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# Dilute Solution Properties of Monodisperse Poly($\alpha$-methyl styrene). I. Sedimentation Coefficient in Theta Solvent

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The sedimentation behavior of anionically polymerized poly($\alpha$-methyl styrene) has been studied as a function of molecular weight, concentration and speed of centrifugation under the theta condition of solvent and temperature, *i. e.*, in cyclohexane at 39°C. Analysis of the data was made by use of Fujita's equation for the pressure- and concentration-dependent sedimentation. It was found that the sedimentation coefficient at zero concentration and one atmosphere was given as $s_0{}^0 = 2.00 \times 10^{-15} M^{1/2}$ sec, where $M$ is molecular weight. The concentration dependence coefficient $k$ and the pressure dependence coefficient $\mu$ appearing in the Fujita equation were obtained as $k = 6.2 \times 10^{-4} M^{1/2}$ dl/g, and $\mu = 1.6 \times 10^{-9}$ cm$^2$/dyne, respectively. The intrinsic viscosity in the theta solvent was also determined as $[\eta]_\theta = 7.60 \times 10^{-4} M^{1/2}$ dl/g.

The purpose of this series is to present the results of systematic measurements carried out on the dilute solution properties of anionically prepared poly($\alpha$-methyl styrene). This polymer was taken as working material since its molecular weight distribution had been reported to be extremely sharp compared with other species of anionically prepared polymers.1) Studies along the same line as the present have been published recently by Bywater and associates,2) and by Nagasawa and associates.3) They studied the behavior of intrinsic viscosity, sedimentation coefficient and polymer coil dimensions as functions of molecular weight and solvent nature, and compared the results with the current theories. However, no extensive measurement on the viscoelastic properties of dilute solutions of monodisperse polymer has been

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1) T. Fujimoto, N. Ozaki and M. Nagasawa, *J. Polymer Sci.*, **A3**, 2259 (1965).

2) A. F. Sirianni, D. J. Worsfold and S. Bywater, *Trans. Faraday Soc.*, **55**, 2124 (1959); J. M. G. Cowie, S. Bywater and D. J. Worsfold, *Polymer*, **8**, 105 (1967).

3) I. Noda, S. Saito, T. Fujimoto and M. Nagasawa, *J. Phys. Chem.*, **71**, 4048 (1967).

published yet but some preliminary measurements.[4,5] Thus, in this series, we intend to investigate not only the viscosity and sedimentation behavior but also the viscoelastic behavior of dilute solutions under varying conditions of molecular weight, concentration and solvent nature.

In this paper, we present a series of velocity sedimentation data obtained for the monodisperse poly($\alpha$-methyl styrene) in a theta solvent. The sedimentation coefficient at zero concentration and one atmosphere is determined as a function of molecular weight using Fujita's equation for the pressure- and concentration-dependent sedimentation.[6]

The Fujita equation for the apparent sedimentation coefficient $s_{app}$ is written in the form that

$$s_{app} = \frac{\ln(r/r_m)}{\omega^2(t-t_0)} = s_c{}^0\left\{1 + K\left[\left(\frac{r}{r_m}\right)^2 - 1\right]\right\} \quad (1)$$

with

$$s_c{}^0 = s_0{}^0/(1 + kc) \quad (2)$$

$$K = \frac{kc - m(1 + kc)}{2(1 + kc)} \quad (3)$$

$$m = \frac{1}{2}\mu\omega^2\rho_0{}^0 r_m{}^2 . \quad (4)$$

Here $r$ is the radial distance of the boundary from the axis of rotation, $r_m$ is the radial distance of the meniscus, $\omega$ is the angular velocity, $t$ is the time measured from the moment the acceleration of the rotor commenced, $t_0$ is the zero-time correction for the acceleration period, and $\rho_0{}^0$ is the density of solvent at one atmosphere. $s_c{}^0$ and $s_0{}^0$ represent values of the sedimentation coefficient at initial concentration $c$ of the solution and at infinite dilution, respectively: the both are referred to one atmosphere of the pressure. $k$ and $\mu$ are constants characteristic of the polymer-solvent system: the former is called the concentration dependence coefficient and the latter is called the pressure dependence coefficient.

