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# Characterization of Polystyrene in Methyl Ethyl Ketone by Small-Angle X-Ray Scattering

By

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Molecular and thermodynamic properties of polystyrene in methyl ethyl ketone were studied by a small-angle X-ray scattering with a Kratky camera. The molecular weight, radius of gyration, second virial coefficient, mass per unit length, hydrodynamic length, radius of gyration of cross section, persistence length, and radius of cross section were estimated. Some of these values were compared with the values determined by other methods. Both values agreed well each other.

## 1. Introduction

It is well known that the molecular and thermodynamic parameters of solute polymer can be obtained from light scattering or small-angle X-ray scattering. While the former is done as routine work now, the latter still has some experimental difficulties. In particular, since the excess scattering from polymer molecules, which is obtained by subtracting the scattered intensity of the solvent from that of the solution, in small-angle X-ray scattering is much smaller than that in light scattering, it is very difficult to determine the intensity of excess scattering of polymer with good accuracy. As has been pointed out by Kratky et al.,<sup>1)</sup> one of the difficulties is to minimize the fluctuation of the intensity of small-angle X-ray scattering. In spite of this difficulty, small-angle X-ray scattering is very important, because it enables us to measure the quantities which cannot be measured by light scattering, e.g. the molecular weight of oligomers and the geometrical shape of polymer molecules.<sup>2)</sup>

For this reason, many biopolymers in solutions have been studied by small-angle X-ray scattering. The characterization of synthetic polymer, on the other hand, has been published by only a few authors.<sup>3,4)</sup> The purpose of this paper is to characterize the synthetic polymer (styrene oligomer) in solution by small-angle X-ray scattering.

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## 2. Experimental

Monodisperse polystyrene (batch no. 12b) manufactured by Pressure Chemical Co., whose nominal molecular weight is 2,100 and  $M_w/M_N < 1.10$ , was used as a sample. As a solvent, spectral grade methy ethyl ketone (MEK) was used without further purification. The  $\theta_L$ -temperature of polystyrene in MEK is 145.7°C.<sup>5)</sup>

All measurements were made with a Kratky camera.<sup>6,7)</sup> As the X-ray source, a Rigaku Denki X-ray generator CN4032A2 with a Phillips broad focus Cu-tube (PW 2103-01) operated at 45 kV and 35 mA was used. The diameter of the tube window is larger than the length of the target, which means that a so-called "open beam" collimation was used.<sup>7)</sup>

Before the measurement, the stabilities of the high voltage and tube current of the generator were checked and found to be better than 0.015% and 0.008% for a week, respectively. The temperature of cooling water for the target affects the scattered intensity appreciably.<sup>7)</sup> An example of the influence of the temperature of cooling water on scattered intensity is shown in Figure 1. We used service water, the iron rust in which was eliminated by a filter, and whose temperature was maintained at  $18 \pm 1^\circ\text{C}$ , as the cooling water for the target.

For determination of the scattered intensity, a scintillation counter was used in connection with a pulse-height analyser focused on the  $\text{CuK}\alpha$  line (1.54 Å) and a 10  $\mu$  Ni filter to eliminate  $\text{CuK}\beta$ . The stability of the counting device was also checked by means of a radioactive calibration sample  $\text{Fe}^{55}$ , and the measured intensity of the radiation was found to decrease linearly by 0.025% a day, apart from the decrease owing to the calibration sample itself.

In order to minimize the fluctuation of the primary and scattered beam intensity,

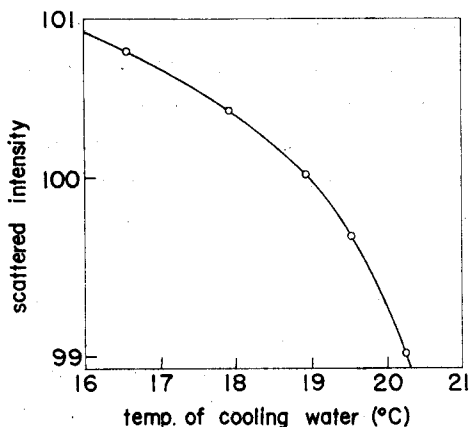


Fig. 1. Effect of temperature of cooling water on scattered intensity.

it was necessary to eliminate the vibration of the camera and the tube shield. Although it was rather easy to eliminate the vibration of the camera, it was difficult to prevent the vibration of the tube shield, because the jet of the cooling water runs through the tube shield, which causes a continual vibration at the top of the X-ray tube. We measured the intensity of the vibration at the top of the tube shield with a vibrometer. It was found that the vibration decreases below 0.02 g (when operated at 45 kV and 35 mA) and that the fluctuation of scattered intensity was minimized, when the following conditions were fulfilled.

