

## Anomalies in Light Scattering from Polyelectrolyte in Semi-Dilute Solution Region

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**ABSTRACT:** Some anomalies in light scattering from polyelectrolyte in semi-dilute solution have been investigated and compared with those observed in high-molecular-weight neutral polymer solutions. Three anomalous in behavior were found: (a) the  $c/R_\theta$  vs.  $\sin^2(\theta/2)$  curve was convex upward at a lower angle  $\theta$ , (b) the  $c/R_\theta$  vs.  $c$  curve was convex upward, and (c) the  $Z_{45}$  vs.  $c$  curve exhibited a minimum.  $R_\theta$  is the reduced scattering intensity at the scattering angle  $\theta$ ,  $c$  the polymer concentration, and  $Z_{45}$  the dissymmetry ratio. Further, it has been pointed out that the plot of logarithm of correlation length  $\xi$  against logarithm of concentration  $c$  changes its slope at a polymer concentration at which  $R_\theta$  vs.  $c$  curve shows a maximum, *i.e.*, at the critical polymer concentration. In the polymer concentration range above the critical point, lumps of molecules are more certain to exist rather than microgels which are conventionally regarded as the origin of the anomalies.

**KEY WORDS** Anomalies / Light Scattering / Polyelectrolyte / Semi-Dilute Solution / High Molecular Weight / Correlation length / Lump /

In the preceding paper,<sup>1</sup> we pointed out that polyelectrolyte in dilute solution below a critical concentration behaves like a polymer in a good solvent, and that such a critical concentration is very low in comparison with that of a neutral polymer solution. For example, a concentration of  $c = 10^{-3}$  g cm<sup>-3</sup> is sufficiently below the critical concentration of neutral polymers having ordinary molecular weights of the order of  $10^4$  to  $10^5$ , but the critical concentration of a polyelectrolyte with the same molecular weight should be far below  $10^{-3}$  g cm<sup>-3</sup>.

Published works on polyelectrolyte solutions have been carried out usually<sup>2-5</sup> in a polymer concentration range from  $10^{-4}$  to  $10^{-3}$  g cm<sup>-3</sup>. We consider that such concentration range covers both regions below and above the critical concentration, thus making data analysis difficult.

On the other hand, the same behaviors have been observed for the neutral polymer having high molecular weight.<sup>6-9</sup> Because the primary purpose of light-scattering studies is to investigate the dilute-solution behavior (*i.e.*, to study an isolated molecule at infinite dilution), a few studies has been carried

out at the semi-dilute region. But these data<sup>6-9</sup> all exhibit anomalies similar to those of polyelectrolyte solution.

In this paper, we discuss anomalies of light scattering in aqueous solutions of poly(acrylic acid) in the presence of a small amount of NaCl, and make comparison with data on high-molecular-weight neutral polymers in good solvent. Senior *et al.*<sup>3</sup> have attributed the origin of such an anomaly to the formation of microgel. However, we show that it is not an unusual but necessary phenomenon, and present a possible model in accordance with that of Edwards<sup>10</sup> for chain molecules in semi-dilute solution above the critical concentration.

### EXPERIMENTAL

Preparation and characterization of the polyacrylic acid (PAA) sample used for the light-scattering measurements were indicated in the preceding paper.<sup>1</sup> The weight-average molecular weight  $M_w$  and the dishomogeneity factor  $M_w/M_n$  of PAA are  $5.0 \times 10^5$  and 2.2, respectively. A high-molecular-weight polystyrene with a narrow-molecular-weight

distribution was purchased from Pressure Chemical Co. The  $M_w$  and  $M_w/M_n$  of the polystyrene used were  $1.81 \times 10^6$  and less than 1.3, respectively. Toluene was used as the solvent for the polystyrene following distillation. Light-scattering measurements were performed according to the procedures mentioned previously.<sup>1</sup>