An experimental test of Eq. (1) has been made by Billick using anionically polymerized polystyrene.[7] He has shown that the pressure and concentration dependence effects of the sedimentation velocity can be treated adequately by Eq. (1) in both poor and good solvents. However, as was noted by Blair and Williams,[8] the evaluation of the pressure dependence coefficient $\mu$ and also of the concentration dependence coefficient $k$ is very sensitive to the zero-time correction $t_0$ applied for the acceleration period, and accordingly it is subjected to a rather large experimental error. In fact, Billick[7] has reported rather scattering values, $\mu = 1.2$—$3.4 \times 10^{-9}$ cm$^2$/dyne; while Blair-Williams[8] and Wales-Rehfeld[9] have reported $(1.6 \pm 0.2) \times 10^{-9}$ and $2.2 \times 10^{-9}$, respectively, for the system polystyrene in cyclohexane.

In view of the existing uncertainty in the value of $\mu$, we found it worthwhile to remeasure the pressure-dependent sedimentation rate using monodisperse polymer samples. After the present work was completed, Noda *et al.*[3] published velocity sedimentation data on the same polymer-solvent system as the present, though their measurements were less extensive with respect to the variation of speed of centrifugation than ours. They reported $\mu = 2.3 \times 10^{-9}$ for the system poly($\alpha$-methyl styrene) in cyclohexane.

## Experimental

**Polymer Samples and Their Molecular Weights.** Nine samples of poly($\alpha$-methyl styrene) with narrow distribution of the molecular weight were prepared in our laboratory by the anionic polymerization technique.[1,10] The initiator used was *n*-butyl lithium for BH-1 and seven samples of BB series, and sodium naphthalene for sample A-1. The terminator used was *n*-butanol for the BB and A series, and water for the BH series. The polymerization was carried out at −78°C in a purified water-free tetrahydrofuran as solvent. All polymers were fractionated in a large-scale Desreux column at 25°C by using benzene-ethanol mixtures, and the middle fraction of each polymer was utilized for measurements. These polymers were then freed from solvents by freeze-drying from benzene solutions followed by evacuation for about 24 hr at 60°C, and were sealed into ampules under argon atmosphere or at $10^{-6}$ mmHg pressure. More details of the sample preparation will be described elsewhere.[11]

The weight-average molecular weights $M_w$ were determined by light scattering in benzene at 30°C and in cyclohexane at 39°C using a Brice type photoelectric photometer. The refractive index increments in these two solvents were 0.134 and 0.200 m*l*/g, respectively, for the light of 436 m$\mu$ wavelength. The number-average molecular weights $M_n$ were determined by osmometry for samples BB-4, 6, 8, BH-1, and A-1 in toluene at 37°C. Details of these measurements will be described in Part II of this series, but a part of the results is given in Table 1.

The ratios $M_w/M_n$ of our samples were in the range 0.93—1.07 if they were evaluated directly from the values of $M_w$ and $M_n$. This ratio $M_w/M_n$, however, can be evaluated with a higher accuracy from the

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[4] J. E. Frederick and J. D. Ferry, *ibid.*, **69**, 346 (1965).

[5] A. Sakanishi and H. Tanaka, *J. Soc. Material Sci.*, **16**, 528 (1967); *Repts. Progr. Polymer Phys. Japan*, **10**, 89 (1967).

[6] H. Fujita, *J. Am. Chem. Soc.*, **78**, 3598 (1956). See also, H. Fujita, "Mathematical Theory of Sedimentation Analysis," Academic Press, Inc., New York, N. Y. (1962).

[7] I. H. Billick, *J. Phys. Chem.*, **66**, 1941 (1962).

[8] J. E. Blair and J. W. Williams, *ibid.*, **68**, 161 (1964).

