

# Light-Scattering Studies on Solutions of High and Low Molecular Weight Polystyrene Mixtures Used as Models of Microgel-Containing Solutions

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## Synopsis

Diluted solutions of linear polystyrene (PS) in toluene and dioxane were studied by the light-scattering method. The solutes were mixtures of high- $\bar{M}_w$  and low- $\bar{M}_w$  PS. The dissolved PS mixtures were regarded as polymer solutions containing microgels, the high- $\bar{M}_w$  PS being looked upon as the microgel counterpart. The calculation method as proposed by Strazielle<sup>1</sup> and Burchard<sup>2</sup> was used to evaluate the microgel percentage and particle size, whereby the method could be verified against mixtures with well-known weight composition and  $(\bar{r}_g^2)^{1/2}$ . The  $(\bar{r}_g^2)^{1/2}$  values evaluated for the mixtures from the experimental data were compared with those estimated from the molecular weights of the components, their weight concentrations, and their  $(\bar{r}_g^2)^{1/2}$  values. The method<sup>1,2</sup> was found to be useful for evaluating the microgel content in a sample, but not for  $(\bar{r}_g^2)^{1/2}$  values as calculated by Guinier's procedure nor those calculated by Zimm's procedure; the former were low and the latter were even incongruous. A comparative analysis of the theoretical function  $P^{-1}(\theta)$ -versus- $\sin^2(\theta/2)$  and experimental  $(Kc/R(\theta))_{c=0}$ -versus- $\sin^2(\theta/2)$  curves allowed to discuss the effect of the course of these curves at small angles from 0° to 30° on  $\bar{M}_w$  and  $(\bar{r}_g^2)^{1/2}$  as determined for the high and low molecular weight polystyrene mixtures in toluene as solvent.

## INTRODUCTION

Microgels occurring in polymer solutions are known to affect their physico-chemical properties. The effect is sometimes so pronounced as to make unequivocal interpretation of the experimental results impossible.<sup>1-4</sup> Rheological<sup>5</sup> and mechanical properties and processability of polymers<sup>6</sup> have also been shown to be related to microgel content.

One of the many problems associated with microgels is the correct determination of microgel percentage and particle size in samples investigated. This problem has been dealt with by numerous investigators, for example, Strazielle,<sup>1</sup> Burchard,<sup>2</sup> Kratochvil,<sup>3</sup> and Lange.<sup>7</sup>

An experimental study of model samples which constitute mixtures of high- $\bar{M}_w$  and low- $\bar{M}_w$  polymers involving macromolecules of well-known shape and size will permit a verification of conventional calculation methods and their underlying theoretical assumptions. In the present study, unfractionated linear polystyrene (PS) samples were used as model samples.

## EXPERIMENTAL

### Apparatus

Scattered light intensity was measured with a Fica 42000 photometer using light of wavelength 5460 Å in vacuo at room temperature. Solvents and solutions were centrifuged for 60 min in a Phywe-Pirouette laboratory centrifuge at 25,000 *g* to remove mechanical impurities.

### Samples

High- $\bar{M}_w$  and low- $\bar{M}_w$  PS samples and mixtures thereof were studied by the light-scattering method (LS) in toluene and dioxane as solvents. The refractive index increments  $dn/dc$  for the solutions in toluene and dioxane were taken as 0.1079 cm<sup>3</sup>/g and 0.171 cm<sup>3</sup>/g, respectively.<sup>8</sup> Weight-average molecular weights  $\bar{M}_w$  were evaluated from Zimm plots.<sup>9</sup> For unmixed PS samples, the radius of gyration  $(\bar{r}_g^2)^{1/2}$  was calculated by two methods, viz., Zimm's<sup>9</sup> and Guinier's.<sup>10</sup> The plots used for the calculations will be published elsewhere.<sup>11</sup> The  $(\bar{r}_g^2)^{1/2}$  values obtained were exaggerated on account of the polydispersity of the unmixed polymer samples. (Low- $M_w$  PS had an  $M_w/M_n$  value of 1.04, and high- $M_w$  PS had an  $M_w/M_n$  value of 1.4.) To estimate the approximately correct values for monodisperse samples of identical  $\bar{M}_w$ ,  $(\bar{r}_g^2)^{1/2}$  values were calculated for the solutions in toluene from the reported  $(\bar{r}_g^2)^{1/2}$ -versus- $\bar{M}$  plots,<sup>12,13</sup> as developed for monodisperse materials. The samples examined in this work are characterized in Table I.

