Revisit to the Intrinsic Viscosity–Molecular Weight Relationship of Ionic Polymers. 2. Viscosity Behavior of Salt-Free Aqueous Solutions of Sodium Poly(styrenesulfonates)

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Abstract: The reduced viscosity of aqueous solutions of sodium poly(styrenesulfonates) of a narrow molecular weight distribution was measured with the utmost care in the absence of a coexisting salt. The possibility of adsorption of the macroions on the glass wall of the viscometer capillary was confirmed to be negligible. The shear rate dependence was quite substantial, particularly at low polymer concentrations. The reduced viscosity was extrapolated to zero shear rate. The general feature of the concentration dependence was that the extrapolated viscosity increased with increasing polymer concentration and decreased after passing a maximum, as was reported earlier by several authors. For the exponent α of the relation $[\eta] = KM^{\alpha}$ ($[\eta]$, intrinsic viscosity; M, molecular weight; and K, a constant), 1.6–1.2 was obtained for samples having molecular weights of 3.7×10^5–1.7×10^6, when use was made of the intrinsic viscosity at zero shear rate. This appears to indicate that the macroions are not fully stretched out like a rod even at the infinite dilution, if the viscosity–molecular weight relation may be used for *ionic* flexible macromolecules.

I. Introduction

In part 1[1] of this series, we reported the viscosity behavior of dilute suspensions of ionic polymer latex particles. The study revealed that (1) the reduced viscosity (η_{sp}/ϕ with ϕ the volume fraction and η_{sp} the specific viscosity) of these suspensions was much higher than the prediction of Einstein, (2) it generally depended on the shear rate, q, (3) it increased with an increasing volume fraction of latex, and after passing through a maximum it decreased sharply in a similar manner as often observed for flexible ionic polymers, and (4) the intrinsic viscosity ($[\eta]$) could be accounted for in terms of the first-order electroviscous effect when the concentration of coexisting salt was not low.

The study of the viscosity of polyelectrolyte solutions was one of central properties which have been intensively studied. As was mentioned in Part 1, we have come to understand that the macroions are stretched out like a rod in dissociating solvents as a result of electrostatic repulsive interaction between ionized groups. This type of conformation has been claimed not only at an infinite dilution but also at a relatively high concentration of polymer. The rationale was the observation by Katchalsky,[2] Doty,[3] and Fuoss[4] that the exponent α in the relation $[\eta] = KM^{\alpha}$ (M, the molecular weight of polymer, and K, a constant) was two for ionic polymers in salt-free solutions. In these papers, it was assumed that the η_{sp}/C monotonously increased with decreasing C (concentration). Soon thereafter several groups reported that the assumption was not justified in light of the existence of a maximum in the $\eta_{sp}/C - C$ curve.[5–8] If this is correct, the intrinsic viscosity cannot be claimed to have been determined judiciously. It seems, however, that the existence of the maximum was not easily accepted because the remaining impurities in the solutions, the adsorption of the macroions onto the wall of viscometer capillary, and other factors were thought to be so influential to cause artifactual results. Very recently, Vink performed highly precise measurements and confirmed the maximum.[9,10] This was further substantiated by Cohen et al.[11] Thus it became clearer that the conventional extrapolation of the viscosity data to the infinite dilution was not justified, endangering the widely accepted conclusion that the macroions assume fully stretched conformation.

It is our presumption that the conformation of the macroions is still a problem requiring more careful scrutiny, as was discussed in a recent review article.[12] In the present paper, we describe the viscosity behavior of salt-free aqueous solutions of sodium poly(styrenesulfonate) (NaPSS), a typical soluble polyelectrolyte having a narrow molecular weight distribution.

II. Experimental Section

A. Materials. Three kinds of poly(styrenesulfonates) were purchased from Pressure Chemical, Pittsburgh, PA, and a higher molecular weight sample was synthesized.

The NaPSS samples from Pressure Chemical (lot nos. 12, 16, and 17) were washed with Milli-Q water by an ultrafilter (Model 202, Amicon Co., Lexington, MA) with membranes PM 30 (exclusion limit, $M_w = 3 \times 10^4$) for no. 12 and XM 50 (exclusion limit, $M_w = 5 \times 10^4$) for nos. 16 and 17 until the optical density of the absorbance at 200 nm of the filtrate became smaller than 0.1. Then the purified samples were passed through a cation- and anion-exchange resin column several times. The amounts of the loaded resins (IR-120B and IRA-400, Organo, Tokyo) were five times and $^1/_4$ times equivalent as much as the polyions, respectively. The acid form of the polyelectrolyte (HPSS) thus obtained was analyzed to obtain the number of sulfonate groups by conductometric titration and then immediately neutralized by a solution of sodium hydroxide, Merck, Darmstadt, FRG. The polymer concentration in the titrated solutions was determined by drying, and the degree of substitution was evaluated by taking into account the number of sulfonate groups determined above. The NaPSS thus obtained was freeze-dried and kept in a dark place with silica gel beads as a desiccating agent.