[9] M. Wales and S. J. Rehfeld, *J. Polymer Sci.* **62**, 179 (1962).

[10] M. Morton, A. A. Rembaum and J. L. Hall, *ibid.*, **A1**, 461 (1963).

[11] Y. Tsunajima, K. Sakato, M. Fukatsu and M. Kurata, *Bull. Inst. Chem. Res. Kyoto Univ.*, **46**, 37 (1968).

TABLE 1. MOLECULAR WEIGHTS, SEDIMENTATION COEFFICIENTS AND INTRINSIC VISCOSITIES OF ANIONICALLY PREPARED POLY($\alpha$-METHYL STYRENE)

| Sample No. | $M_w$ $\times 10^{-4}$ | $M_n$ $\times 10^{-4}$ | $[\eta]_\theta$ (d$l$/g) | $k'$ | $s_0{}^0$ $\times 10^{13}$ (sec) | $k$ (d$l$/g) |
|---|---|---|---|---|---|---|
| BB-7 | 168[a] | — | 0.983 | 0.55 | — | — |
| BB-5 | 143[a] | — | 0.910 | 0.53 | 23.9±0.5 | 0.79±0.15 |
| A-1 | 97.0[a] | 93.2 | 0.706 | 0.53 | 19.3±0.5 | 0.52±0.10 |
| BB-10 | 64.0[a] | — | 0.600 | 0.53 | — | — |
| BB-6 | 48.8[a] | 48.7 | 0.528 | 0.58 | 13.0±0.3 | 0.44±0.07 |
| BB-9 | 35.5[b] | — | 0.430 | 0.53 | — | — |
| BH-1 | 26.0[c] | 24.2 | 0.395 | 0.59 | 10.25±0.20 | 0.28±0.07 |
| BB-4 | 4.87[c] | 5.26 | 0.177 | 0.53 | 4.26±0.10 | 0.16±0.04 |
| BB-8 | 4.03[b] | 4.07 | 0.142 | 0.56 | — | — |

a) Determined in both benzene and cyclohexane.
b) Determined in benzene. c) determined in cyclohexane.

sedimentation boundary curve obtained in theta solvent.[12] The results of such measurements indicated that $M_w/M_n$ were less than 1.01 for the samples BB-4, 5, 6, BH-1 and A-1. It is clear from these measurements that all our samples have an extremely narrow molecular weight distribution.

**Theta Solvent and Temperature.** Reagent grade cyclohexane was dried over a molecular sieve of 4A after the removal of a trace of benzene by a silica gel column, and was fractionally distilled with metallic sodium. The theta temperature was 38.6°C in cyclohexane as determined by the light-scattering second virial coefficient $A_2$. Figure 1 shows the $A_2$ *versus* temperature relationship obtained for sample A-1.

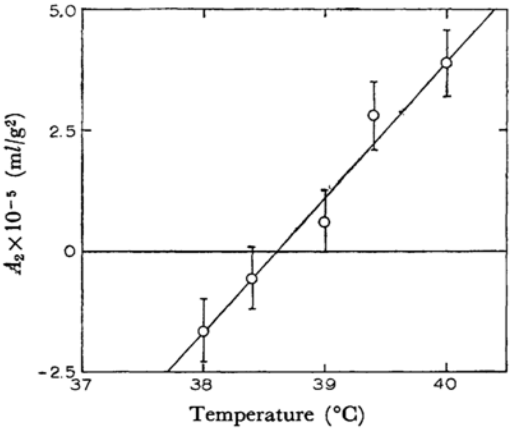

Fig. 1. Variation of the light-scattering second virial coefficient with temperature of sample A-1 in cyclohexane.