## RESULTS AND DISCUSSION

### Comparison with Neutral Polymer

Before discussing light-scattering anomalies in

semi-dilute polyelectrolyte solutions, we first consider light scattering in high-molecular-weight neutral polymer solutions. In Figure 1(a) is shown a Zimm plot,  $Kc/R_\theta$  vs.  $\sin^2(\theta/2) - 50c$ , obtained for polystyrene ( $M_w = 1.81 \times 10^6$ ) in toluene at 25°C in the ranges of  $c = 5.0 \times 10^{-4} \sim 1.97 \times 10^{-2} \text{ g cm}^{-3}$ , and  $\theta = 15^\circ \sim 150^\circ$ .  $R_\theta$  and  $K$  denote the reduced scattered intensity at angle  $\theta$ , and light-scattering constant, respectively. Figure 1(b) is the  $(Kc/R_\theta)^{1/2}$  vs.  $\sin^2(\theta/2) - 50c$  plot (square-root plot) which makes it possible to analyze in greater details the results obtained at a lower concentration range. In

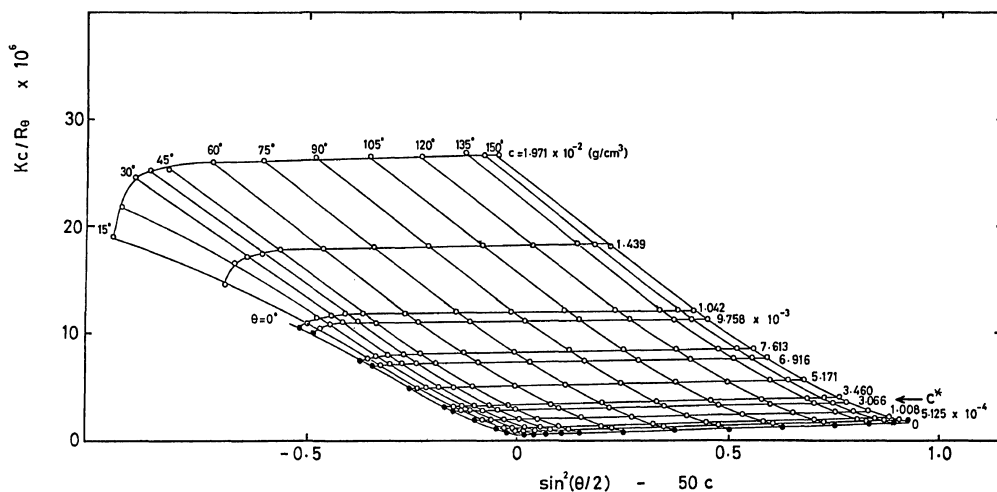


Figure 1(a). Zimm plot for polystyrene in toluene at 25°C.

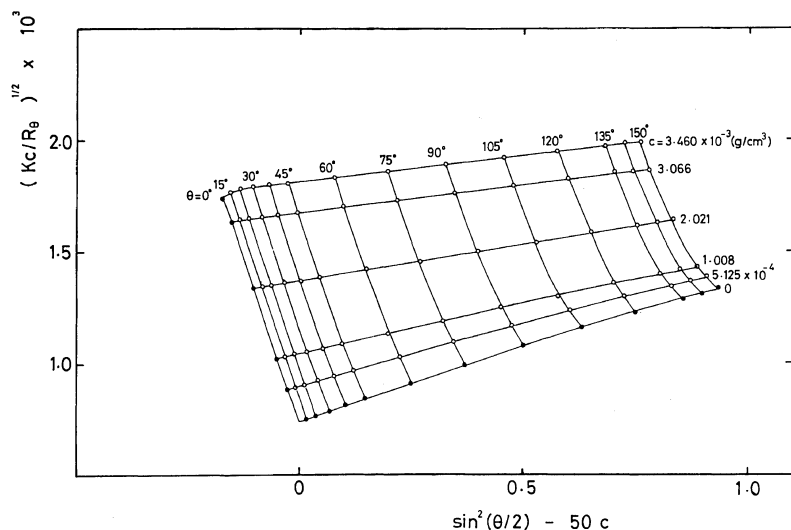


Figure 1(b). Square-root plot at a lower concentration for the same system as Figure 1(a).