- (1) The camera and tube shield should be fixed tightly on a firm table equipped with a vibration-proof device. We fixed them on a box-like surface plate mounted on vibration-absorbing rubbers.
- (2) The flux of cooling water should be minimized as far as the target is cooled sufficiently.
- (3) A nozzle with an appropriate size should be used, since the intensity of vibration of the tube shield is very sensitive to the condition of the jet.

After such conditions were fulfilled, we checked the fluctuation of the primary beam intensity by determining the scattered intensity of the Lupolen standard sample continuously, which was given us by Kratky. It was found that the fluctuation of the intensity, as a whole, is better than 0.3% for a week, including the statistical error of 0.1%. In addition, the angular shift in the primary beam position was checked before and after each experiment, and found to be less than  $5 \times 10^{-6}$  rad. The room temperature was controlled at  $21 \pm 0.5^\circ\text{C}$  by combining a cooler and heaters.

The scattered intensity of the sample was measured by the step scanning method by means of a full automatic step controller. About fifty steps were scanned for each curve, and  $10^5$  pulses were recorded for each measurement, which correspond to a statistical error of 0.3%.

The solution samples were investigated in a thin-walled quartz capillary, the inside diameter of which was 0.1617 cm, which was determined by a microscope. The temperature of the sample was kept at  $21 \pm 0.01^\circ\text{C}$  by circulating thermostated water. The measurements were made with about 1, 2, 3, 4, and 5 g/dl solutions. The density of the solution, from which the partial specific volume of the solute can be calculated, was measured to five places of decimals by a "precision density meter" developed by Kratky et al.<sup>8)</sup>

An entrance slit of 60  $\mu$  width was used for all scattering angles. In this case, full illumination could be achieved, because the effective width of the line focus is 100  $\mu$ . The width of the counter slit was changed from 150 to 1000  $\mu$ , as the scattering angle increased. The distance from the sample to the counter slit was 20.5 cm. In order to obtain high scattered intensity, we used the primary beam with a line-shaped cross

section, which causes a collimation error. This error was eliminated (desmeared) by the method of Schmidt.<sup>9)</sup> Corrected intensity corresponds to the intensity obtained by an idealized point collimation. In the following, we designate the measured (smeared) scattered intensity with a long and narrow slit by  $\tilde{I}$  and that of the desmeared scattered intensity by  $I$ .

The measurement of the absolute intensity, which is defined as the ratio of the scattered intensity to that of the primary beam, was carried out by using a secondary standard sample, a Lupolen platelet, calibrated by Kratky et al.<sup>10)</sup> During the measurements, the primary beam intensity was checked at least once a day.

### 3. Theoretical

#### Zimm plot

In the same manner as the light scattering, the following equation is used to estimate the weight-average molecular weight  $M_{Zimm}$ , the  $z$ -average radius of gyration  $\langle S^2 \rangle^{1/2}$ , and the second virial coefficient  $A_2$  of polymer in solution, from the Zimm plot.

$$Kc/I_n(\theta) = (1/M_{Zimm})[1 + (16\pi^2/3\lambda^2)\langle S^2 \rangle \sin^2\theta + \dots] + 2A_2 + \dots \quad (1)$$

where  $c$  is the concentration of the solution,  $\theta$  is half of the scattering angle,  $\lambda$  is the wave length, and  $I_n(\theta)$  is the absolute intensity normalized as follows.

$$I_n(\theta) = (I/P)(r^2/d) \quad (2)$$

where  $P$  is the primary beam intensity,  $r$  is the distance between the sample and the plane of registration and  $d$  is the thickness of the sample. According to the theory of Thomson, the value of the constant  $K$  is given by

$$K = i_e(z_e)^2 N_A \quad (3)$$

where  $i_e$  is the Thomson-scattering constant of a free electron,  $7.9 \times 10^{26}$ ,  $N_A$  is Avogadro's number, and  $z_e$  is the number of mole excess electrons per g of solute, which is determined by

$$z_e = z_2 - \bar{v}_2 \rho_1 \quad (4)$$

where  $z_2$  denotes the mole electrons in 1 g of solute,  $\bar{v}_2$  is the partial specific volume of the solute, and  $\rho_1$  is the electron density of the solvent.