**Sedimentation Velocity.** Sedimentation velocity measurements were carried out in a Spinco model E ultracentrifuge equipped with an RTIC temperature control unit. In all experiments, the temperature was controlled at 39.0±0.1°C. A double sector cell of 12 mm long was used, and measurements were made at four rotor speeds, *i. e.*, 59780, 50740, 42040 and 29500 rpm, and at three or four initial concentrations of about 0.03 to 0.25 g/d$l$. Schlieren diagrams were read on a' 'Universal" contour projector (made by Nihon Kogaku Co., Ltd., Tokyo, Japan) to the accuracy of some 0.005 mm. The boundary position $r$ in Eq. (1) was determined from the maximum of the refractive index gradient, since the schlieren diagrams were of good gaussian distribution curves.

**Partial Specific Volume.** A measuring-cylinder pycnometer of the Lipkin type was used to determine solution densities. The volume was approximately 10 m$l$. The density $\rho_0$ of cyclohexane was 0.7598 at 39°C. The partial specific volume $v$ of poly($\alpha$-methyl styrene) was found to be 0.882 m$l$/g in this solvent.

**Intrinsic Viscosity.** Viscosity measurements were carried out in cyclohexane at 39°C using dilution viscometers of the Ubbelohde type. The corrections for the kinetic energy and shear rate effect were both negligible under the experimental conditions. The intrinsic viscosity $[\eta]_\theta$ and the Huggins coefficient $k'$ determined are given in Table 1. The solvent viscosity $\eta_0$ was 0.730 centi-poise at 39°C.

## Results

**Zero-time Correction for Sedimentation.** Among several methods so far proposed for the evaluation of the zero-time correction $t_0$ in sedimentation experiments, the so-called "best-fit" method of Blair and Williams[8] was found to be most appropriate for analysis of the present measurements. In this method, the value of $t^0$ is determined so as to minimize the "standard deviation" $\sigma$ which is defined by

$$\sigma = [(1/n)\sum_{i=1}^{n} R_i{}^2]^{1/2} \tag{5}$$

with

$$R = s_c{}^0\omega^2(t-t_0) + s_c{}^0K\omega^2(t-t_0)[(r/r_m)^2-1] - \ln(r/r_m) \tag{6}$$

Here $n$ denotes the number of observation in a given run of experiments. Figure 2 illustrates

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12) T. Homma, K. Kawahara, H. Fujita and M. Ueda, *Makromol. Chem.*, **67**, 132 (1963).

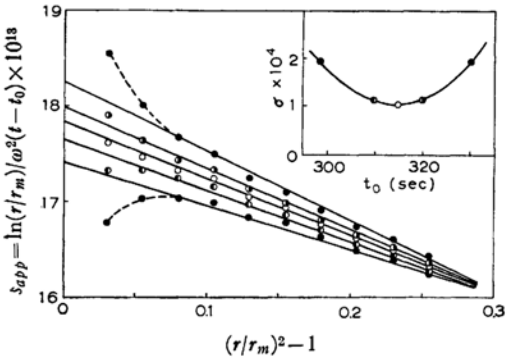

Fig. 2. Determination of the zero-time correction $t_0$ by the "best-fit" method of Blair and Williams. The five lines and different marks show the apparent sedimentation coefficients plotted against the quantity $(r/r_m)^2-1$ with five different choices of $t_0$ value. The insert shows variation of the standard deviation $\sigma$ with the assumed values of $t_0$. Sample, A-1; rotor speed, 50740 rpm; concentration, 0.131 g/d*l*.

the procedure for the determination of $t_0$, in which the apparent sedimentation coefficients $s_{app}$ obtained for various assumed values of $t_0$ are plotted against the quantity $(r/r_m)^2-1$. With aid of the best-fit line to each set of experimental points, a pair of values of $s_c{}^0$ and $K$ can be determined, and then the standard deviation $\sigma$ can be calculated using Eqs. (5) and (6). The values of $\sigma$ thus obtained are shown in the insert of Fig. 2 as a function of $t_0$, and the "best-fit" value of $t_0$ is determined to be 315 sec. This value of $t_0$ was considerably larger than the time, 260 sec in this example, required for the so-called "2/3-acceleration".[7,13]