A higher molecular weight sample, NaPSS-H, was prepared by the modified Vink's method.[10,13] One hundred thirty milligrams of polystyrene (Batch 80323, Pressure Chemical Co.) was dissolved in 60 mL of cyclohexane. Sulfuric acid was added at 55 °C into the solution and stirred for 80 min. After keeping the mixture standing for 70 min, 20 g of ice was added, and the solution was cooled to 0 °C. HPSS was precipitated, dissolved into 120 mL of water, and neutralized with a solution of sodium hydroxide after filtration. The NaPSS thus prepared was dialyzed against Milli-Q water. The completeness of the dialysis was judged by conductance measurements. The NaPSS sample was obtained after ion-exchange and neutralization as described above.

The extinction coefficient ϵ_{262} at the peak top near 262 nm of NaPSS was determined by using the freeze-dried samples. The concentrations of the polymer in the viscosity measurements were evaluated spectro-

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Table I. Properties of Sodium Poly(styrenesulfonates)

sample	M_W	M_W/M_n	degree of sulfonation	ϵ_{262} (dL g^{-1} cm^{-1})
no. 12	3.7×10^5	1.10^a	0.85	18.6
no. 16	6.7×10^5	1.10^a	0.73	18.2
no. 17	1.1×10^6	1.10^a	0.81	19.2
NaPSS-H^b	1.7×10^6	1.10^c	0.88	18.8

[a] From the brochure of Pressure Chemical. [b] Synthesized from polystyrene by Vink's method. [c] The polydispersity for the parent polystyrene reported by the supplier.

photometrically by using the ϵ_{262} thus obtained. One serious problem in the correct estimations of the degree of substitution, and ϵ_{262}, is the water bound with NaPSS samples which could not be eliminated completely even by drying. This leads to an overestimation of the sample mass. In the present paper, the water content was determined by the Karl-Fischer method both on the dried samples and freeze-dried ones as follows. A known amount of the sample was dissolved under a nitrogen atmosphere into formamide, Wako Pure Chemical Ind. Ltd., Osaka, Japan, the final concentration being about 0.6%. Before use, formamide was dehydrated by keeping it with molecular sieves 4A, Wako Pure Chemical, for several days. The analysis was carried out in the presence of a large amount of methanol by using a Karl-Fischer moisture meter (MK-SS, Kyoto Electronics MRF. Co., Kyoto) and a Karl-Fischer reagent of Mitsubishi Kasei, Tokyo. The water content of the sample was determined by subtracting that of formamide (about 0.03 vol %). The measurements were repeated at least three times to take the average.

The weight-average molecular weight, M_w, was calculated by using the degree of polymerization supplied by Pressure Chemical Co. and the degree of sulfonation determined above. Light scattering measurements were performed for sample no. 12 in 0.1 M aqueous NaCl solutions (about 0.05–0.3 g/dL) by Chromatix KMX-6, Mountain View, CA, to estimate the M_w directly. The calculated and measured M_w's were in good agreement within experimental error.

Table I gives the properties of NaPSS samples used in the present paper. The IR and ^{1}H NMR measurements were kindly done by Dr. Takashi Yamamoto, Tokyo Research Center, Tosoh Company Ltd., Kanagawa, Japan. Two peaks at 1800 and 1930 cm^{-1} were taken as implying the existence of 1,4-disubstituted benzene rings. The signal pattern of the benzene rings was as clear as a standard sample of 100% sulfonated polystyrene. These analyses implied that the sulfonate groups were introduced at the para position; the ortho and meta substitutions and polysubstitution were concluded to be implausible. Furthermore, Dr. Yamamoto carried out the SO_3^- analysis by the combustion flask ion chromatography, which confirmed the degree of sulfonation obtained independently by us.

The water used in the present paper was purified immediately before use by deionization with cation- and anion-exchange resins (Puric-G., Organo) and further purified by a Milli-Q system (Type I, Millipore, Bedford, MA). The ion-exchange resins, which were used for the purification of the samples, were washed thoroughly by hydrochloric acid, sodium hydroxide, and ethanol. The preparation of sample solutions was performed in a nitrogen box to minimize the contamination by carbon dioxide in air, as described in part 1. Polyethylene (instead of glass) bottles were used to avoid contamination of ionic impurities from the glass wall.

