

## Further Test of the Two-Parameter Theory of Dilute Polymer Solutions: Poly(*p*-bromostyrene)

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**ABSTRACT:** Light-scattering and intrinsic-viscosity data are presented for fractions of poly(*p*-bromostyrene) in monochlorobenzene and dioxane at 30°C, and in benzene at temperatures ranging from 25 to 50°C. The theta temperature for this polymer in benzene is 26.3°C. With the data for the statistical-radius expansion factor  $\alpha_S$  and the interpenetration function  $\Psi$  appearing in the second virial coefficient, the agreement between theory and experiment is examined with respect to the same two criteria as those employed in the previous study on poly(*p*-methylstyrene). The Yamakawa—Tanaka theory of  $\alpha_S$  and also the modified Flory theory are again found to satisfy both criteria. The data also reproduce the relationship between the cubed viscosity-radius expansion factor  $\alpha_\eta^3$  and the excluded-volume parameter  $z$  if  $z$  is estimated using the Yamakawa—Tanaka equation for  $\alpha_S$ . Specifically, the first-order perturbation theory of  $\alpha_\eta^3$  recently developed by Yamakawa and Tanaka compares well with the data near the theta temperature. The recent critical comments by Isihara and Nagasawa are also replied to.

**KEY WORDS** Two-Parameter Theory/Excluded-Volume Effect/Mean-Square Radius/Second Virial Coefficient/Intrinsic Viscosity/Expansion Factor/Light Scattering/Poly(*p*-bromostyrene)

Recently, extensive experimental tests of the two-parameter theory of dilute polymer solutions have been made by four research groups. The foremost of these is the work of Berry<sup>1</sup> who carried out light-scattering and viscosity measurements on solutions of polystyrene. Subsequently similar studies were made on polychloroprene by Fujita, *et al.*,<sup>2,3</sup> on poly(*p*-methylstyrene) by Yamakawa, *et al.*,<sup>4</sup> and on poly( $\alpha$ -methylstyrene) by Nagasawa, *et al.*<sup>5,6</sup> The raw data of the first three groups are consistent with one another, but those of Nagasawa, *et al.*, are somewhat different from others in behavior. In addition, no definite conclusion has been reached.

In this work, our primary attention is directed to the behavior of the mean-square radius  $\langle S^2 \rangle$  and intrinsic viscosity  $[\eta]$  of a polymer chain, or the statistical-radius expansion factor  $\alpha_S$  and viscosity-radius expansion factor  $\alpha_\eta$ , as defined by

$$\alpha_S^2 = \langle S^2 \rangle / \langle S^2 \rangle_0 \quad (1)$$

$$\alpha_\eta^3 = [\eta] / [\eta]_0 \quad (2)$$

where  $\langle S^2 \rangle_0$  and  $[\eta]_0$  denote the unperturbed

values of  $\langle S^2 \rangle$  and  $[\eta]$  in the theta state, respectively. Berry<sup>1</sup> has concluded that the Flory—Fisk theory<sup>7</sup> of  $\alpha_S$  is in good agreement with experiment, and that  $\alpha_\eta$  is not a function of only the excluded-volume parameter  $z$ , indicating the existence of the draining effect, where  $z$  is defined for the chain of  $n$  effective bonds with length  $a$  by the equation

$$z = (3/2\pi a^2)^{3/2} \beta n^{1/2} = (4\pi \langle S^2 \rangle_0)^{-3/2} \beta n^2 \quad (3)$$

with  $\beta$  the binary-cluster integral, or the effective excluded volume, for a pair of segments. Fujita, *et al.*,<sup>2,3</sup> and Yamakawa, *et al.*,<sup>4,8</sup> have criticized Berry's procedure of analyzing data, especially of estimating  $z$ , and set forth two criteria to examine the agreement between theory and experiment. Their conclusions are the following. (1) the modified Flory theory<sup>9,10</sup> of  $\alpha_S$

$$\alpha_S^5 - \alpha_S^3 = 1.276z \quad (\text{F, m}) \quad (4)$$

and also the Yamakawa—Tanaka theory<sup>11</sup>

$$\alpha_S^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \quad (\text{YT}) \quad (5)$$

are in satisfactory agreement with experiment, and (2) if  $z$  is estimated using eq 5, the observed

$\alpha_\eta$  is a function of only  $z$ . Reanalysis of Berry's data has also led to the same conclusions.

On the other hand, Nagasawa's conclusions<sup>5,6</sup> are as follows: (1) for good-solvent systems, the F, m equation (eq 4) is valid for polymer molecular weights greater than  $10^6$  but its validity is inconclusive for smaller molecular weights, and (2) the observed  $\alpha_\eta$  is not a function of only  $z$  if  $z$  is estimated using eq 4, and this does not necessarily indicate the existence of draining effect but rather the inadequacy of using eq 4. In this connection, we must refer to the claim of Isihara<sup>12</sup> that the data of Fujita, *et al.*, for  $\alpha_\eta$  compare well with his own theory, which predicts the existence of the draining effect in  $\alpha_\eta$ .

There therefore seems to be some confusion in the present situation regarding experimental tests of the theory of the excluded volume effect in polymer solutions. For this reason, we present some light-scattering and viscosity data recently obtained for poly(*p*-bromostyrene) in theta, intermediate, and good solvents, and add further discussion to the previous work, together with replies to criticism by Isihara and Nagasawa.

## EXPERIMENTAL

### Materials

The procedure for the preparation of the monomer, *p*-bromostyrene, was described in the previous paper.<sup>13</sup> It was prepared from *p*-bromobenzaldehyde, which was obtained by the oxidation of *p*-bromotoluene prepared from *p*-toluidine by the Sandmeyer method, but the details are not reproduced here. The boiling point of the monomer obtained was 57°C at 4.0 mmHg, and its refractive index at 17.1°C for the sodium D line was 1.5950.

We prepared 54.7 g (71% conversion) of poly(*p*-bromostyrene) by thermal polymerization of 77.0 g of *p*-bromostyrene at 70°C for 164 hr. Elementary analysis of the polymer was carried out; the results were C, 52.78; H, 3.94; Br, 43.38; the calculated values being C, 52.49; H, 3.85; Br, 43.66.