## RESULTS AND DISCUSSION

It is not possible to prepare model systems that correspond exactly to microgel-containing solutions. Binary mixtures composed of low- $\bar{M}_w$  (component 1) and high- $\bar{M}_w$  (component 2) polymers may be looked upon as models of microgel-containing polymers. However, the macromolecules of the high- $\bar{M}_w$  PS are regarded as the counterparts of microgel particles. Actually microgels occurring in solutions of PE, polyethylene oxide, PVC, and other polymers have certainly a more compact structure than have high- $M_w$  PS samples. In the solutions of the PS mixtures under study, of overall concentration  $c = c_1 + c_2$ , the component concentrations are made highly disparate,  $c_2 \ll c_1$ . The light intensity of mixture solutions may be described by the equation

TABLE I  
Characteristics of PS Samples

Sample	Component	Solvent	LS experimental data			Literature data	Ref.
			$\bar{M}_w \times 10^{-3}$	Zimm $(\bar{r}_g^2)^{1/2}$ , Å	Guinier $(\bar{r}_g^2)^{1/2}$ , Å	$(\bar{r}_g^2)^{1/2}$ , Å	
PS 48	1	toluene	79	380		100	12
PS 48	1	dioxane	70.4	120			
PS 8M	2	toluene	6170	1750	1160	1150	13
PS 8M	2	dioxane	6100	1750	1150		
PS 22	2	toluene	6800	1750	1100	1210	13

$$R(\theta) = R_1(\theta) + R_2(\theta) \quad (1)$$

or on extrapolation to zero concentration

$$R(\theta) = Kc\bar{M}_1P_1(\theta) + Kcy\bar{M}_2P_2(\theta) \quad (2)$$

where  $R(\theta)$  is the Rayleigh ratio determined for the mixtures,  $K$  is the optical constant for the system,  $P_1(\theta)$  and  $P_2(\theta)$  are the functions characteristic of the dimensions of the small and large macromolecules, and  $y$  is the fraction by weight of microgel defined as

$$y = c_2/(c_1 + c_2). \quad (3)$$

For mixtures, the values of  $\bar{M}_w$ ,  $r_g^2$ , and  $P(\theta)$  can be described by the following equations:

$$\bar{M}_w = \bar{M}_1c_1 + \bar{M}_2c_2 \quad (4)$$

$$r_g^2 = \frac{c_1\bar{M}_1\bar{r}_1^2 + c_2\bar{M}_2\bar{r}_2^2}{c_1\bar{M}_1 + c_2\bar{M}_2} \quad (5)$$

$$P(\theta) = \frac{c_1\bar{M}_1P_1(\theta) + c_2\bar{M}_2P_2(\theta)}{c_1\bar{M}_1 + c_2\bar{M}_2} \quad (6)$$

where  $\bar{M}_1$  and  $\bar{M}_2$  are the weight-average molecular weights of the two components and  $\bar{r}_1^2$  and  $\bar{r}_2^2$  are their mean-square gyration radii.

Equation (4) results from eq. (1). Relation (6) is given by Kratochvil.<sup>3</sup> Equation (5) is obtained by substituting the following values into eq. (1):

$$R_1(\theta) = Kc_1M_1 \left( 1 - \frac{\mu^2}{3} \bar{r}_1^2 \right)$$

$$R_2(\theta) = Kc_2M_2 \left( 1 - \frac{\mu^2}{3} \bar{r}_2^2 \right)$$

where  $\mu = (4\pi/\lambda) \sin(\theta/2)$ . Therefore,

$$\frac{R(\theta)}{c} = K \frac{c_1\bar{M}_1 + c_2\bar{M}_2}{c_1 + c_2} \left[ 1 - \frac{\mu^2}{3} \left( \frac{c_1\bar{M}_1\bar{r}_1^2 + c_2\bar{M}_2\bar{r}_2^2}{c_1\bar{M}_1 + c_2\bar{M}_2} \right) \right].$$