B. Viscometers. As described in part 1, three kinds of viscometers were used: an Ubbelohde viscometer (type 0A, Kusano Scientific, Tokyo), a precision rotational viscometer (RV20, Haake, Karlsruhe, FRG), and a variable shear viscometer. The temperature was 25 ± 0.02 °C. The capillary viscometers were filled with nitrogen gas during the viscosity measurements. The details of the measurements themselves and the determination of the viscosity were as described in part 1.

Figure 1 shows the reduced viscosities of an NaPSS solution measured by the variable shear viscometer and by the rotational viscometer as a function of the shear rate. The correspondence between the two viscometers is satisfactory.

C. Adsorption Experiments. A glass tube (inner diameter, 4.7 mm, and length, 55.5 mm) filled with porous glass beads gel CPG 10 (mesh, 200–350 , mean diameter, 59 μm; pore size, 86 Å), a product of Electro-Nucleonics Inc., Fairfield, NJ, was connected with a conventional low-pressure chromatography apparatus. The column was first washed with water at a rate of 1 mL/min. Then 10 μL of an aqueous solution (1.5×10^{-3} g/dL) of NaPSS (molecular weight, 1.7×10^6) was repeatedly injected into the column. The amount of NaPSS in the effluent was estimated by UV absorbance at 230 nm. The NaPSS concentration in contact with the glass beads was estimated to be about 1.2×10^{-4} g/dL, which is very close to the lowest concentration in the viscosity measurements. A similar experiment was also carried out for a low molecular weight sample (3×10^5).

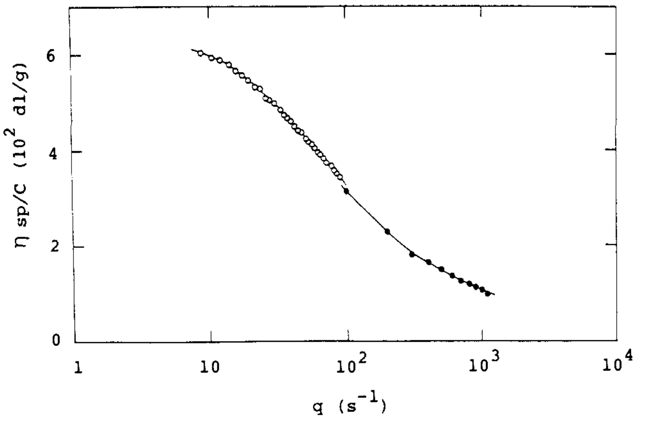

Figure 1. Comparison of the reduced viscosities determined by the variable shear viscometer (open circles) and by the rotational viscometer (filled circles): NaPSS, no. 17; concn, 0.13 g/dL, at 25 °C.

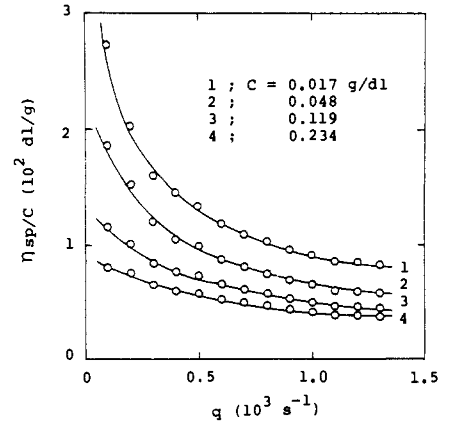

Figure 2. The shear rate dependence of the reduced viscosity: NaPSS, no. 17.

III. Results and Discussion

A. Dilute Regions. Figure 2 shows the reduced viscosities (η_{sp}/C) measured by the rotational viscometer for sample no. 17. Graphically the shear-thinning behavior is clear: the reduced viscosity increases with decreasing shear rate (q). Similar shear-thinning behavior was reported by Vink for poly(styrenesulfonic acid) and its sodium and potassium salts.[10] Albeit not on the same materials, the apparent viscosity of ionic polymer solutions was demonstrated to be non-Newtonian by many authors including Mark,[14] Fuoss and Strauss,[15] and Hall and Fuoss.[16] Fujita and Homma studied the viscosity of sodium carboxymethylcellulose in the q range between 50 and 1000 s^{-1} and reported conspicuous non-Newtonian behavior.[6] Obviously, these data and ours are at variance with those by Cohen et al.[11] who claimed the absence of the shear rate dependence for sodium poly(styrenesulfonates). The discrepancy is supposed to be due to the narrow range of shear rates (300–600 s^{-1}) covered by Cohen et al.

In part 1, we showed substantial shear-thinning effects of salt-free dilute suspensions of ionic polymer latex. This behavior was supposed to be due to the second-order electroviscous effects, which was caused by an electrostatic interaction between particles strong enough to form an ordered arrangement in suspensions.