51 g of poly(*p*-bromostyrene) was successively divided into five crude fractions by the addition of methanol to its 2-% solution in toluene at 30°C. The last three fractions were further

fractionated by successive precipitations in a similar manner. Thus we obtained 18 fractions in all. Each final fraction was dissolved in toluene, filtered through a 30- $\mu$ -sintered glass filter, precipitated into methanol, and dried by evacuation at 50°C.

We chose benzene, dioxane, and monochlorobenzene as theta, intermediate, and good solvents for poly(*p*-bromostyrene), respectively. Light-scattering and viscosity measurements were carried out in the intermediate and good solvents at 30°C, and in benzene at temperatures ranging from 25 to 50°C. Osmotic pressure measurements were also carried out in toluene at 30°C. Benzene and toluene were purified according to standard procedures, and fractionally distilled. Dioxane was refluxed over sodium for two days, and fractionally distilled. Monochlorobenzene was washed according to the standard procedure, dried over calcium chloride for one day, refluxed over calcium hydride for one day, and fractionally distilled. The density of dioxane was measured pycnometrically at 30°C; the result was 1.0233 g/ml. For the densities of other solvents at temperatures of measurement, literature values<sup>14</sup> were used. Refractive indices of benzene, dioxane, and monochlorobenzene for light of wavelength 436 m $\mu$  were calculated according to the same procedure as before.<sup>4</sup> The results thus obtained at 30°C are 1.515<sub>5</sub> for benzene, 1.424<sub>5</sub> for dioxane, and 1.541<sub>1</sub> for monochlorobenzene. For benzene, the values at 25 and 50°C are 1.519<sub>3</sub> and 1.500<sub>4</sub>, respectively.

In the case of dioxane, monochlorobenzene, and toluene solutions, the most concentrated solution of each fraction was stirred continuously for two days at room temperature and sequential dilutions were made to obtain test solutions. Monochlorobenzene solutions were handled in the dark as much as possible to prevent photo and oxidative degradation of the polymer. The most concentrated solution of each fraction in benzene was stirred continuously for 1–2 weeks at 48°C and sequential dilutions were made. The concentrations of the most concentrated solutions were determined gravimetrically except for light-scattering measurements on fractions III-1 and III-3. In the case of these high-molecular-weight fractions, sedimentation of a detectable amount of the polymer occurred in the course

of optical purification by centrifugation, and the concentrations were determined by dry weights. Those of all the diluted solutions were determined from known dilution factors.

#### Light Scattering

Light-scattering measurements were carried out in a Shimadzu photometer with a cylindrical cell. The apparatus was calibrated according to the same procedure as before.<sup>4</sup> Optical purification of both the most concentrated solutions and solvents was carried out by centrifugation at 20000 rpm for 1 hr using a Marusan centrifuge. Each purified benzene solution was stirred in a cell at 35°C for 20 hr before measurements. All measurements were carried out with unpolarized light of wavelength 436 m $\mu$ , and data were obtained for four polymer concentrations for scattering angles from 35 to 145°C. The sample temperature was held to  $\pm 0.05^\circ\text{C}$  over the range of temperature from 25 to 50°C.

Refractive-index-increment measurements were carried out at 30°C using a Shimadzu differential refractometer. The sample temperature was held to  $\pm 0.03^\circ\text{C}$ . The results for 436-m $\mu$  light were 0.103 (ml/g) for benzene, 0.167 for dioxane, and 0.088<sub>8</sub> for monochlorobenzene.

Analysis of all but the scattering data for fractions III-1 and III-3 in monochlorobenzene

was carried out according to the procedure of Berry,<sup>1</sup> plotting the square root of  $Kc/R_\theta$  against  $c$  and  $\sin^2(\theta/2)$  with  $R_\theta$  the Rayleigh ratio,  $c$  the polymer concentration in conventional units,  $\theta$  the scattering angle, and  $K$  the well-known constant involving the refractive index and its increment. Although second virial coefficients  $A_2$  for these two fractions in monochlorobenzene were determined from the Berry plots, their weight-average molecular weights  $M_w$  and  $z$ -average mean-square radii  $\langle S^2 \rangle_z$  were determined applying a method recently proposed by Fujita,<sup>15</sup> since the plots of  $(Kc/R_\theta)^{1/2}$  against  $\sin^2(\theta/2)$  exhibited marked deviations from linearity.

Fujita's procedure is based on the recent experimental fact that Debye's scattering function<sup>16</sup> is valid over a wide range for chains with excluded volume as well as for unperturbed chains.<sup>17</sup> The following basic equations<sup>15</sup> result

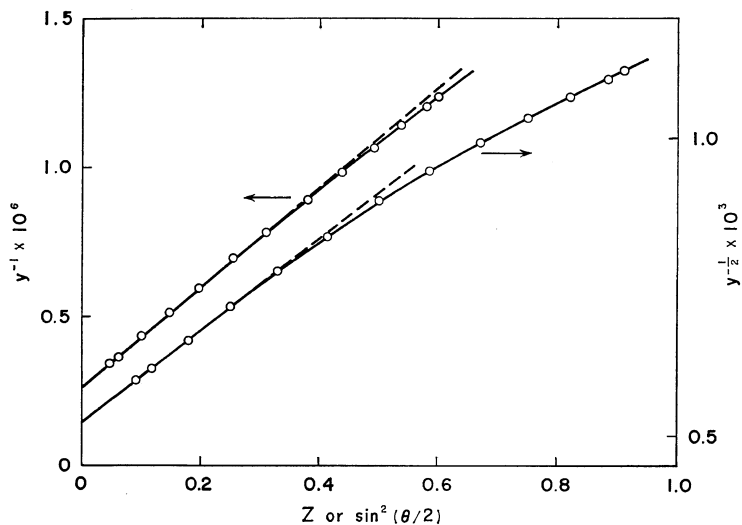
$$(Kc/R_\theta)_{c=0} \equiv 1/y(u) = 1/M_w + bZ(u) + O(Z^2) \quad (6)$$

$$b = (32\pi^2/3\lambda^2) \langle S^2 \rangle_z / M_w \quad (7)$$

$$Z(u) = [y(u)u^{4/3}]^{-1} \int_0^u y(u)u du \quad (8)$$

$$u = \sin^3(\theta/2) \quad (9)$$

where  $\lambda$  is the wavelength of light in the medium. For homogeneous unperturbed chains,



**Figure 1.** Comparison between the Fujita plots and the Berry plots of  $(Kc/R_\theta)_{c=0}$  for fraction III-1 of poly(*p*-bromostyrene) in monochlorobenzene at 30°C.