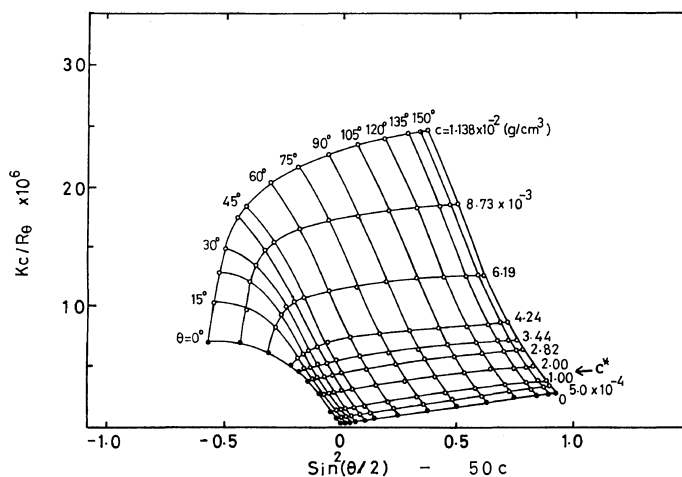


Figure 2. Zimm plot for polystyrene in benzene (recast from Benoit and Picot's data<sup>7</sup>).

Figure 2, the original data in light scattering of Benoit and Picot<sup>7</sup> for polystyrene having high molecular weight ( $M_w = 7.5 \times 10^6$ ;  $M_w/M_n = 1.9$ ) in benzene are recast in the form of Zimm plot. The following anomalies were observed in these figures: (1) the  $Kc/R_\theta$  vs.  $c$  curves are concave upward below the concentration indicated by  $c^*$ , but above this concentration the curves are convex upward; (2) the  $Kc/R_\theta$  vs.  $\sin^2(\theta/2)$  curves are approximately linear (normal) below  $c^*$ , but are remarkably convex upward above  $c^*$ . The dissymmetry ratio  $Z_{45}$  is plotted against the concentration  $c$  in Figure 3 for the polystyrene ( $M_w = 1.81 \times 10^6$ )–toluene system. As is obvious from Figure 3,  $Z_{45}$  decreases monotonously, passes through a minimum, and then increases monotonously with an increase in  $c$ . The same behavior was also found in recast data of Benoit.<sup>7</sup>

The anomalies pointed out above in neutral polymer solution are suitable for discussing similar behavior reported in some papers on polyelectrolyte solutions.<sup>1-5</sup> In order to study the origin of these anomalies,  $R_\theta$  of the PAA–NaBr and PAA–NaCl aqueous solutions was plotted against  $c$ , according to Debye,<sup>11</sup> in Figure 4(a)–(d). As indicated in a preceding paper,<sup>1</sup> PAA in a 1.5 M NaBr aqueous solution is regarded as a  $\theta$  state at 15°C. Obviously from Figure 4(a), it may be said that the scattered intensity is proportional to  $c$  for the  $\theta$  solvent system, wherein no intermolecular interaction exists. With a decrease in the concentration  $c_s$  of added salt, intermolecular interaction increases, *i.e.*, the