#### Cross-section factor

According to Kratky et al.,<sup>11-13)</sup> the intensity of the tail end of the scattering curve for coiled macromolecules which have a finite cross section area is given by

$$I = I_q(1/2\theta) \quad (5)$$

where  $I_q$  is the so-called cross-section factor, which is determined by the dimension of

the cross section. If  $I_q$  can be approximated by a Gaussian function, a plot of  $\log(I \cdot 2\theta)$  against  $(2\theta)^2$  shows a straight line. From the inclination  $(\tan \alpha)_0$  of the tangent at a very low angle in this plot, the radius of gyration  $\langle S_q^2 \rangle^{1/2}$  of the cross section can be obtained.

$$\langle S_q^2 \rangle^{1/2} = (\lambda/\pi)[2.303(-\tan \alpha)_0/2]^{1/2} \quad (6)$$

Furthermore, analogous to the determination of the molecular weight, mass  $M_q$  per unit length can be estimated from the cross-section factor extrapolated to a zero angle.<sup>13)</sup>

$$M_q = (z_e N_A)^{-1} [(I \cdot 2\theta)_0 / P] [r^2 / dc(z_e)^2] \quad (7)$$

From Eqs. 1, 2, 3, and 7, the hydrodynamic length  $L$ , which is the fully extended length of the real chain, is estimated.<sup>13)</sup>

$$L = M / M_q = I_0 / (I \cdot 2\theta)_0 \quad (8)$$

where  $I_0$  is the scattered intensity extrapolated to a zero angle.

As the molecular weight  $M_m$  and the length  $l$  of the monomer unit are known from the chemical structure of the polymer, the molecular weight  $M_{I \cdot 2\theta}$  from  $I \cdot 2\theta$  is determined from the ratio of  $I_0$  to  $(I \cdot 2\theta)_0$  without knowing the absolute intensity and the excess electrons  $z_e$ .

$$M_{I \cdot 2\theta} = (\lambda/l) [I_0 / (I \cdot 2\theta)_0] M_m \quad (9)$$

### Invariant

A third method for the determination of the molecular weight is to use the invariant  $\bar{Q}$ , which is obtained directly from the measured intensity  $\bar{I}$ . Invariant was first introduced by Porod<sup>14)</sup> and defined by

$$\bar{Q} = \int \bar{I} \cdot 2\theta d(2\theta) \quad (10)$$

Volume  $V$  of each polymer molecule is calculated from  $\bar{Q}$  by

$$V = (\lambda^3 / 2\pi) (I_0 / \bar{Q}) \quad (11)$$

Knowing the partial specific volume  $\bar{v}_2$  of the polymer, the molecular weight  $M_{\bar{Q}}$  from  $\bar{Q}$  can be calculated.

$$M_{\bar{Q}} = N_A V / \bar{v}_2 \quad (12)$$

### Persistence length

The persistence length  $a$  is related to the position of the transition point  $(2\theta)^*$  by<sup>15)</sup>

$$a = 2.3\lambda / 2\pi(2\theta)^* \quad (13)$$

The persistence length for the random coil is also related to  $\langle S^2 \rangle^{1/2}$  and the hydrodynamic length  $L$  by the following equation,<sup>16)</sup>

$$3\langle S^2 \rangle = a[L - a - a \cdot \exp(-L/a)] \quad (14)$$

The transition point  $(2\theta)^*$  can be obtained from either the plot of  $I \cdot (2\theta)^2$  against  $2\theta$ , the plot<sup>17)</sup> of  $I \cdot 2\theta$  against  $1/2\theta$  or the plot<sup>17)</sup> of  $[dI/d(2\theta)]2\theta$  against  $2\theta$ .

### Radius of cross section

If the molecular chain is supposed to be a long, flexible cylinder of uniform electron density, the radius of the cross section can be calculated in various ways. The radius  $r_q$  of the cross section is related to the radius of gyration  $\langle S_q^2 \rangle^{1/2}$  of the cross section by

$$r_q = \sqrt{2} \langle S_q^2 \rangle^{1/2} \quad (15)$$

In the analogy with the rod-like particles,  $r_q$  can be also calculated from the cross-section area  $F$ , which in its turn is obtained from the cross-section factor  $I \cdot 2\theta$  and the invariant  $\bar{Q}$ .

$$\begin{aligned} F &= (\lambda^3 r^3 / \pi) [(I \cdot 2\theta)_0 / \bar{Q}] \\ F &= r_q^2 \pi \end{aligned} \quad (16)$$

According to Fedorov and Ptitsyn,<sup>18)</sup>  $r_q$  is obtained from the maximum in the plot of  $I \cdot (2\theta)^2$  against  $2\theta$ . The relation is

$$\gamma J_0(\gamma/2) = 3J_1(\gamma/2) \quad (17)$$

with the solution  $\gamma_1 = 2.72$ , where  $\gamma = 4\pi \cdot 2r_q \sin \theta / \lambda$  and  $J_\nu(\gamma)$  is the Bessel function of  $\nu$ th order.

