Observation of Cluster Formation in Polyelectrolyte Solutions by Small-Angle Neutron Scattering. 1.[1] A Steep Upturn of the Scattering Curves from Solutions of Sodium Poly(styrenesulfonate) at Scattering Vectors below 0.01 Å^{-1}

Scattering experiments on ionic polymer solutions and colloidal dispersions have shown a single, broad, but distinct, interference peak at low-salt conditions.[2,3] This peak indicates a more or less ordered arrangement of ionic solutes in the solution or suspension due to an electrostatic interaction. For high charge density polymers, the intermacroion spacing calculated from the peak position by Bragg's equation ($2D_{exp}$) is shorter than the average distance ($2D_0$) calculated from the concentration.[4] For aqueous solutions of high molecular weight sodium poly(styrenesulfonates) (NaPSS), for example, the $2D_{exp}$ is smaller than $2D_0$ by a factor of 2.[5] From this experimental finding, we have proposed a "two-state structure" model: ordered regions of a high polymer density coexist with disordered regions of a low polymer density.[4] Such a two-state structure has directly been confirmed for ionic latex dispersions by an ultramicroscopic technique.[3] In the two-state structure model, density fluctuations exist between the ordered clusters and the disordered regions, which should give rise to scattering in very small scattering vector (q) regions. In previous works,[2,3] however, such a scattering due to the density fluctuation has not been observed. This may be due to the limited small-angle resolution ($q > 0.03$ Å^{-1}) or due to an insufficient scattering contrast or both. In the present work, we performed small-angle neutron (SANS) experiments with 1 order of magnitude higher small-angle resolution for NaPSS in deuterated water (D_2O) to obtain a high scattering contrast.

NaPSS used was a product of Pressure Chemical Co. (Pittsburgh, PA). SANS measurements were performed at the FRJ2 reactor in Forschungszentrum Jülich by using the 40-m instruments, KWS 1 and 2. The details of the apparatus can be found elsewhere.[6] D_2O (Merck, Darmstadt) was used as a solvent to minimize incoherent scattering and to maximize the scattering contrast. The scattering patterns were calibrated in absolute units of reciprocal centimeters by using a (vanadium-calibrated) Lupolen standard.

Figure 1 shows the SANS patterns of NaPSS in D_2O at different polymer concentrations without added salt in a double-logarithmic scale. In addition to an intermacroion interference peak at $q = 0.04$–0.10, where $q = 4\pi \sin(\theta/\lambda)$, where 2θ is the scattering angle and λ is the wavelength of the neutrons (7 Å in the present), a steep, distinct upturn of scattered intensity was observed below $q = 0.01$ Å^{-1}.

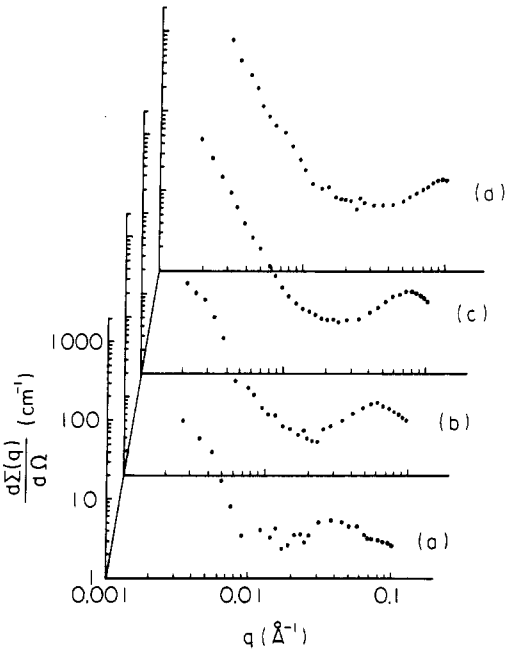

Figure 1. SANS curves of a NaPSS–D_2O solution at different polymer concentrations without added salt. Polymer concentration: (a) 0.01, (b) 0.02, (c) 0.04, (d) 0.08 g/mL.