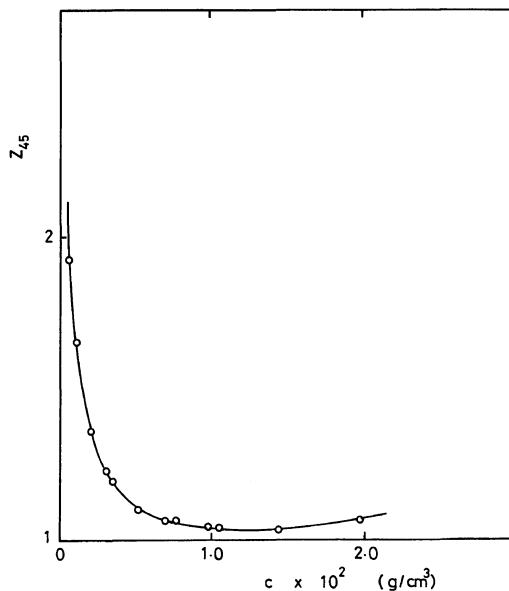
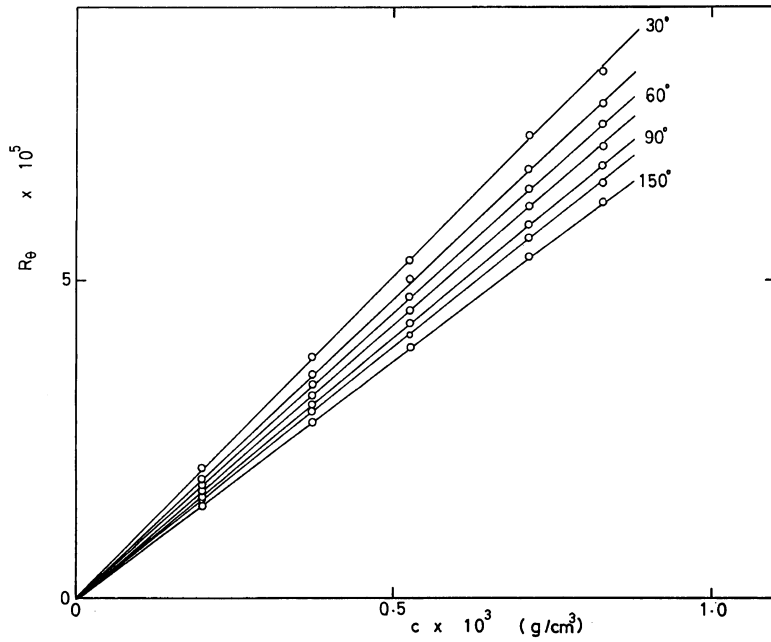
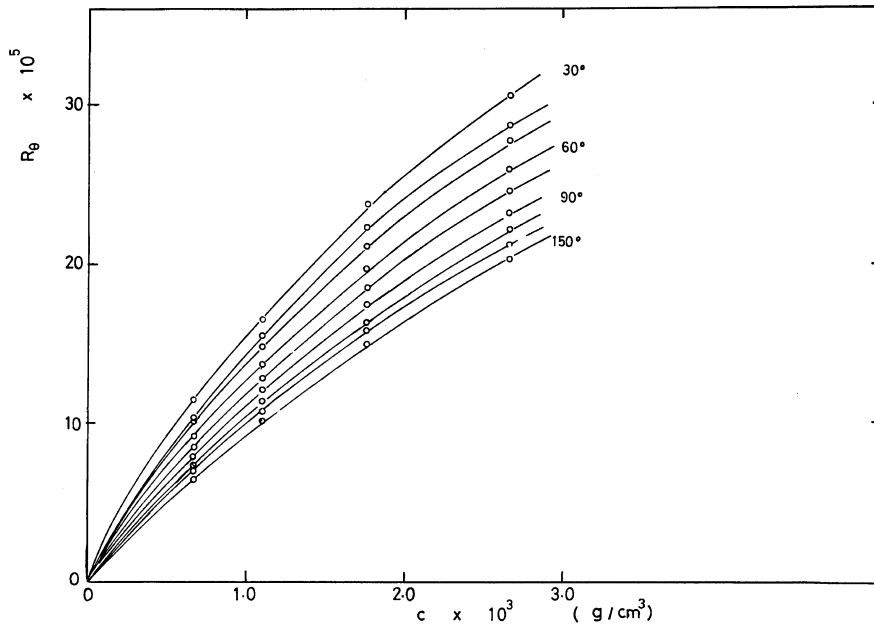


Figure 3. Concentration dependence of the dissymmetry ratio  $Z_{45}$  for polystyrene in toluene.

solvent behaves better as a solvent. At  $c_s = 1$  M (Figure 4(b)), the curves are convex upward; that is, the increment of the scattered intensity decreases with an increase in  $c$ . Such behavior is brought about by intermolecular interaction, which makes the order in the solution to produce a destructive intermolecular interference. At  $c_s = 0.1$  M (Figure 4(c)) and  $c_s = 0.01$  M (Figure 4(d)), this intermolecular interaction further increases, and there ap-



(a)