$y^{-1}$  is given exactly by the equation linear in  $Z$ . Thus  $M_w$  and  $\langle S^2 \rangle_z$  can be obtained from the plot of  $y^{-1}$  against  $Z$ , which can be estimated by performing the integration in eq 8 graphically. An example of this plot is shown in Figure 1, using the data for fraction III-1 in monochlorobenzene. For comparison, the square-root plot of Berry ( $y^{-1/2}$  vs.  $\sin^2(\theta/2)$ ) for the same system is also shown in the figure. The new method is seen to appreciably decrease deviations from linearity.

#### Viscosity

Intrinsic-viscosity measurements were carried out using a viscometer of the Ubbelohde type at the same temperatures as those for the light-scattering measurements. The sample temperature was held to  $\pm 0.02^\circ\text{C}$ . Both shear-rate and kinetic-energy corrections were unnecessary. The data were extrapolated to infinite dilution to determine intrinsic viscosities, plotting  $\eta_{sp}/c$  against  $c$ , and also  $(\ln \eta_r/c)$  against  $c$  for benzene solutions, where  $\eta_{sp}$  and  $\eta_r$  are the specific and relative viscosities of the solutions, respectively.

#### Osmotic Pressure

From the previous study,<sup>18</sup> the present samples were expected to be fairly homogeneous in molecular weight. Thus, osmotic-pressure measurements were carried out only on two fractions in toluene at  $30^\circ\text{C}$ , using osmometers of the modified Zimm—Myerson type<sup>18</sup> fitted with adequately conditioned gel-cellophane membranes. The sample temperature was held to  $\pm 0.005^\circ\text{C}$ . The data were extrapolated to infinite dilution to determine number-average molecular weights  $M_n$ , plotting the square root of  $\pi/c$  against  $c$  with  $\pi$  the osmotic pressure.

## RESULTS

Table I summarizes light-scattering and intrinsic-viscosity data for fractions III-3, III-5, and III-7 of poly(*p*-bromostyrene) in benzene at various temperatures  $t$  ( $^\circ\text{C}$ ) ranging from 25 to  $50^\circ\text{C}$ , the molecular weights being given in the second column of Table II. With these data, we plotted the product  $A_2 M_w$  against temperature  $t$ , and found  $\theta = 26.3^\circ\text{C}$  as the theta temperature

Table I. Light-scattering and intrinsic-viscosity data for poly(*p*-bromostyrene) in benzene

$t$ , $^\circ\text{C}$	III-3			III-5			III-7		
	$A_2 \times 10^4$ , ml mol/g <sup>2</sup>	$\langle S^2 \rangle_z \times 10^{12}$ , cm <sup>2</sup>	$[\eta]$ , dl/g	$A_2 \times 10^4$ , ml mol/g <sup>2</sup>	$\langle S^2 \rangle_z \times 10^{12}$ , cm <sup>2</sup>	$[\eta]$ , dl/g	$A_2 \times 10^4$ , ml mol/g <sup>2</sup>	$\langle S^2 \rangle_z \times 10^{12}$ , cm <sup>2</sup>	$[\eta]$ , dl/g
50	0.21 <sub>0</sub>	18.3	0.992	0.26 <sub>7</sub>	13.2	0.877	—	—	—
45	0.18 <sub>6</sub>	17.6	0.968	0.22 <sub>1</sub>	12.8	0.841	—	—	—
40	0.15 <sub>6</sub>	16.8	0.927	0.17 <sub>9</sub>	12.2	0.810	—	—	—
35	0.10 <sub>8</sub>	16.1	0.857	0.13 <sub>2</sub>	11.3	0.761	—	—	—
30	0.05 <sub>3</sub>	15.1	0.820	0.07 <sub>4</sub>	10.9	0.703	0.05 <sub>6</sub>	5.72	0.452
28	0.03 <sub>4</sub>	14.6	0.793	0.04 <sub>8</sub>	10.6	0.686	0.02 <sub>8</sub>	5.63	0.447
27	0.01 <sub>8</sub>	14.3	0.777	0.02 <sub>2</sub>	10.4	0.677	0.01 <sub>4</sub>	5.61	0.444
26	-0.01 <sub>6</sub>	14.0	0.766	—	—	—	-0.04 <sub>4</sub>	5.53	0.440
25	-0.03 <sub>8</sub>	13.9	0.752	-0.01 <sub>7</sub>	10.1	0.660	-0.06 <sub>9</sub>	5.46	0.436

Table II. Mean-square radii and intrinsic viscosities in benzene at the theta temperature ( $26.3^\circ\text{C}$ )

Fraction	$M_w \times 10^{-4}$	$\langle S^2 \rangle_{\theta,z} \times 10^{12}$ , cm <sup>2</sup>	$\langle S^2 \rangle_{\theta,z} / M_w \times 10^{18}$	$[\eta]_\theta$ , dl/g	$[\eta]_\theta / M_w^{1/2} \times 10^5$	$M_n \times 10^{-4}$	$M_w / M_n$
III-3	250	14.1	5.68	0.771	48.8	—	—
III-4 <sup>a</sup>	206	11.7	5.68	0.741	51.7	—	—
III-5	179	10.2	5.70	0.672	50.2	176 <sup>b</sup>	1.0 <sub>2</sub>
IV-2 <sup>a</sup>	113	6.44	5.70	0.543	51.2	—	—
III-7	84.0	5.54	6.60	0.442	48.2	77.7 <sup>b</sup>	1.0 <sub>8</sub>

<sup>a</sup> From direct measurements at the  $\theta$  temperature ( $26.3^\circ\text{C}$ ).

<sup>b</sup> From osmotic-pressure measurements in toluene at  $30^\circ\text{C}$ .

at which  $A_2$  vanishes.