Results of the studies on mixtures carried out at varying high- $\bar{M}_w$  and low- $\bar{M}_w$  PS weight concentrations are summarized in Table II. The plots employed in the calculations will be published elsewhere.<sup>11</sup>

For the present PS mixture solutions treated as solutions containing aggregates or microgels, the procedure suggested earlier<sup>1,2</sup> is applicable, and the equation

$$\log(Kc/R_2(\theta)_{\theta=0}) = \log(1/yM_2) \quad (7)$$

where  $r_2(\theta)$  is the Rayleigh ratio for the light scattering of microgel particles and  $\bar{M}_2$  is the weight-average molecular weight of the microgel, allows construction of a plot of  $\log(Kc/I_2)$  versus  $\sin^2(\theta/2)$ . This plot characterizes the microgel content in the polymer, because  $I_2$  is the scattered-light intensity due to microgel particles,

$$I_2 = I - I_1. \quad (8)$$

Zimm plots corresponding to the scattering of microgel particles made possible

TABLE II  
Characteristics of PS Mixture Samples

Mixture	Solvent	$c_1, \text{wt-\%}$	$c_2, \text{wt-\%}$	Experimental data			Estimates based on			
				$\bar{M}_w \times 10^{-3} \text{ }^a$	Zimm $(r_g^2)^{1/2} \text{ }^b \text{ \AA}$	Guinier $(r_g^2)^{1/2} \text{ }^c \text{ \AA}$	Experimental pure component authors' data $\bar{M}_w \times 10^{-3} \text{ }^d$	Pure-component literature data $(r_g^2)^{1/2} \text{ }^e \text{ \AA}$	Literature $(r_g^2)^{1/2}$ versus $\bar{M}$ plot, $(r_g^2)^{1/2} \text{ }^f \text{ \AA}$	
PS 48 + PS 22	toluene	99.5	0.5	106	700	600	109.5	1010	670	120
PS 48 + PS 8M	toluene	99	1	117	700	610	140.0	1190	770	120
PS 48 + PS 8M	dioxane	99	1	—	—	580	109.0	—	—	—

<sup>a,b</sup> Calculated by Zimm's method from the data measured for the PS mixtures.

<sup>c</sup> Calculated by Guinier's method from the data measured for the PS mixtures.

<sup>d</sup>  $\bar{M}_w$  calculated by eq. (4) with measured molecular weights  $M_1$  and  $M_2$  and specified experimental concentrations  $c_1$  and  $c_2$ .

<sup>e</sup> Calculated by eq. (5) with the  $(r_1^2)^{1/2}$  and  $(r_2^2)^{1/2}$  values measured for the pure components.

<sup>f</sup> Calculated by eq. (5) with the  $(r_1^2)^{1/2}$  and  $(r_2^2)^{1/2}$  values obtained from the literature data listed in Table I.<sup>12,13</sup>

<sup>g</sup> Evaluated graphically from experimental  $\bar{M}_w$  with the aid of  $(r_g^2)^{1/2}$ -versus- $M$  plots reported<sup>12,13</sup> for monodisperse materials.

evaluation of the  $y\overline{M}_2$  product and thus finding  $y$  and the radius of gyration of the microgel particles. The  $\overline{M}_2$  value is known from the individual measurements for the samples used as the components of the mixtures investigated (Table I).

Irrespective of the possibilities presented above, a Guinier plot of  $\log(I_2(\theta))$  versus  $\sin^2(\theta/2)$  permits the direct calculation of the radius of gyration of the microgel portion, designated  $(\overline{\rho_2^2})^{1/2}$  to avoid confusion. By a comparison of the known values with those obtained by the method suggested earlier<sup>1,2</sup> from the measurements performed for the mixtures, the reliability of this method can be checked (Table III).