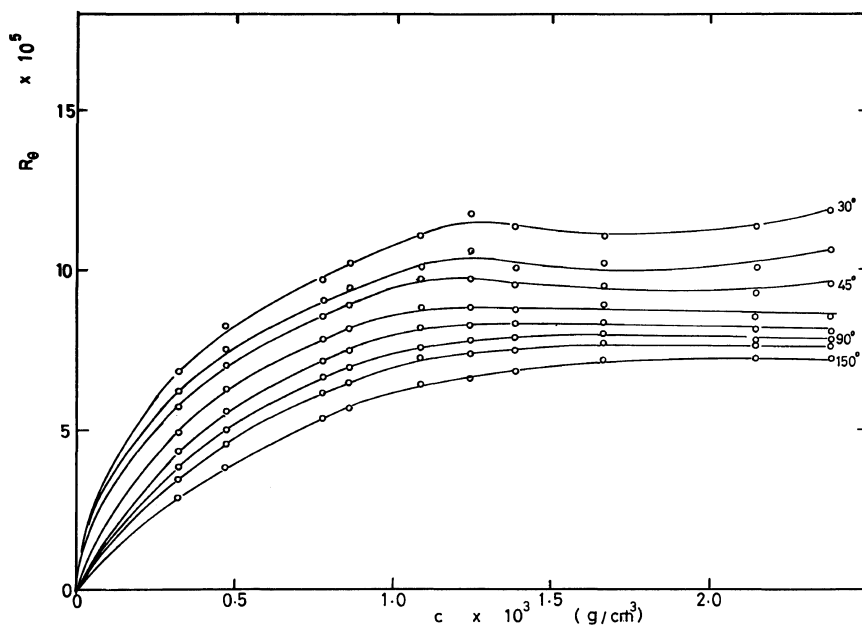


(b)

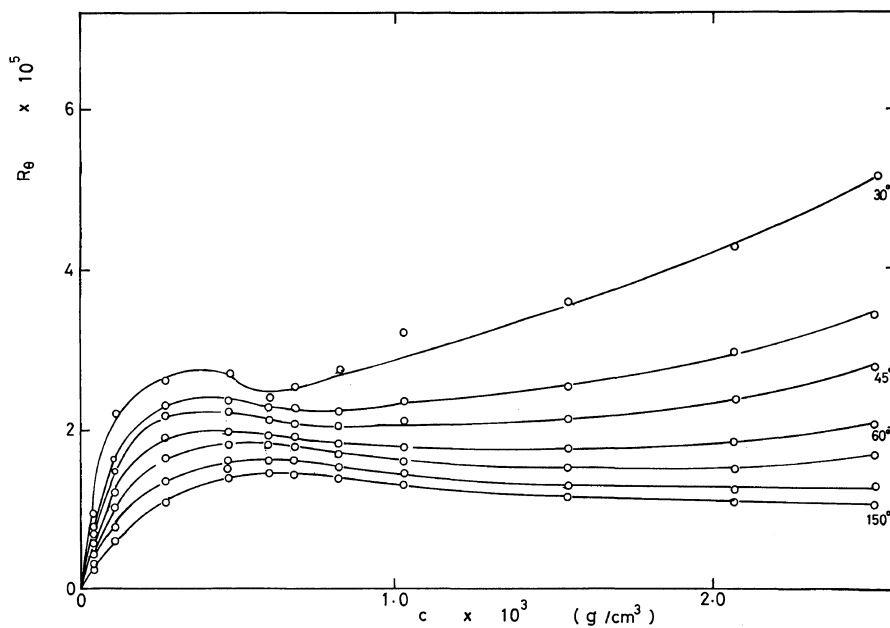
pears a maximum point in each curve. The existence of the order has recently been shown by small-angle neutron<sup>12</sup> and X-ray scattering.<sup>13</sup> The concentration at the maximum point agrees well with the critical

concentration  $c^*$  mentioned above, and shifts to the lower concentration side with increasing solvent power *i.e.*, when there is a decrease in  $c_s$ . The same sort of behavior is observed with polystyrene

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(c)



(d)

Figure 4. Concentration dependence of reduced scattered intensity  $R_\theta$  for PAA in NaCl aqueous solutions: (a) PAA in 1.5 M NaBr at 15°C; (b) PAA in 1 M NaCl at 25°C; (c) PAA in 0.1 M NaCl at 25°C; (d) PAA in 0.01 M NaCl at 25°C.

( $M_w = 1.81 \times 10^6$ ) in toluene as in Figure 5, and with polystyrene<sup>7</sup> ( $M_w = 7.5 \times 10^6$ ) in benzene.