From plots of  $\langle S^2 \rangle_z$  and  $[\eta]$  against  $t$  for the same systems as above, values of  $\langle S^2 \rangle_{0,z}$  and  $[\eta]_\theta$  at the  $\theta$  temperature were obtained by interpolation to 26.3°C. The results thus obtained are given in Table II, where the results for fractions III-4 and IV-2 were obtained from direct light-scattering and viscosity measurements in benzene at 26.3°C. The expected constancies of the ratios  $\langle S^2 \rangle_{0,z}/M_w$  and  $[\eta]_\theta/M_w^{1/2}$  are observed within experimental uncertainty, though the former ratio for fraction III-7 with the lowest molecular weight is a little too large. Thus we assign the following values to these ratios

$$\langle S^2 \rangle_{0,z}/M_w = 5.69 \times 10^{-18} \quad (10)$$

$$[\eta]_\theta/M_w^{1/2} = 50.0 \times 10^{-5} \quad (11)$$

$\langle S^2 \rangle_{0,z}$  being expressed in centimeters squared and  $[\eta]_\theta$  in deciliters per gram. In the previous study on polar polymers,<sup>13</sup> we obtained the corresponding values for the same polymer in toluene by extrapolation methods. The value given by eq 10 is in good agreement with the previous one, while the value given by eq 11 is somewhat greater than the corresponding value previously obtained. This difference does not necessarily indicate the existence of a solvent effect, but rather may be regarded as arising from an error in extrapolation. If we adopt the values given by eq 10 and 11, we obtain  $\Phi_0 = 2.5 \times 10^{21}$  for the Flory-Fox viscosity con-

**Table III.** Light-scattering and intrinsic-viscosity data for poly(*p*-bromostyrene) in dioxane at 30°C.

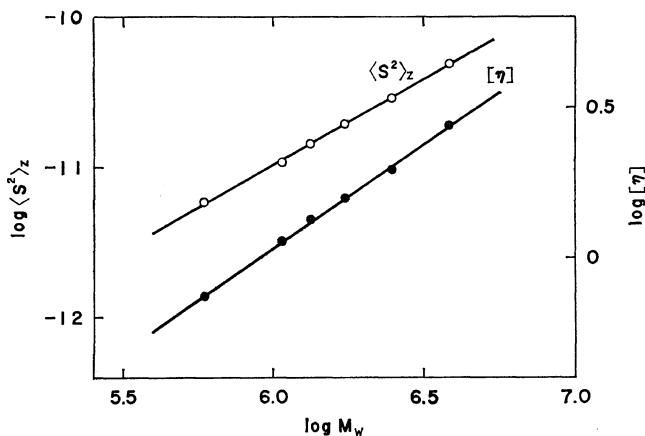
Fraction	$M_w \times 10^{-4}$	$A_2 \times 10^4$ , m <sup>2</sup> mol/g <sup>2</sup>	$\langle S^2 \rangle_z \times 10^{12}$ , cm <sup>2</sup>	$[\eta]$ , dl/g
III-4	218	0.59 <sub>2</sub>	20.2	1.26
III-7	78.4	0.85 <sub>8</sub>	7.89	0.681
V-2	59.2	0.91 <sub>9</sub>	5.06	0.599

**Table IV.** Light-scattering and intrinsic-viscosity data for poly(*p*-bromostyrene) in monochlorobenzene at 30°C.

Fraction	$M_w \times 10^{-4}$	$A_2 \times 10^4$ , m <sup>2</sup> mol/g <sup>2</sup>	$\langle S^2 \rangle_z \times 10^{12}$ , cm <sup>2</sup>	$[\eta]$ , dl/g
III-1	384	0.72 <sub>0</sub>	49.0	2.76
III-3	248	0.85 <sub>5</sub>	28.8	1.96
III-5	173	0.95 <sub>3</sub>	19.4	1.57
III-6	133	1.10	14.4	1.34
IV-2	107	1.15	10.9	1.13
V-2	59.2	1.32	5.87	0.741

stant<sup>19</sup> at the  $\theta$  temperature. In Table II are also given values of  $M_n$  and of the ratio  $M_w/M_n$  for fractions III-5 and III-7. It is reasonable to ignore corrections for heterogeneity in molecular weight in this work.

Light-scattering and viscosity data in dioxane and monochlorobenzene at 30°C are given in Tables III and IV, respectively. Figure 2 shows log-log plots of  $\langle S^2 \rangle_z$  vs.  $M_w$  and of  $[\eta]$  vs.  $M_w$  for poly(*p*-bromostyrene) in monochloro-



**Figure 2.** Double logarithmic plots of  $\langle S^2 \rangle_z$  against  $M_w$  and of  $[\eta]$  against  $M_w$  for poly(*p*-bromostyrene) in monochlorobenzene at 30°C.

benzene at 30°C. The equations for the straight lines in the figure are

$$\langle S^2 \rangle_z = 1.54 \times 10^{-18} M_w^{1.14} \quad (12)$$

$$[\eta] = 7.43 \times 10^{-5} M_w^{0.69} \quad (13)$$

which were determined by the method of least squares,  $\langle S^2 \rangle_z$  and  $[\eta]$  being expressed in the same units as in eq 10 and 11, respectively.

We calculated values of  $\alpha_S$  and  $\alpha_\eta$  according to the same procedures as those in the previous work on poly(*p*-methylstyrene).<sup>4</sup>

## DISCUSSION

### Behavior of $\alpha_S$ and $A_2$

We test approximate theories of  $\alpha_S$  and  $A_2$  using two criteria proposed by Fujita and Yamakawa. First, we consider the interpenetration function  $\Psi$  appearing in the second virial coefficient

$$A_2 = 4\pi^{3/2} N_A (\langle S^2 \rangle^{3/2} / M^2) \Psi \quad (14)$$

where  $N_A$  is Avogadro's number (and  $M$  is the molecular weight of the homogeneous polymer).

If  $h$  is, as usual, the correction to the single-contact approximation of  $A_2$ , then  $\Psi$  may be related to  $h$  by the equation

$$\Psi = \bar{z}h(\bar{z}) \quad (15)$$

with

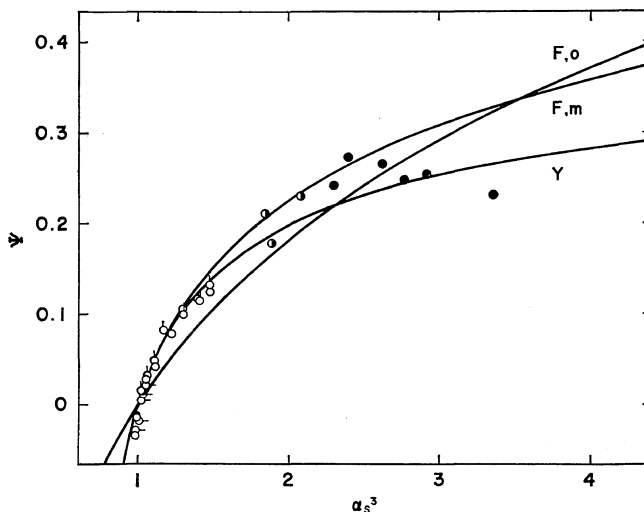
$$\bar{z} = z/\alpha_S^3 \quad (16)$$

Values of  $\Psi$  were calculated from eq 14 with observed values of  $M_w$ ,  $A_2$ , and  $\langle S^2 \rangle_z$  given in the tables, and are plotted against the corresponding values of  $\alpha_S^3$  in Figure 3. Curves F, m and Y in the figure represent the theoretical values predicted by the modified Flory—Krigbaum—Orofino theory<sup>10,20,21</sup> of  $\Psi$  with the modified Flory theory of  $\alpha_S$ , eq 4, and by the Kurata—Yamakawa theory<sup>8,22</sup> of  $\Psi$  with the Yamakawa—Tanaka theory of  $\alpha_S$ , eq 5, respectively. These read