For the quantitative analysis of the data, the Guinier method may be the most convenient and useful technique although its application should be limited to homogeneous entities, strictly speaking. Thus, the following data should be judged as giving not so highly precise information. An example of the Guinier plot is shown in Figure 2. From the slope of the straight line in very small angle regions (shown as a dotted line in the figure), R_g of the scatterer was found to be 686 Å with a statistical error of 13 Å by the Guinier law

$$I(q) = I(0) \exp[-(1/3)R_g^2 q^2]$$

where $I(q)$ is the intensity of scattered radiation.

Table I summarizes the SANS data for various NaPSS concentrations. The $2D_{exp}$ was consistent with our previous SAXS results[4] and also smaller than the $2D_0$, which supports the two-state structure. If the experimental uncertainty is duly taken into account, we can say that the ordered clusters have size (R or R_g) on the order of 500–900 Å and appear to increase with increasing polymer concentration, which is reasonable if one considers the progressively enhanced electrostatic intermacroion interaction. However, we may have to be careful about the value of R_g obtained because the angle limit is not yet

Table I
SANS Data of NaPSS–D_2O Solutions[a]

run no.	[NaPSS], g/mL	[NaCl], M	R_g, Å	R, Å	V, 10^9 Å^3	$2D_{exp}$, Å	$2D_0$, Å	n	$d\Sigma(0)/d\Omega$, cm^{-1}
1	0.01	0	407 ± 17	525	0.61	166	255	130	194 ■ 21
2	0.02	0	516 ± 15	666	1.24	103	202	1100	532 ± 38
3	0.04	0	686 ± 13	886	2.90	85	160	4700	2590 ■ 174
4[b]	0.08	0	(630 ■ 13)[a]	813	2.25	64	128	8600	3043 ± 210

[a] R_g is the radius of gyration of the cluster obtained by Guinier's method. R and V are the radius and volume of the spherical cluster calculated from R_g. $2D_{exp}$ is the distance between the macroions in a cluster estimated from the peak position in the scattering curve by Bragg's equation. $2D_0$ is the average intermacroion distance calculated from the concentration with an assumption of a uniform distribution of the macroions throughout the solution. N is the number of macroions in one cluster calculated from $2D_{exp}$ and R. $d\Sigma(0)/d\Omega$ is the scattered intensity at $q = 0$ estimated by the intercept of the straight line in the Guinier plot, which should be proportional to the number of clusters, the square of the cluster volume, and the square of the difference of the scattering length density between the ordered clusters and disordered regions. [b] The linearity of the Guinier plot was not as good as that for the other three samples: it might be possible that the R_g and the forward scattering intensity would be higher than those given in the table.

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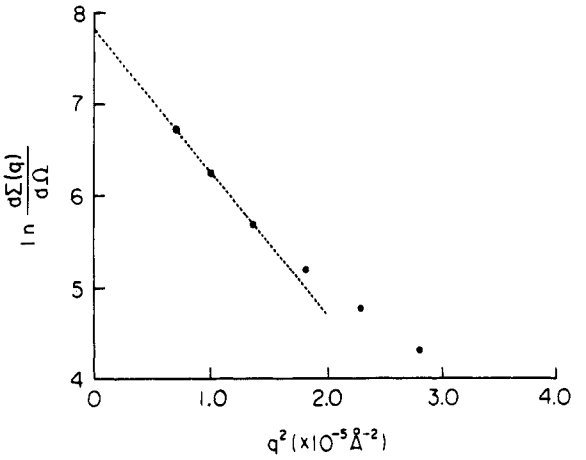

Figure 2. Guinier plot of the scattering intensity at [NaPSS] = 0.04 g/mL.

small enough for the Guinier extrapolation. The number of macroions in one cluster also increased significantly with increasing polymer concentration, which is also acceptable.

In conclusion, a steep upturn behavior in very small-angle regions was observed for a NaPSS–D_2O system. Together with the evidences previously obtained,[2,3] this upturn substantiates the existence of localized ordered clusters in solution. A similar upturn in very small angle regions has also been observed in SAXS curves for ionomer films,[7] which was explained by cluster formation. It is to be noted that the upturn cannot be accounted for in terms of other existing models[8-10] such as the parallel rod model and the isotropic model, which were invoked to explain the scattering peak. More detailed analyses, such as salt concentration dependence and a model calculation for the densities of both ordered and disordered regions from the absolute intensity measurements, are now in progress. Furthermore, we are trying to reach smaller scattering angles using neutron radiation of longer wavelengths.

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