Analysis of the data listed in Tables II and III allows the following conclusions to be drawn:

The microgel percentages  $y$  calculated according to Strazielle<sup>1</sup> and Burchard<sup>2</sup> differ from the actual concentrations  $c_2$  by 0.24% on the average (Table III).

The gyration radii of microgel particles calculated after Strazielle and those calculated after Guinier,  $(\overline{\rho_2^2})^{1/2}$  (Table III), are close to, though invariably lower than, the actual  $(\overline{r_2^2})^{1/2}$  values (Table IIIa).

Zimm's  $(\overline{r_2^2})^{1/2}$  values, also calculated by the methods of Strazielle and Burchard (Table IIIf), are two to three times as high as the actual  $(\overline{r_2^2})^{1/2}$  values. The differences between the  $(\overline{r_2^2})^{1/2}$  values increase with increase in  $(\overline{r_2^2})^{1/2}$  values calculated according to Strazielle and Burchard.

The  $(\overline{r_g^2})^{1/2}$  values calculated by eq. (5) for the samples of high- $\overline{M}_w$  and low- $\overline{M}_w$  polymer mixtures with the aid of the experimental  $(\overline{r_1^2})^{1/2}$  and  $(\overline{r_2^2})^{1/2}$  values (Table IIe) are closer to (though 1.6 times as high as) Zimm's  $(\overline{r_g^2})^{1/2}$  values based on the data observed for the mixtures (Table IIb) than to Guinier's  $(\overline{r_g^2})^{1/2}$  values (Table IIc).

The  $(\overline{r_g^2})^{1/2}$  values found experimentally for the mixtures by the Guinier method (Table IIc) and by the Zimm method (Table IIb) differ only slightly from those calculated by eq. (5) with the  $(\overline{r_1^2})^{1/2}$  and  $(\overline{r_2^2})^{1/2}$  values (Table IIe) for monodisperse materials taken from the literature.

A comparison of the  $(\overline{r_g^2})^{1/2}$  values evaluated from the experiments performed for the mixtures (Table IIb,c) with the  $(\overline{r_g^2})^{1/2}$  data evaluated graphically by using the literature<sup>12,13</sup>  $(\overline{r_g^2})^{1/2}$ -versus- $\overline{M}$  or  $h^2$ -versus- $\overline{M}$  plots discloses that the high- $\overline{M}_w$  fraction greatly affects (nearly sixfold) the  $(\overline{r_g^2})^{1/2}$  value in samples containing very large macromolecules, though in a low proportion.

In order to study the effect of the experimental error associated with the high polydispersity of the mixtures on the data obtained, a comparative analysis was performed in terms of the theoretical function  $P^{-1}(\theta)$  versus  $\sin^2(\theta/2)$  and experimental  $(Kc/R(\theta))_{c=0}$ -versus- $\sin^2(\theta/2)$  curves for the mixtures dissolved in toluene.

The values of  $P_1(\theta)$  and  $P_2(\theta)$  required for the calculation of  $P(\theta)$  from eq. (6) were obtained by using the equation<sup>14</sup>

$$x = (8\pi^2/3\lambda^2)h^2 \sin^2(\theta/2) \quad (9)$$

where  $h^2$  is the mean square distance between the ends of a coil chain and  $\lambda$  is the wavelength of light in the medium. For the low- $\overline{M}_w$  and high- $\overline{M}_w$  PS of known  $\overline{M}_1$  and  $\overline{M}_2$  (Table I), the  $\overline{h_1^2}$  and  $\overline{h_2^2}$  values were evaluated from earlier reports,<sup>12,13</sup> respectively. In the studies referred to, monodisperse samples were examined and the gyration radius (or the distance between the ends of a coil

TABLE III  
Comparison of Results Obtained by the Method of Strazielle<sup>1</sup> and Burchard<sup>2</sup> with Starting Data