$$\Psi = [\ln(1 + 5.73\bar{z})]/5.73 \quad (\text{F, m}) \quad (17)$$

$$\Psi = 0.547[1 - (1 + 3.903\bar{z})^{-0.4683}] \quad (\text{Y}) \quad (18)$$

The values of the numerical constants in eq 18 have been recalculated with the use of revised



**Figure 3.** Plots of  $\Psi$  against  $\alpha_S^3$  for fractions of poly(*p*-bromostyrene): ●, in monochlorobenzene at 30°C; ◐, in dioxane at 30°C; ○ (III-3), ◑ (III-5), ◒ (III-7), in benzene at various temperatures. The three curves represent the theoretical values: curve F, o, the original Flory—Krigbaum—Orofino theory of  $\Psi$  (eq 19) with the original Flory theory of  $\alpha_S$  (eq 20); curve F, m, the modified Flory—Krigbaum—Orofino theory of  $\Psi$  (eq 17) with the modified Flory theory of  $\alpha_S$  (eq 4); curve Y, the Kurata—Yamakawa theory of  $\Psi$  (eq 18) with the Yamakawa—Tanaka theory of  $\alpha_S$  (eq 5).

value of 9.202 recently obtained by Tagami and Casassa<sup>23</sup> for the coefficient of the triple-contact term in  $h(\bar{z})$ , the corresponding value originally obtained by Albrecht<sup>24</sup> being 9.726. However, this change affects only slightly the values of the Kurata—Yamakawa form of  $\Psi$ . In Figure 3 are also shown the theoretical values predicted by the original Flory—Krigbaum—Orofino theory<sup>20,21</sup> of  $\Psi$  with the original Flory theory<sup>9</sup> of  $\alpha_S$

$$\Psi = [\ln(1 + 2.30\bar{z})]/2.30 \quad (\text{F, o}) \quad (19)$$

with

$$\alpha_S^5 - \alpha_S^3 = 2.60z \quad (\text{F, o}) \quad (20)$$

It is seen that the present results are consistent with the previous ones<sup>4</sup> for poly(*p*-methylstyrene), and also with those of Berry<sup>1</sup> for polystyrene and of Fujita, *et al.*,<sup>3</sup> for polychloroprene. In precise terms, however, our values of  $\Psi$  previously obtained for poly(*p*-methylstyrene) are somewhat smaller than the present ones. This may be regarded as arising from the fact that the previous samples were more heterogeneous in molecular weight, thereby giving larger values of  $\langle S^2 \rangle_z$  and smaller values of  $\Psi$ . As discussed previously,<sup>4</sup> the square-root plot leads to underestimates of  $A_2$  for high-molecular-weight fractions

in good solvents. For this reason, the value of  $\Psi$  for fraction III-1 in monochlorobenzene (with the highest value of  $\alpha_S$  in Figure 3) may be considered to be a little too small.

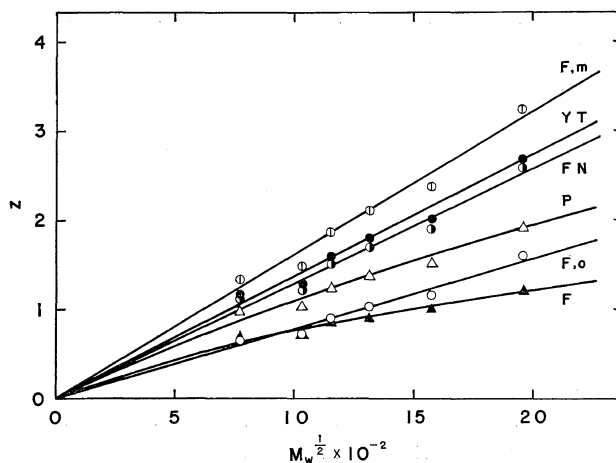
Next we test approximate theories of  $\alpha_S$  with respect to the second criterion, *i. e.*, the linearity between  $z$  and  $M_w^{1/2}$ . We estimated values of  $z$  from observed values of  $\alpha_S$  for poly(*p*-bromostyrene) in monochlorobenzene at 30°C using the F, m equation (eq 4), the YT equation (eq 5), the F, o equation (eq 20), the Fixman equation<sup>25</sup>

$$\alpha_S^3 = 1 + 1.914z \quad (\text{F}) \quad (21)$$

the Ptitsyn equation<sup>26</sup>

$$5.12\alpha_S^2 = 4.12 + (1 + 9.79z)^{2/3} \quad (\text{P}) \quad (22)$$

and also the theoretical curve obtained by Fujita and Norisuye (FN).<sup>27</sup> The values of  $z$  thus obtained are plotted against  $M_w^{1/2}$  in Figure 4. The results displayed in this figure do not alter our previous conclusion. That is, the data points obtained from all but the F and P equations fall around the indicated lines passing through the origin. Thus, the F, m equation for  $\alpha_S$  and also the YT equation satisfy both criteria, as in the case of polystyrene, polychloroprene, and poly(*p*-methylstyrene).



**Figure 4.** Test of the linearity between  $z$  and  $M_w^{1/2}$  with the data for poly(*p*-bromostyrene) in monochlorobenzene at 30°C. The values of  $z$  were calculated from various theories of  $\alpha_S$ : ○, from the original Flory theory (eq 20); ⊙, from the modified Flory theory (eq 4); ●, from the Yamakawa—Tanaka theory (eq 5); ⊕, from the Fujita—Norisuye theory; ▲, from the Fixman theory (eq 21); △, from the Ptitsyn theory, (eq 22).

