, the difference in molecular weights seems to be within experimental error.

From the experimental results, it may be concluded that the present method is very simple and useful for estimating molecular weight distribution of randomly branched polymer. However, branching degrees can't be straightforwardly obtained from the present method. Further investigations are in progress on this problem.

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