Sample	Solvent	$c_2$ , wt-%	A <sup>d</sup>		B <sup>e</sup>			
			Zimm ( $r_2^2$ ) <sup>1/2</sup> , Å	$\bar{M}_2 \times 10^{-3}$	Guinier ( $\rho_2^2$ ) <sup>1/2</sup> , Å	$y\bar{M}_2 \times 10^{-4}$	$y$ , <sup>b</sup> wt-%	Zimm ( $r_2^2$ ) <sup>1/2</sup> , Å
PS 48 + PS 22	toluene	0.5	1750	6800	1200	2.6	0.4	5200
PS 48 + PS 8M	toluene	1	1750	6170	1150	4.43	0.72	4800
PS 48 + PS 8M	dioxane	1	1750	6100	1030	4.56	0.74	2990

<sup>a</sup> ( $\bar{\rho}_2^2$ )<sup>1/2</sup> is the radius of gyration of microgel particles in the mixtures as determined by Guinier's relation  $\log(I_2(\theta))$  versus  $\sin^2(\theta/2)$ .

<sup>b</sup> Microgel percentage evaluated from eq. (7) according to Strazielle<sup>1</sup> and Burchard.<sup>2</sup>

<sup>c</sup> Radius of gyration of microgel particles calculated according to Zimm from the plots  $\log(Kc/I_2)$  versus  $\sin^2(\theta/2) + kc$ .

<sup>d</sup> Results obtained from studies on the individual components of the mixtures (cf. Table I).

<sup>e</sup> Results obtained from studies on the mixtures by the methods of Strazielle<sup>1</sup> and Burchard.<sup>2</sup>

chain) was plotted as a function of  $\bar{M}$ . With the known  $h_1^2$  and  $h_2^2$  values,  $x$  values were calculated. The tables published in Stacey's monograph<sup>15</sup> and the known  $x^{1/2}$  values allowed us to calculate the functions  $P_1(\theta)$  and  $P_2(\theta)$ .

A comparative study of the theoretical function  $P^{-1}(\theta)$  versus  $\sin^2(\theta/2)$  and experimental  $(Kc/R(\theta))_{c=0}$ -versus- $\sin^2(\theta/2)$  curves for the 99.5% PS 48 + 0.5% PS 8M and 99% PS 48 + 1% PS 8M mixtures in toluene as solvent (Figs. 1 and 2) allows the following conclusions to be deduced:

Extrapolation of the two experimental curves results in mixture  $\bar{M}_w$  values lower than those calculated by eq. (4) from the component molecular weights and the composition of the mixture (Table IIa,d); thus, for 99% PS 48 + 1% PS 8M,  $\bar{M}_w \text{ exptl} = 117,000$ , whereas  $\bar{M}_w \text{ calcd} = 140,000$ ; and, for 99.5% PS 48 + 0.5% PS 22,  $\bar{M}_w \text{ exptl} = 106,000$ , whereas  $\bar{M}_w \text{ calcd} = 109,500$ . The greater bend of the experimental than the theoretical curves at small angles where measurements could no longer be made may well be responsible for these differences. The bending of these curves at small angles can be readily examined in terms of the theoretical function  $P^{-1}(\theta)$ . This function could be evaluated at angles of  $0^\circ$  and  $30^\circ$ , experimentally inaccessible by the Fica photometer, and thus the correct courses of the plots could be established. The mean-square radius of gyration

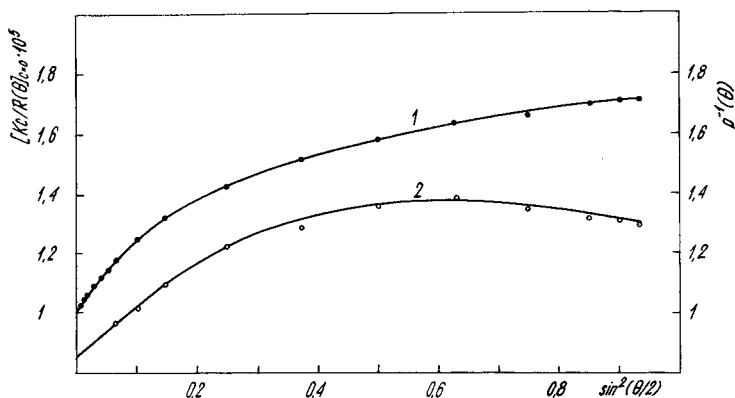


Fig. 1. Plots of  $(Kc/R(\theta))_{c=0}$  vs  $\sin^2(\theta/2)$  and  $P^{-1}(\theta)$  vs  $\sin^2(\theta/2)$  for a 99% PS 48 + 1% PS 8M mixture dissolved in toluene: (1) theoretical curve; (2) experimental curve.