*Behavior of  $\alpha_\eta$* 

Figure 5 shows plots of  $\log \alpha_\eta^3$  against  $\log \alpha_S^3$  for poly(*p*-bromostyrene), as proposed by Fujita, *et al.*<sup>3,28</sup> Curve 1 represents the best fit to the data for polychloroprene<sup>2,3</sup> and poly(*p*-methylstyrene).<sup>4</sup> The present data in benzene reproduce well the relationship between  $\alpha_\eta$  and  $\alpha_S$ , while the data points for dioxane and monochlorobenzene solutions lie only a little below curve 1. This does not necessarily lead to the conclusion that such plots form no single-composite curve, considering the experimental accuracy. However, the determination of  $\alpha_S$  and  $\alpha_\eta$  requires some comments. Possibly there occurs splitting of the curves of  $\alpha_\eta$  against  $\alpha_S$  in different solvents, if  $\langle S^2 \rangle_0$  is dependent on solvent and we ignore this effect to determine  $\alpha_S$  and  $\alpha_\eta$ . The local dipolar interactions in the chains of poly(*p*-halostyrene)s are rather weak compared to those in the chains of cellulose derivatives. In fact, no remarkable effect of solvent on  $\langle S^2 \rangle_0$  has been observed in the case of poly(*p*-chlorostyrene).<sup>29,30</sup> For comparison, the theoretical values predicted by the Kurata—Yamakawa theory<sup>31</sup>

$$\alpha_\eta^3 = \alpha_S^{2.43} \quad (23)$$

and the boson-operator theory of Fixman<sup>32,33</sup>

are also represented by line 2 and curve 3, respectively, in Figure 5. The latter values were calculated from the Fixman theory<sup>32</sup> of  $\alpha_\eta$  combined with the Stidham—Fixman theory<sup>33</sup> of  $\alpha_S$ .

We may examine, instead of  $\alpha_\eta$ , the behavior of the viscosity constant  $\Phi$ , as defined by the equation<sup>19</sup>

$$[\eta] = 6^{3/2} \Phi \langle S^2 \rangle^{3/2} / M \quad (24)$$

since there is the relationship between them

$$\Phi / \Phi_0 = \alpha_\eta^3 / \alpha_S^3 \quad (25)$$

Values of  $\Phi / \Phi_0$  calculated from eq 25 for poly(*p*-bromostyrene) are plotted against  $\alpha_S^3$  in Figure 6. Curves 1—3 correspond to curves 1—3, respectively, in Figure 5. The rapid decrease in  $\Phi$  near the  $\theta$  temperature is again observed. However, the data scatter appreciably for  $\alpha_S^3 > 2$ , and in this work, we cannot definitely conclude that  $\Phi$  increases gradually for  $\alpha_S^3 > 2$ .

Figure 7 shows plots of  $\alpha_\eta^3$  against  $z$  for poly(*p*-bromostyrene), where the values of  $z$  were determined from the values of  $\alpha_S$  using the YT equation (eq 5) as before. Curve 1 represents the best fit to the data for polychloroprene<sup>2,3</sup> and poly(*p*-methylstyrene).<sup>4</sup> The results displayed in Figures 5—7 do not require much change in

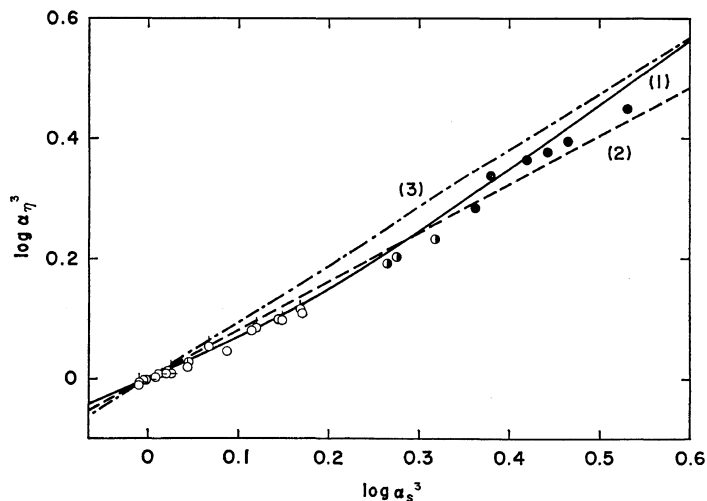
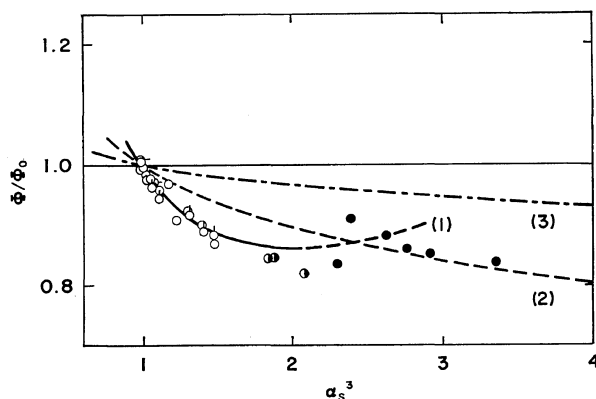


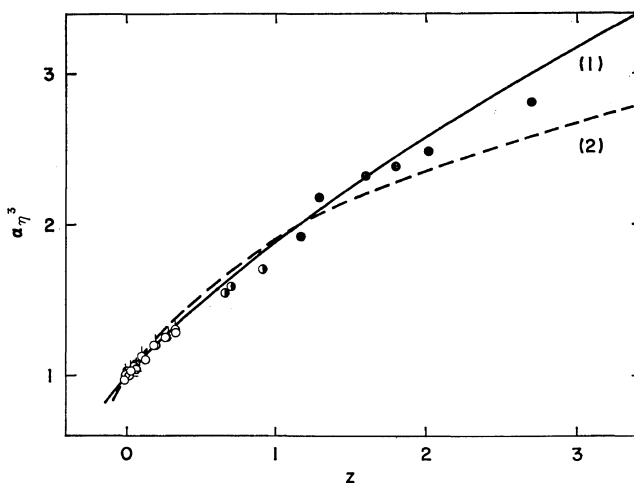
Figure 5. Double logarithmic plots of  $\alpha_\eta^3$  against  $\alpha_S^3$  for fractions of poly(*p*-bromostyrene). The symbols have the same significance as those in Figure 3. Curve 1 (—), the best fit to the data for polychloroprene<sup>2,3</sup> and poly(*p*-methylstyrene);<sup>4</sup> line 2 (---), the Kurata—Yamakawa theory (eq 23); curve 3 (-·-·-), the boson-operator theory of Fixman.