*Critical Concentration*

The experimental results mentioned above are

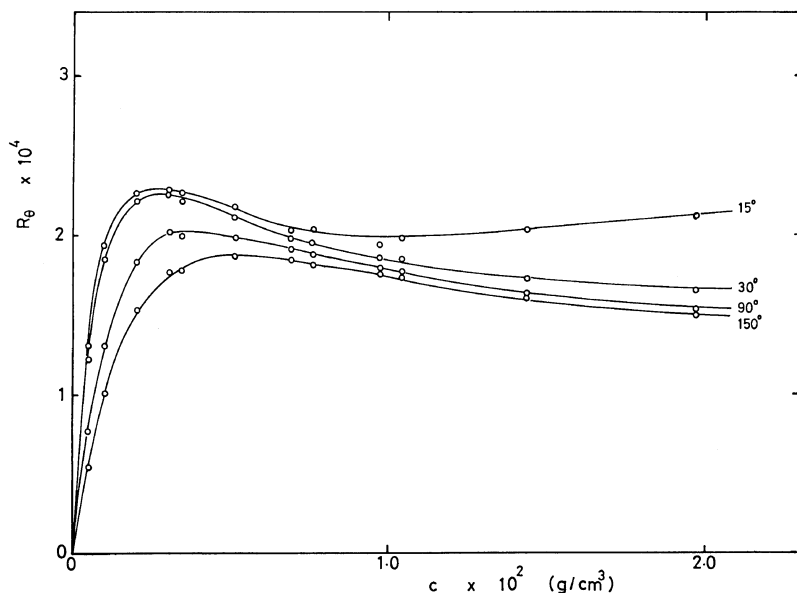


Figure 5. Concentration dependence of  $R_\theta$  for polystyrene in toluene.

discussed from another point of view. The osmotic pressure  $\pi$  is given by a series of powers of the concentration  $c$ .

$$\frac{\pi}{c} = RT \left( \frac{1}{M} + A_2 c + \dots \right) \quad (1)$$

where  $M$  is the molecular weight of the polymer,  $A_2$  is the second virial coefficient, and  $R$  is the gas constant. The first term of eq 1 is concerned with an isolated polymer molecule, and the second term, with the intermolecular interaction. Hence, the ratio of the second to first term,  $A_2 M c$ , indicates the degree of intermolecular interaction. Thus, at a definite concentration, the intermolecular interaction increases with an increase in the  $A_2 M$  value. The  $M$  of PAA used is  $5.0 \times 10^5$  and the values of  $A_2$  in  $\text{cm}^3 \text{mol}^{-1} \text{g}^{-2}$  unit in 0.1 M and 0.01 M NaCl aqueous solutions are  $1.3 \times 10^{-3}$  and  $8.8 \times 10^{-3}$ , respectively,<sup>1</sup> thus  $A_2 M$  is of the order of  $10^2$ – $10^3$  in the range of  $c_0 = 0.1$ – $0.01$  M. On the other hand, for polystyrene having a molecular weight as high as  $1.81 \times 10^6$ ,  $A_2$  in toluene obtained from Figure 1(b) is  $2.14 \times 10^{-4}$ , and so  $A_2 M$  is of the order of  $10^2$ . For neutral polymer systems having ordinary molecular weight ( $M$  is of the order of  $10^5$ ) in a good solvent,  $A_2$  is of the order of  $10^{-4}$  or less, and hence,  $A_2 M$  is of the order of 10 or less. These calculations indicate that the  $A_2 M$  values for both PAA in 0.01–0.1 M

NaCl, and polystyrene of  $M = 10^6$  in toluene systems are about 10 times that of a neutral polymer of ordinary molecular weight in a good solvent. In other words, the critical concentration  $c^*$  for each PAA solution mentioned above is about 1/10 that of a neutral polymer of ordinary molecular weight.

Recent studies<sup>14,15</sup> on light scattering in polyelectrolyte solutions have been carried out at concentrations  $c$  having the order of  $10^{-4} \text{ g cm}^{-3}$ , which is lower than those of the order of  $10^{-3}$  used previously<sup>2-5</sup> for carrying out measurements on polyelectrolyte solutions. This means that lower concentration range is necessary for obtaining more definitive information.