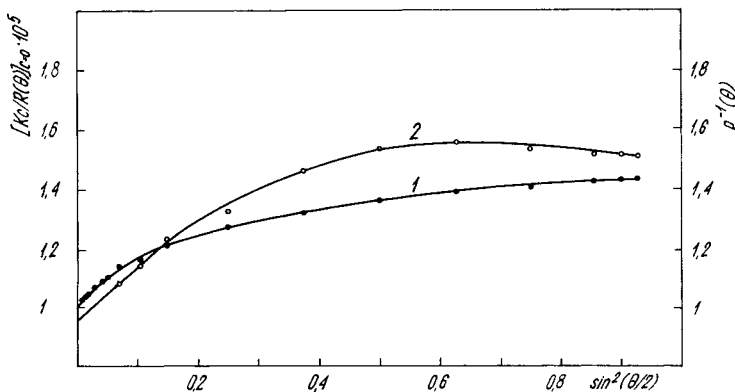


Fig. 2. Plots of  $(Kc/R(\theta))_{c=0}$  vs  $\sin^2(\theta/2)$  and  $P^{-1}(\theta)$  vs  $\sin^2(\theta/2)$  for a 99.5% PS 48 + 0.5% PS 22 mixture dissolved in toluene: (1) theoretical curve; (2) experimental curve.

is proportional to the initial slope of  $P^{-1}(\theta)$ . With systems as highly polydisperse as the present ones, the curvature, in the angular range inaccessible to measurements, is crucial for the determination of  $r_g^2$ . If so, this curvature can be established by an approximate procedure. The differences between the gyration radii as determined from the pure component data and observed for the mixtures are most likely to stem from this approximation.

Consideration of the experimental plots of  $(Kc/R(\theta))_{c=0}$  versus  $\sin^2(\theta/2)$  constructed for the mixtures (Figs. 1 and 2) reveals that of the foregoing problems discussed here, the following puzzling point still remains: that for the low- $\bar{M}_w$  PS samples the  $Kc/R(\theta)$  ratio should be a constant independent of the angle of measurement. If the high- $\bar{M}_w$  polymer did not contribute to the light scattering of the mixtures at high angles, the maximum value of  $(Kc/R(\theta))_{c=0}$  should be approximately  $M_w^{-1}(\text{PS } 48) = 1.27 \times 10^{-5}$ . Since the high- $\bar{M}_w$  polymer does contribute somewhat to the scattering intensity even at high angles, one would expect to find  $(Kc/R(\theta))_{c=0}^{\text{max}} < 1.27 \times 10^{-5}$ . It is not clear why in the first case  $(Kc/R(\theta))_{c=0}^{\text{max}} = 1.38 \times 10^{-5}$  and in the second case  $(Kc/R(\theta))_{c=0}^{\text{max}}$  is as high as  $1.56 \times 10^{-5}$ . (Compare experimental curves in Figs. 1 and 2.)

The above findings suggest that the Strazielle and Burchard calculation method<sup>1,2</sup> is useful for evaluating the microgel content in samples. However, when applied to the calculation of the gyration radii of microgel particles, the Guinier method, using a  $\log(I_2(\theta))$ -versus- $\sin^2(\theta/2)$  plot, yields low data, whereas the Zimm method, using a  $Kc/I_2$ -versus- $\sin^2(\theta/2) + kc$  plot, affords entirely incongruous data. The latter relation has no logical support.

Contrary to Lange's findings,<sup>16</sup> the PS mixture solutions in toluene and dioxane disclosed no appreciable solvent effect on the high- $\bar{M}_w$  to occur.

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