Test of the Two-Parameter Theory: Poly(*p*-bromostyrene)



**Figure 6.** Plots of  $\Phi/\Phi_0$  against  $\alpha_S^3$  for fractions of poly(*p*-bromostyrene). The symbols have the same significance as those in Figure 5: curve 1 (—), the best fit to the data for polychloroprene<sup>2,3</sup> and poly(*p*-methylstyrene);<sup>4</sup> curve 2 (---), the Kurata—Yamakawa theory; curve 3 (— · —), the boson-operator theory of Fixman.



**Figure 7.** Plots of  $\alpha_\eta^3$  against  $z$  for fractions of poly(*p*-bromostyrene). The symbols have the same significance as those in Figure 5: curve 1 (—), the best fit to the data for polychloroprene<sup>2,3</sup> and poly(*p*-methylstyrene);<sup>4</sup> curve 2 (---), the boson-operator theory of Fixman. The values of  $z$  were calculated from the values of  $\alpha_S$  using eq 5.

our previous conclusion regarding the behavior of  $\alpha_\eta$ . Curve 2 in Figure 7 represents the theoretical values predicted by the boson-operator theory of Fixman.<sup>32</sup> It is seen that the curvature of curve 2 is too large compared to that of curve 1. Note that the interrelation between curves 1 and 2 in Figure 7 is different from that between the corresponding curves 1 and 3 in Figure 5; that is, the Fixman theory predicts

values of  $\alpha_\eta^3$  greater than the observed ones only in the range of relatively small (positive)  $z$  in Figure 7 but over a wide range in Figure 5. This arises from the fact that the boson theory of Fixman and our theory predict different dependences of  $\alpha_S$  on  $z$ .

Our attention is now directed to the behavior of  $\alpha_\eta$  for small  $z$ . Figure 8 is an enlargement of the region of small  $z$  in Figure 7. Curve 1

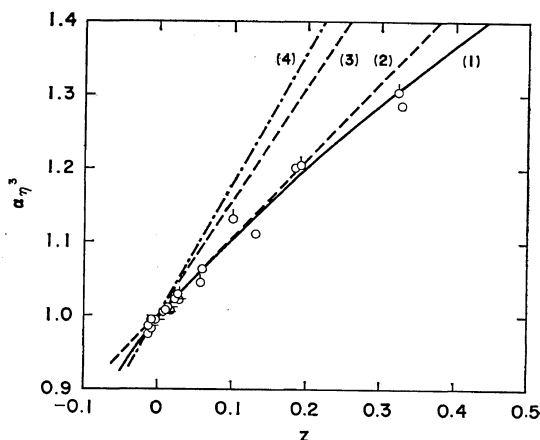
is an empirical fit to the data. Straight line 2 represents the first-order perturbation theory prediction recently obtained by Yamakawa and Tanaka<sup>34</sup>

$$\alpha_\gamma^3 = 1 + C_1 z - \dots \quad (26)$$

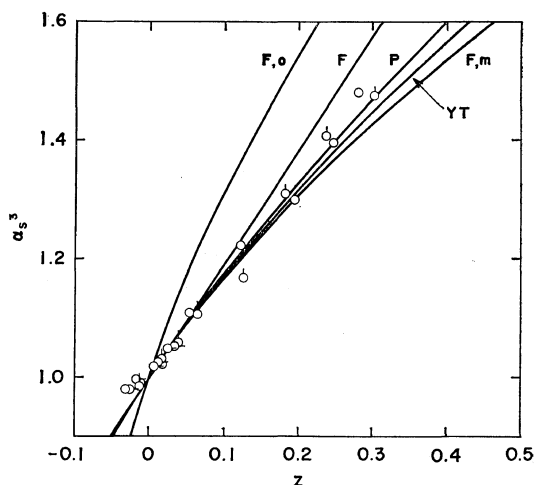
with  $C_1=1.06$ . We note that this theory has been derived by introducing the excluded-volume effect into the viscosity theory of Zimm<sup>34</sup> in Hearst's version.<sup>36</sup> Straight lines 3 and 4 represent the approximate first-order perturbation theory predictions (eq 26) with  $C_1=1.55$  of Kurata and Yamakawa<sup>31</sup> and with  $C_1=1.80$  of Fixman,<sup>32,34</sup> respectively. As pointed out previously,<sup>3,4</sup> it is clear that both the Kurata—Yamakawa theory and the Fixman theory overestimate  $\alpha_\gamma^3$  for positive small  $z$ . On the other hand, the new theory of Yamakawa and Tanaka is seen to be in satisfactory agreement with experiment for  $z < 0.3$ . This is also the case for poly(*p*-methylstyrene) in diethyl succinate.<sup>4</sup> Fujita, *et al.*,<sup>3</sup> have assigned the experimental value of 1.24 to  $C_1$  for polychloroprene, while we have predicted that  $1.05 < C_1 < 1.55$ .<sup>4</sup> At present, it is difficult to determine accurately the experimental value of  $C_1$ . It depends, to some extent, on the range of  $z$  over which the first-order perturbation theory of  $\alpha_\gamma^3$  may be regarded as experimentally valid.

In this connection, we examine the range of validity of the first-order perturbation theory of  $\alpha_S^3$ . Figure 9 shows plots of  $\alpha_S^3$  against  $z$  for poly(*p*-bromostyrene) in benzene. In this case, the values of  $z$  were calculated from the values of  $\Psi$  using eq 18.<sup>8</sup> We note that if we use any approximate expressions for  $\Psi$  which give the exact first-order perturbation theory of  $h$ , we obtain almost the same values of  $z$  as long as  $\Psi$  is smaller than 0.18. The curves in Figure 9 represent the theoretical values calculated from various approximate theories, the symbols attached to the curves having the same significance as those in Figure 4. Straight line F represents just the exact first-order perturbation theory of  $\alpha_S^3$ , and it is seen to be valid for  $z < 0.1-0.15$ . This is consistent with the earlier conclusion obtained by Kurata, Yamakawa, and Teramoto<sup>37</sup> by a different method of analyzing data. We may expect that the  $z$  series of  $\alpha_\gamma^3$  converges more rapidly than does that of  $\alpha_S^3$ , since the

value of 1.06 for  $C_1$  in  $\alpha_\gamma^3$  is much smaller than the corresponding value of 1.914 in  $\alpha_S^3$  and the



**Figure 8.** Plots of  $\alpha_\gamma^3$  against  $z$  for fractions of poly(*p*-bromostyrene) in benzene at various temperatures: curve 1 (—), empirical fit to the data; line 2 (---), the first-order perturbation theory of Yamakawa and Tanaka (eq 26) with  $C_1=1.06$ ; line 3 (-·-·), the Kurata—Yamakawa theory with  $C_1=1.55$ ; line 4 (— — —), the Fixman theory with  $C_1=1.80$ .