**Pressure- and Concentration-dependence Coefficients.** The values of $s_c{}^0$ and $K$ corresponding to the best-fit value of $t_0$ were determined for samples BB-4, 5, 6, BH-1 and A-1 under various conditions of the concentration and the speed of centrifugation. The results are summarized in Table 2. For illustration, the values of $s_c{}^0$ of sample BB-5 thus determined are plotted in Fig. 3 against the concentration $c$. No systematic effect of the speed of centrifugation is observed in these $s_c{}^0$ *versus* $c$ plots, and we can evaluate the concentration dependence coefficient $k$ within an accuracy of about ten or twenty percent. The values of $k$ thus obtained are listed in Table 1, and are plotted against the square-root of the molecular weight in Fig. 4. This plot suggests the relationship,

$$k = 6.2\times10^{-4}\,M^{1/2}\ \mathrm{d}l/\mathrm{g}.$$

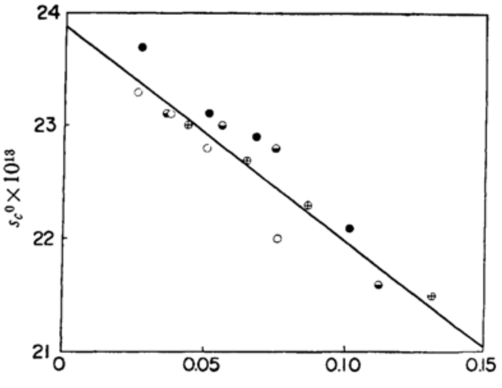

Fig. 3. Variation of sedimentation coefficient $s_c{}^0$ with the concentration $c$ of sample BB-5 in cyclohexane at 39°C. Rotor speeds: ○, 59780; ⊕, 50740; ◒, 42040; ●, 29500 rpm.

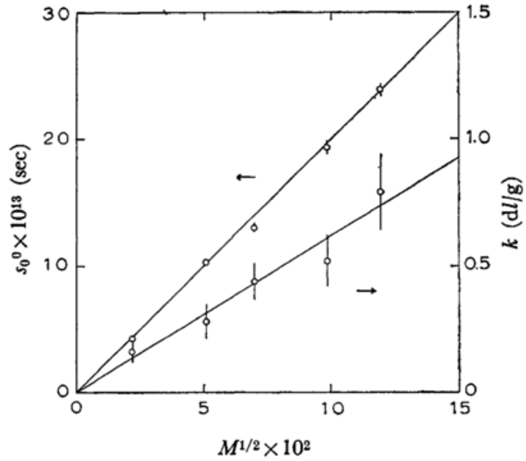

Fig. 4. The sedimentation coefficient $s_0{}^0$ and its concentration dependence coefficient $k$ as functions of the molecular weight $M$.

The pressure dependence coefficient $\mu$ can be readily evaluated by substituting the values of $K$ and $k$ into Eqs. (3) and (4). The results are tabulated in Table 2. No systematic variation of the $\mu$ values with the polymer molecular weight nor concentration is observed, and the averaging of these sixty four values of $\mu$ yields

$$\mu = (1.6\pm0.2)\times10^{-9}\ \mathrm{cm^2/dyn}. \tag{8}$$

**Sedimentation Coefficient at Infinite Dilution.** The sedimentation coefficient $s_0{}^0$ at zero concentration of the polymer and at one atmosphere are listed in Table 1. As shown in Fig. 4, this quantity $s_0{}^0$ is proportional to the square root of the molecular weight:

$$s_0{}^0 = (2.00\pm0.03)\times10^{-15}\,M^{1/2}\ \mathrm{sec}. \tag{9}$$

**Intrinsic Viscosity.** The intrinsic viscosities given in Table 1 are also proportional to the square root of the molecular weight:

$$[\eta]_\theta = (7.60\pm0.07)\times10^{-4}\,M^{1/2}\ \mathrm{d}l/\mathrm{g}. \tag{10}$$

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[13] R. Trautman, *J. Phys. Chem.*, **60**, 1211 (1956).