According to Cotton *et al.*,<sup>16</sup> the reduced scattered intensity  $R_\theta$  is related to the correlation length  $\xi$  by

$$R_\theta = kc / (q^2 + \xi^{-2}) \quad (2)$$

where  $q = (4\pi/\lambda') \sin(\theta/2)$

and  $k$  is a constant.  $\xi$  is obtained from the  $c/R_\theta$  vs.  $\sin^2(\theta/2)$  plot by extrapolating  $c/R_\theta$  at high  $\theta$  values which satisfy the relation,

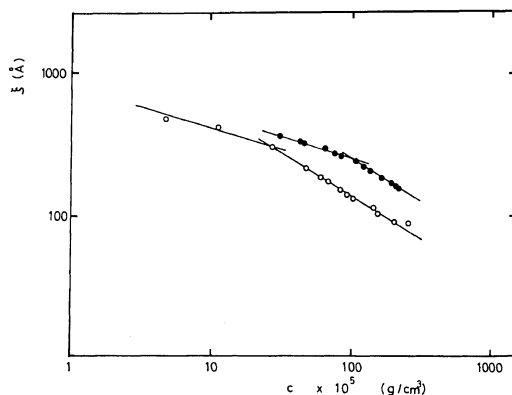
$$1 < q \langle S^2 \rangle^{1/2} \quad (3)$$

where  $\langle S^2 \rangle^{1/2}$  denotes the radius of gyration. In light scattering, such a region appears at higher angles compared with the X-ray and the neutron

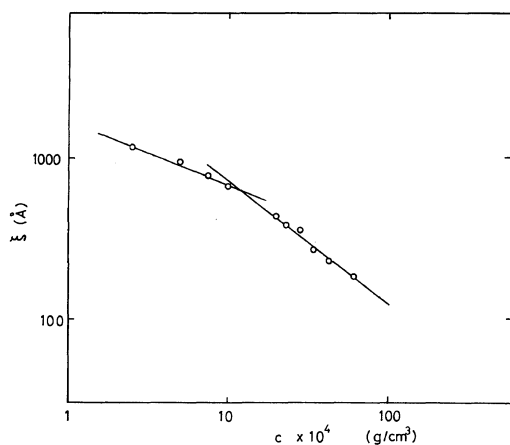
scattering because of the difference in the wavelength. In Figure 6,  $\log \xi$  is plotted against  $\log c$  for PAA in 0.01 and 0.1 M NaCl aqueous solutions. As is obvious from the figure, the slope of the plot changes at a polymer concentration where the  $R_\theta$  vs.  $c$  curve shows a maximum, *i.e.*, at the critical concentration  $c^*$ . The same behavior can also be observed for polystyrene of high molecular weight, as shown in Figure 7.

#### Molecular Arrangement in Semi-Dilute Region

Anomalies in light scattering as a function of  $c$  for polyelectrolyte solution have always been attributed by Senior *et al.*<sup>3</sup> to the formation of microgel.



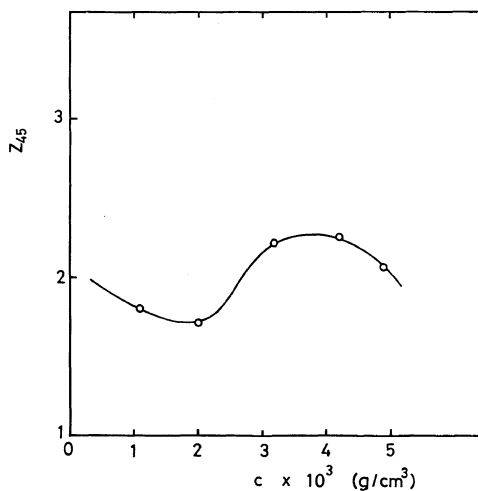
**Figure 6.**  $\log \xi$  plotted against  $\log c$  for PAA in NaCl aqueous solutions: filled circles: 0.1 M NaCl; open circles: 0.01 M.