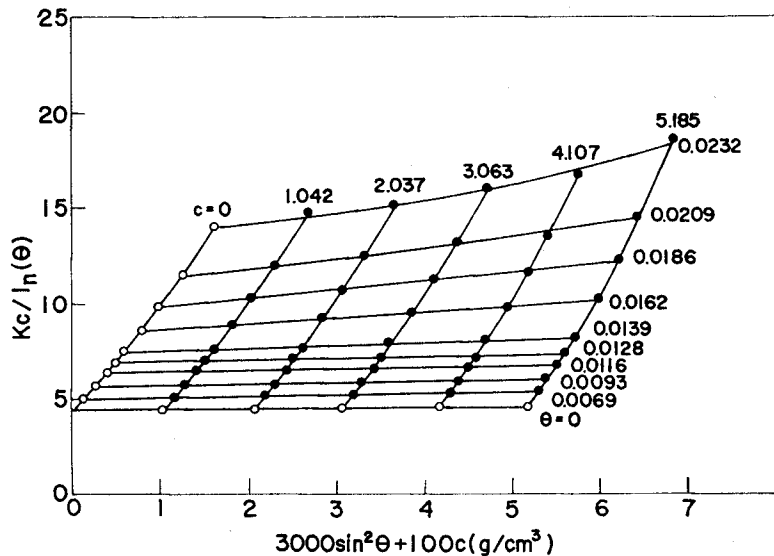


Fig. 2. Zimm plot of polystyrene in MEK at 21°C.

#### 4. Results and Discussion

Figure 2 shows the Zimm plot, from which the weight average molecular weight  $M_{Zimm}$ , the  $z$ -average radius of gyration  $\langle S^2 \rangle^{1/2}$  and the second virial coefficient  $A_2$  can be calculated.

Figure 3 shows the Guinier plot of the cross-section factor, from which the mass  $M_q$  per unit length, the radius of gyration  $\langle S_q^2 \rangle^{1/2}$  of the cross section, the hydrodynamic length  $L$ , and the molecular weight  $M_{I,2\theta}$  can be calculated.

Figure 4 shows the plot of  $\tilde{I} \cdot 2\theta$  against  $2\theta$  for the determination of the invariant  $\tilde{Q}$ , from which the molecular weight  $M_{\tilde{Q}}$  and the cross-section area  $F$  or the radius of the cross section  $r_q$  can be calculated.

Figure 5 shows the plot of  $I \cdot (2\theta)^2$  against  $2\theta$  and that obtained after division by the cross-section factor,<sup>4,19)</sup> which in its turn is obtained from Figure 3. The corrected curve apparently shows the transition point, which makes it possible to calculate the

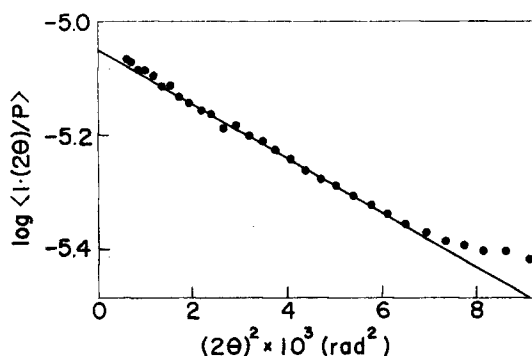


Fig. 3. Guinier plot of cross-section factor of polystyrene in MEK.

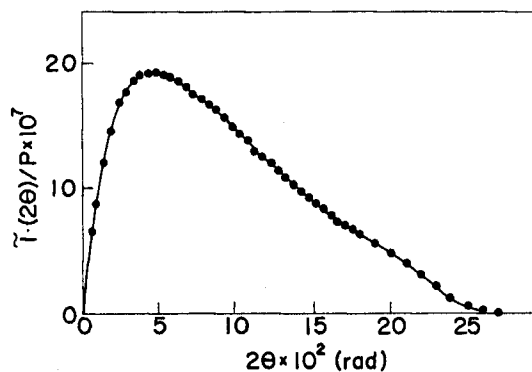


Fig. 4. Plot of  $\tilde{I} \cdot 2\theta$  vs.  $2\theta$  for determination of invariant of polystyrene in MEK.



persistence length  $a$  according to Eq. 13. The uncorrected curve has a maximum point, from which the radius of the cross section  $r_q$  can be calculated.

Figures 5, 6, and 7 show other ways of determining the transition point  $(2\theta)^*$ .