TABLE 2. PRESSURE- AND CONCENTRATION-DEPENDENCE OF THE SEDIMENTATION COEFFICIENT OF POLY($\alpha$-METHYL STYRENE) IN CYCLOHEXANE AT 39°C

| Sample | $\omega$ (rpm) | $c$ (g/d$l$) | $s_c^0\times10^{13}$ (sec) | $-K$ | $\mu\times10^9$ (cm$^2$/dyne) | $\sigma\times10^4$ |
|---|---|---|---|---|---|---|
| BB-5 | 59780 | 0.026 | 23.3 | 0.43 | 1.5 | 0.7 |
| | | 0.038 | 23.1 | 0.44 | 1.6 | 1.0 |
| | | 0.051 | 22.8 | 0.45 | 1.6 | 1.5 |
| | | 0.076 | 22.0 | 0.46 | 1.7 | 0.9 |
| | 50740 | 0.044 | 23.0 | 0.31 | 1.6 | 1.4 |
| | | 0.065 | 22.7 | 0.30 | 1.5 | 1.8 |
| | | 0.087 | 22.3 | 0.32 | 1.7 | 1.3 |
| | | 0.131 | 21.5 | 0.33 | 1.8 | 1.7 |
| | 42040 | 0.037 | 23.1 | 0.24 | 1.7 | 1.3 |
| | | 0.056 | 23.0 | 0.24 | 1.8 | 1.1 |
| | | 0.075 | 22.8 | 0.24 | 1.8 | 1.2 |
| | | 0.112 | 21.6 | 0.21 | 1.7 | 1.8 |
| | 29500 | 0.027 | 23.7 | 0.11 | 1.7 | 0.9 |
| | | 0.051 | 23.1 | 0.070 | 1.3 | 0.8 |
| | | 0.068 | 22.9 | 0.12 | 2.1 | 0.8 |
| | | 0.102 | 22.1 | 0.14 | 2.4 | 0.6 |
| A-1 | 59780 | 0.040 | 18.9 | 0.44 | 1.6 | 1.6 |
| | | 0.061 | 18.6 | 0.46 | 1.7 | 2.0 |
| | | 0.122 | 17.9 | 0.46 | 1.7 | 0.8 |
| | | 0.159 | 17.5 | 0.48 | 1.7 | 1.3 |
| | 50740 | 0.036 | 18.8 | 0.31 | 1.6 | 1.8 |
| | | 0.066 | 18.7 | 0.33 | 1.7 | 1.3 |
| | | 0.087 | 18.2 | 0.31 | 1.6 | 0.9 |
| | | 0.131 | 17.8 | 0.32 | 1.7 | 1.0 |
| | 42040 | 0.099 | 18.7 | 0.23 | 1.7 | 1.5 |
| | | 0.149 | 18.2 | 0.23 | 1.7 | 1.4 |
| | | 0.199 | 17.7 | 0.23 | 1.8 | 1.0 |
| | | 0.298 | 16.9 | 0.24 | 1.9 | 1.1 |
| | 29500 | 0.077 | 18.6 | 0.092 | 1.6 | 1.5 |
| | | 0.102 | 18.5 | 0.092 | 1.7 | 1.6 |
| | | 0.152 | 18.0 | 0.072 | 1.5 | 0.7 |
| BB-6 | 59780 | 0.049 | 12.92 | 0.49 | 1.8 | 1.0 |
| | | 0.074 | 12.55 | 0.41 | 1.5 | 1.4 |
| | | 0.098 | 12.48 | 0.43 | 1.6 | 1.9 |
| | | 0.147 | 12.30 | 0.44 | 1.6 | 0.9 |
| | | 0.294 | 11.43 | 0.41 | 1.5 | 1.2 |
| | 50740 | 0.047 | 12.63 | 0.30 | 1.6 | 1.6 |
| | | 0.067 | 12.44 | 0.31 | 1.6 | 0.8 |
| | | 0.089 | 12.23 | 0.29 | 1.5 | 1.0 |
| | | 0.134 | 12.07 | 0.29 | 1.6 | 1.1 |
| | 42040 | 0.038 | 12.76 | 0.20 | 1.5 | 2.3 |
| | | 0.051 | 12.81 | 0.21 | 1.6 | 1.3 |
| | | 0.077 | 12.70 | 0.22 | 1.7 | 2.0 |
| | | 0.102 | 12.46 | 0.21 | 1.6 | 1.0 |
| | 29500 | 0.075 | 12.62 | 0.095 | 1.6 | 1.9 |
| | | 0.150 | 12.38 | 0.056 | 1.1 | 1.1 |
| | | 0.225 | 11.90 | 0.10 | 1.9 | 1.2 |
| BH-1 | 59780 | 0.077 | 9.98 | 0.40 | 1.5 | 1.5 |
| | | 0.115 | 9.90 | 0.38 | 1.4 | 1.5 |
| | | 0.153 | 9.78 | 0.45 | 1.6 | 1.3 |
| | | 0.230 | 9.40 | 0.40 | 1.5 | 0.7 |
| | 50740 | 0.062 | 10.10 | 0.34 | 1.7 | 2.0 |
| | | 0.093 | 10.00 | 0.31 | 1.6 | 3.5 |
| | | 0.124 | 9.87 | 0.31 | 1.6 | 1.6 |
| | | 0.187 | 9.71 | 0.34 | 1.7 | 1.4 |
| | 42040 | 0.077 | 10.03 | 0·17 | 1.3 | 1.4 |
| | | 0.153 | 9.90 | 0.20 | 1.5 | 2.7 |
| | | 0.230 | 9.64 | 0.24 | 1.8 | 2.3 |
| | 29500 | 0.153 | 9.83 | 0.082 | 1.5 | 0.8 |
| | | 0.229 | 9.64 | 0.093 | 1.8 | 1.2 |
| BB-4 | 59780 | 0.176 | 4.15 | 0.44 | 1.6 | 1.0 |
| | | 0.264 | 4.07 | 0.39 | 1.4 | 1.1 |
| | | 0.396 | 4.00 | 0.38 | 1.4 | 1.6 |
| | | 0.528 | 3.90 | 0.38 | 1.4 | 1.0 |