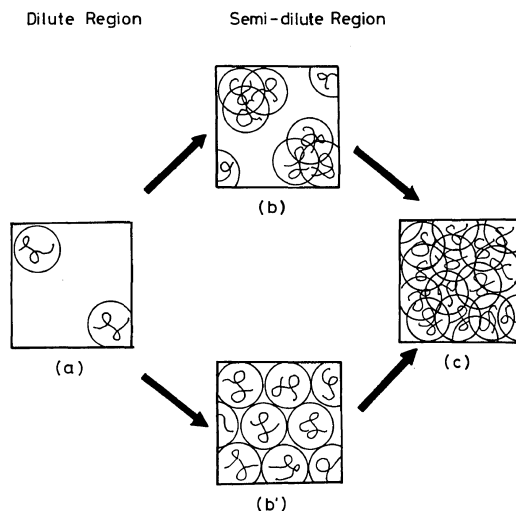
**Figure 7.**  $\log \xi$  plotted against  $\log c$  for polystyrene in benzene (Cotton *et al.*<sup>16</sup> from the data of Benoit and Picot<sup>7</sup>).

However, the experimental results obtained here do not support this concept for the following reasons, (1) Formation of microgel has been recognized for solutions of polyethylene, polypropylene, polyvinyl chloride, and others, for which the  $c/R_\theta$  vs.  $\sin^2(\theta/2)$  curves in the Zimm plot are convex upward for the entire concentration range considered. But the curves for our PAA systems are approximately linear (normal) below the critical concentration  $c^*$ , and above which, the curves are convex upward. (2) The anomalies become more significant when the solvent power becomes stronger for the PAA system. However, this is inconsistent with the fact that the stronger intermolecular interaction (repulsion) causes the formation of microgel to become more difficult. (3) The light-scattering data reported by Kratochvil<sup>17</sup> for poly(vinyl chloride) in cyclohexanone, an example of a system containing microgel, was recast in the form of the  $Z_{45}$  vs.  $c$  plot in Figure 8. Obviously, such a curve is quite different from those of our PAA–NaCl aqueous solution systems shown in the preceding paper (*cf.* Figure 9 in reference 1).

As can be clearly seen from Figure 4(d),  $R_\theta$  passes through a maximum and then increases with increasing concentration. If the polymer molecules are interpenetrated uniformly at concentrations higher than the concentration at the maximum point, *i.e.*, the critical concentration, then  $R_\theta$  should



**Figure 8.** Concentration dependence of dissymmetry ratio  $Z_{45}$  for poly(vinyl chloride) in cyclohexanone (recast from Kratochvil's data<sup>17</sup>).



**Figure 9.** Schematic representation for molecular arrangement in solution: (a) monomolecular dispersion; (b) interpenetrated lumps; (b') uniform distribution of molecules; (c) interpenetrated uniform matrix.

decrease monotonously with concentration, as pointed out by Koyama.<sup>18</sup> Such an increase in  $R_\theta$  at higher concentrations is related to the formation of some kind of cluster in the semi-dilute region mentioned in the preceding paper.<sup>1</sup> As mentioned above, formation of microgel would not support our experimental results. As an alternative, we propose to adopt a model presented first by Edwards.<sup>10</sup> According to our proposal, polymer molecules in the semi-dilute region interpenetrate each other and forms lumps as is indicated in Figure 9(b) (by repulsion); this is in contrast to the uniform distribution of molecules in Figure 9(b'). In a dilute region, polymer molecules are dispersed monomolecularly. Thus, the transition concentration from a dilute region to a semi-dilute region corresponds to the critical concentration  $c^*$ . The lumps are larger in size than the polymer molecules as a matter of course, and so the scattered intensity increases. Recently, Qui and Nishijima<sup>19</sup> showed from transient measurements that there existed two phases, one is solvent-rich and the other is polymer-rich, in moderately concentrated solutions. Also Nose and Chu<sup>20</sup> showed, from dynamic light-scattering measurements, the existence of a pseudogel like mode even in a fairly dilute solution. These seem to be the same as what we call a lump.

With increasing  $c$  in the semi-dilute region, the

lump size becomes large, and finally forms an interpenetrated uniform matrix as shown in Figure 9(c).

In conclusion, we point out that the anomalies observed in light scattering in polyelectrolyte solutions are not unusual but necessary phenomena which can be explained by the model as mentioned above.

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