All the results are compiled in Table 1, together with values measured by other methods. As shown in Table 1, the values obtained by different analyses agreed well with one another and also with the values estimated by other methods.

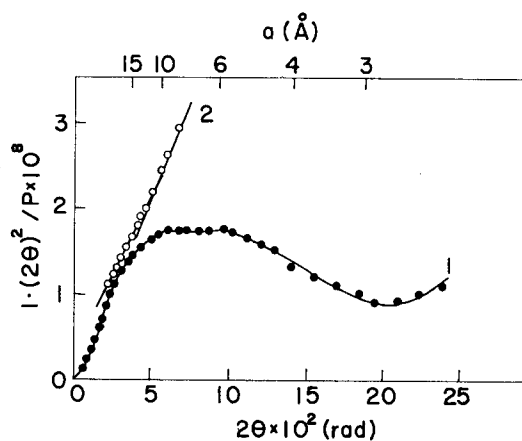


Fig. 5. Plot of  $I \cdot (2\theta)^2$  vs.  $2\theta$  for determination of persistence length of polystyrene in MEK: Curve 1, scattered curve subject to cross-section factor; Curve 2, after deviding by cross-section factor.

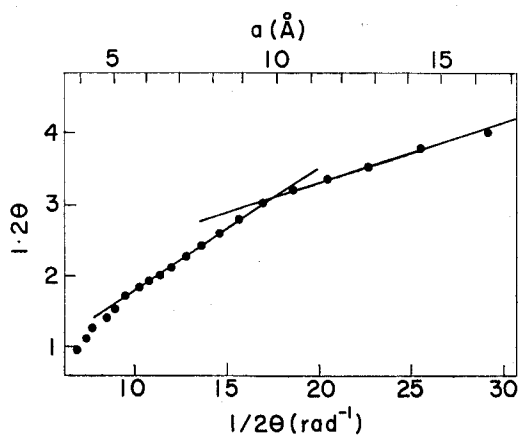


Fig. 6. Plot of  $I \cdot 2\theta$  vs.  $1/2\theta$  for determination of persistence length of polystyrene in MEK.

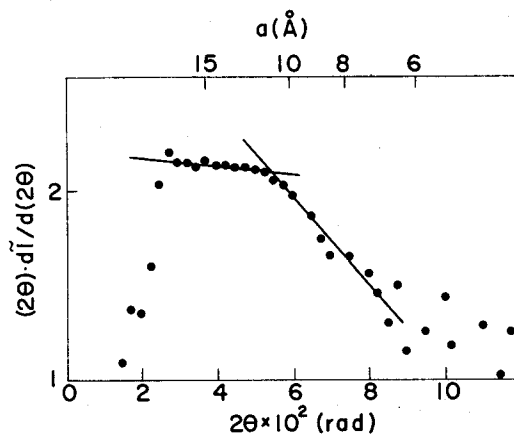


Fig. 7. Plot of  $[d\tilde{I}/d(2\theta)] \cdot 2\theta$  for determination of persistence length of polystyrene in MEK.

Table 1. Parameters of polystyrene in MEK at 21°C.

Parameter	Experimental value	Value observed by other methods
$M_{\text{zimm}}$	2280	2100 <sup>a</sup>
$M_{1,2\theta}$	2110	
$M_Q$	1820	
$\langle S^2 \rangle^{1/2}$	14.0 Å	12.5 Å <sup>b</sup> , 12.3 Å <sup>c</sup>
$A_2$	$5 \times 10^{-4} \text{ cm}^3 \text{g}^{-2}$	$4.5 \times 10^{-4} \text{ cm}^3 \text{g}^{-2}$ <sup>d</sup>
$M_q$	45.6	41.4 <sup>e</sup>
$L$	51.0 Å	50.7 Å <sup>f</sup>
$\langle S_q^2 \rangle^{1/2}$	3.90 Å	
$a_{1,(2\theta)^2}$	11.5 Å	
$a_{1,2\theta}$	9.9 Å	
$a_{\text{diff}}$	10.6 Å	
$r_q, \langle S_q^2 \rangle^{1/2}$	5.51 Å	
$r_q, \tilde{q}$	4.49 Å	
$r_{q, \text{max}}$	3.63 Å	

a Nominal value of the sample.

b Calculated from the characteristic ratio of polystyrene.<sup>20)</sup>

c Calculated from  $a$  and  $L$  obtained in this work using Eq. 14.

d Calculated from the equation proposed by Sotobayashi<sup>21)</sup> and the data of Outer et al.<sup>22)</sup>

e Calculated from the structure of polystyrene.

f Calculated from the structure and the nominal molecular weight.

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