## Discussion

The present measurements indicate that the concentration dependence of the sedimentation coefficient does not vanish at the theta temperature. According to Pyun and Fixman,[14] the concentration dependence coefficient $k$, as expressed in units of d$l$/g, is given as:

$$k = k^{\varphi}(4/300)(M/\boldsymbol{N_A}\pi)^2[(1-v\rho_0)^2/6\eta_0 s_0^0]^3 \quad (11)$$

where $\boldsymbol{N_A}$ is the Avogadro number, and $\rho_0$ and $\eta_0$ are the density and viscosity of solvent. $k^{\varphi}$ denotes the value of the concentration dependence coefficient when the concentration is expressed in the volume fraction. The Pyun and Fixman theory shows that $k^{\varphi}$ depends on the thermodynamic interaction between polymer segmants and that it takes a value between 2 and 3 at the theta point. The substitution of the present results, Eqs. (7) and (9), into Eq. (11) yields $k^{\varphi}=3.08$. This value is favorably compared with the above theoretical estimate, especially with the value, $k^{\varphi}=2.96$, which is derived by their "spherocylinder" approximation.[14]

As for the pressure dependence coefficient $\mu$ of the sedimentation coefficient, Noda *et al.* have reported the value, $\mu=2.3\times10^{-9}$, for the same polymer-solvent system as the present.[3] They referred to the agreement of this value with the theoretical value, $\mu=2.0\times10^{-9}$, which is calculated from the pressure-dependence coefficient $\lambda$ of the solvent viscosity using the relationship,[15]

$$\mu = \lambda + [v\rho_0/(1-v\rho_0)]\kappa. \quad (12)$$

Here $\kappa$ is the isothermal compressibility of the solution. The value of $\lambda$, however, is known only roughly in the case of cyclohexane,[15] and therefore the above comparison of $\mu$ values will not be given a much significance. The present estimate of $\mu$ given in Eq. (8) is in good agreement with the values which were obtained for polystyrene in cyclohexane by Blair-Williams,[8] Billick,[*3] and Cowie-Bywater.[16] Thus, we prefer the present estimate $\mu=1.6\times10^{-9}$, and conclude that $\mu$ is primarily independent of polymer species but characteristic of solvent.