**Figure 9.** Plots of  $\alpha_S^3$  against  $z$  for fractions of poly(*p*-bromostyrene) in benzene at various temperatures. The values of  $z$  were calculated from the values of  $\Psi$  using eq 18. The curves represent the theoretical values calculated from various approximate theories, the symbols attached to the curves having the same significance as those in Figure 4.

experimental curve of  $\alpha_\eta^3$  against  $z$  has a very weak curvature. Thus the range of validity of the first-order perturbation theory of  $\alpha_\eta^3$  must be wider than that of  $\alpha_S^3$ . The above conclusion regarding the agreement between theory and experiment in Figure 8 therefore does not seem unreasonable.

#### Comments on Criticism by Ishihara

Ishihara<sup>12</sup> has claimed that Fujita's plots of  $\log \alpha_\eta^3$  against  $\log \alpha_S^3$  form no single-composite curve and the data points may be split into two groups, one for theta- and intermediate-solvent systems and the other for good-solvent systems, which may be fitted by two curves calculated from his theory. According to the theory of Ishihara, who has employed the Oseen hydrodynamic interaction tensor, as in other theories of this type,  $\alpha_\eta$  is a function of  $z$  and also of the draining parameter

$$h = n^{1/2} \zeta / (12\pi^3)^{1/2} a \eta_0 \quad (27)$$

where  $\zeta$  is the friction constant of a polymer segment in a solvent medium with viscosity coefficient  $\eta_0$ . The two groups of data correspond to two different values of  $h$ , the assigned values of  $h$  being relatively small. In other words, Ishihara has claimed that the draining effect cannot be ignored. In this respect, his opinion is essentially equivalent to Berry's conclusion.<sup>1</sup> On the other hand, in all the theories displayed in Figure 8,  $h$  is formally taken as infinity, corresponding to the non-draining limit.

Now it is well known that no draining effect in flexible chains has been observed at theta temperatures. In order to explain this fact by Ishihara's theory and also by all other theories of this type, we must take  $h$  as infinity at the theta temperature. Therefore Ishihara assumes implicitly that  $h$  takes small values in the non-theta state, depending on solvent. This is equivalent to assigning much smaller values to the Stokes radius of the segment and/or much larger values to the effective bond length in the non-theta state than in the theta state. Such solvent effects are not easy to understand. Moreover, Ishihara's theoretical curves of  $\log \alpha_\eta^3$  against  $\log \alpha_S^3$  are concave downward, contrary to experimental results; presumably he has misread the data. It is more reasonable to consider the

data points of this plot to fall on a single curve within experimental uncertainty. However, the assignment of finite values to  $h$  is plausible. Although Yamakawa<sup>38</sup> has recently attempted to deduce the constancy of  $[\eta]_0/M^{1/2}$  with finite values of  $h$ , this theory is difficult to extend to show whether  $\alpha_\eta$  is apparently a function of only  $z$  for finite values of  $h$ .

#### Comments on Criticism by Nagasawa

Values of  $\Psi$  obtained by Nagasawa, *et al.*,<sup>5</sup> for poly( $\alpha$ -methylstyrene) reach only about 0.2 in toluene, or for large  $\alpha_S$ , while the corresponding values obtained by the other groups reach 0.25–0.30. Their values of  $\Psi$  in toluene are too small, and this seems to result from the overestimation of  $\langle S^2 \rangle$ , though the reason is not clear. In fact, even though they used the monodisperse samples, their values of  $\Phi$  are too small, the value of  $\Phi_0$  being only about  $2.0 \times 10^{21}$ .

According to Nagasawa, *et al.*, values of  $z/M_w^{1/2}$  for their poly( $\alpha$ -methylstyrene) in toluene are plotted against  $\log M_w$  in Figure 10 a, where the values of  $z$  were calculated from the

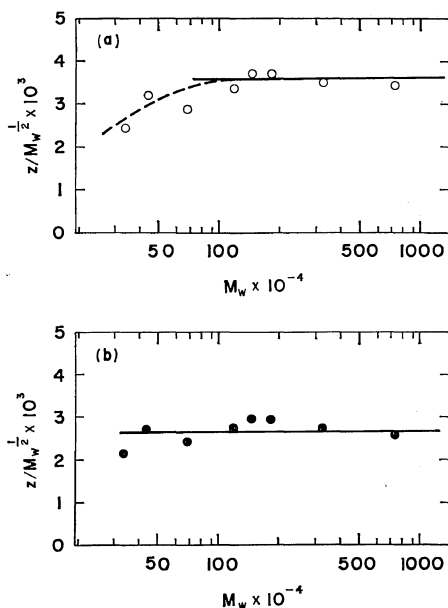


Figure 10. Plots of  $z/M_w^{1/2}$  against  $\log M_w$  with the data of Nagasawa, *et al.*,<sup>5</sup> for poly( $\alpha$ -methylstyrene) in toluene. The values of  $z$  were calculated from the values of  $\alpha_S$  using the F, m equation (eq 4) in (a) and the YT equation (eq 5) in (b).

values of  $\alpha_S$  using the F, m equation (eq 4). Although they have reserved their conclusion, the displayed data show that the F, m equation is invalid for  $M_w < 10^6$  in good solvents. Furthermore, they have shown that plots of  $\alpha_\eta^3$  against  $z$  form no single-compositite curve if  $z$  is estimated using the F, m equation. As shown in Figure 10b, however, the constancy of  $z/M_w^{1/2}$  is improved if we estimate  $z$  using the YT equation (eq 5). We shall not pursue this point any further, since the raw data obtained by Nagasawa, *et al.*, differ from ours in behavior.

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