In spite of the above discrepancy in $\mu$ values, no discrepancy is observed in the values of $s_0^0$ between the measurements by Noda *et al.*[3] and ours. This can be demonstrated by plotting $s_0^0$ against $[\eta]_\theta$. As shown in Fig. 5, the two series of data support the single correlation line:

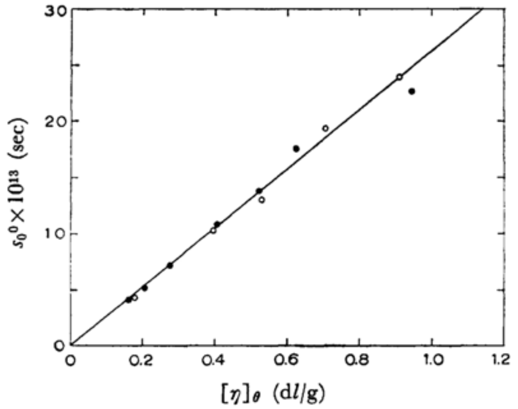

Fig. 5. Relationship between the sedimentation coefficient and the intrinsic viscosity. White circles, the present data; black circles, the data of Noda, Saito, Fujimoto and Nagasawa.[3]

$$s_0^0 = 2.63 \times 10^{-12}\,[\eta]_\theta. \quad (13)$$

This is probably due to the fact that in measurements of Noda *et al.*, the rotor speed was chosen as slow as possible to reduce the pressure effect. At such a low speed of centrifugation, the estimation of the pressure coefficient $\mu$ is subjected to a rather large experimental error, but the determination of $s_0^0$ itself can be performed with a sufficient accuracy.

The sedimentation coefficient *vs.* molecular weight relationship, Eq. (9), is slightly different from the relationship presented by Noda *et al.*:[3]

$$s_0^0 = 2.04 \times 10^{-15}\,M^{1/2} \quad \text{(in cyclohexane at 39°C)}. \quad (14)$$

The intrinsic viscosity *vs.* molecular weight relationship, Eq. (10), is also different from the relationships,

$$[\eta]_\theta = 7.13 \times 10^{-4}\,M^{0.51} \quad \text{(in cyclohexane at 39°C)} \quad (15)$$

$$[\eta]_\theta = 7.80 \times 10^{-4}\,M^{0.50} \quad \text{(in cyclohexane at 37°C)} \quad (16)$$

which were presented by Noda *et al.*[3] and Cowie *et al.*,[2] respectively. These discrepancies seem to arize from small but systematic errors involved in the molecular weight determination in these three laboratories. With the present data, we obtain from Eqs. (9) and (10)

$$\beta = \frac{s_0^0[\eta]_\theta^{1/3}\eta_0\boldsymbol{N}_\mathrm{A}}{(1-v\rho_0)M^{2/3}} = \Phi^{1/3}P^{-1}$$
$$= (2.41 \pm 0.07) \times 10^6, \quad (17)$$

where $P$ and $\Phi$ are the Flory universal constants for the sedimentation coefficient and the intrinsic viscosity, respectively. This value of the Scherage-Mandelkern constant $\beta$ is slightly lower than the value $(2.5—2.6)\times10^6$ which is predicted by the

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[*3] The average of thirteen values of $\mu$ given in Table IIa of Ref. 7 yields $1.75\times10^{-9}$ cm²/dyne.

current theories. It is, however, difficult to decide whether this discrepancy is attributed to underestimate of $M$ in our light scattering measurements or to overestimate of $\Phi$ in the current theories.

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