The marked shear-thinning effect, or the non-Newtonian behavior observed here, seems also highly reasonable in light of the observed distinct scattering peaks for solutions of various ionic polymers including NaPSS under comparable experimental conditions,[17] which indicate the formation of an ordered ar-

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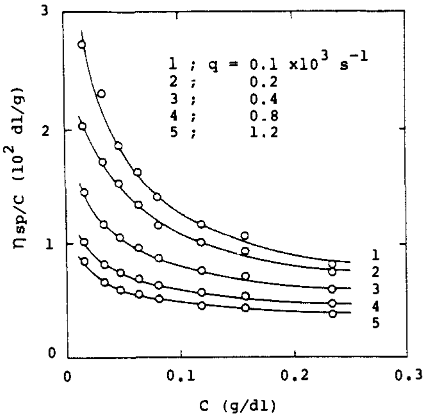

Figure 3. The reduced viscosity–concentration plot at various shear rates: NaPSS, no. 17.

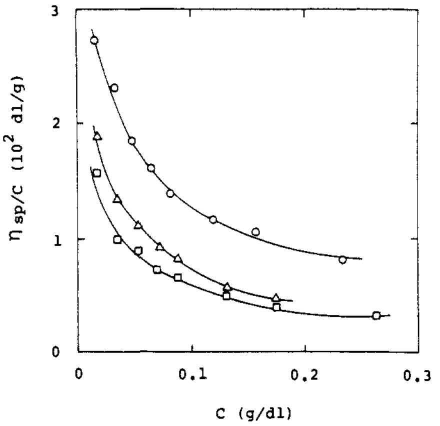

Figure 4. The concentration dependence of the reduced viscosity of three samples of various molecular weights at a shear rate of 100 s^{-1}: square, no. 12; triangle, no. 16; circle, no. 17.

rangement of the macroions in solutions. For linear macroions, the flexible nature and orientation of the polymer chains in streaming solvent would also be related to the shear-thinning behavior.

Figure 3 is the concentration dependence of the η_{sp}/C. Clearly the viscosity became larger with decreasing polymer concentration in the concentration range covered. The shear-thinning effect was substantial at low concentrations.

The concentration dependence of η_{sp}/C at $q = 100\ s^{-1}$ for the three NaPSS of various molecular weight is shown in Figure 4. The η_{sp}/C is found to increase with decreasing C for all the samples investigated.

As is well-known, Fuoss proposed the following relation[4]

$$\eta_{sp}/C = A/(1 + BC^{1/2})$$

or

$$C/\eta_{sp} = 1/A + (B/A)C^{1/2}$$

where A is the intrinsic viscosity and B is a constant. Figure 5 shows the Fuoss plot for no. 17 at various shear rates, from which we can see a satisfactory linearity. However, for low molecular weight samples, the plot led us to a physically unreasonable situation, as is shown in Figure 6: constant A assumed a negative value for nos. 12 and 16. The data in this figure were at $q = 100$ s^{-1}. If use is made of the extrapolated value to $q = 0$, the expected A value would be more negative. This situation clearly shows that the Fuoss plot is not universally valid.

The sharp increase in the η_{sp}/C with decreasing concentration was accounted for in terms of expansion of the macroions (with decreasing concentration) due to progressively enhanced dissociation of the ionizable groups. The more marked q dependence of the η_{sp}/C at a lower concentration (for example, Figure 3) appears to be consistent with such an explanation. However, as was shown in part 1, a similar upturn of the $\eta_{sp}/C - C$ curve was also found for suspensions of polymer latex particles, whose size is expected not to change with concentration. Thus we believe that the conformational change is not a primary reason for the observed increase of the η_{sp}/C. This belief has been further enforced by a recent study by Hara et al.[18] who observed also a similar upturn of the viscosity of halato-telechelic ionomer. This ionomer molecule has only one ionic end group, so that *intra*-molecular Coulombic interaction does not come into question. In other words, the observed upturn is definitely *intermolecular* in nature. Thus, the earlier proposed interpretation in terms of the intramolecular interaction and hence the conformation change would need reconsideration.

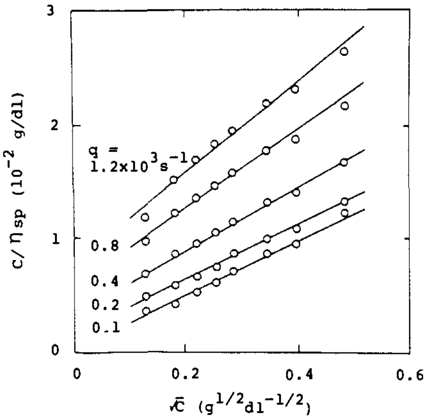

Figure 5. The Fuoss plot at various shear rates: NaPSS, no. 17.

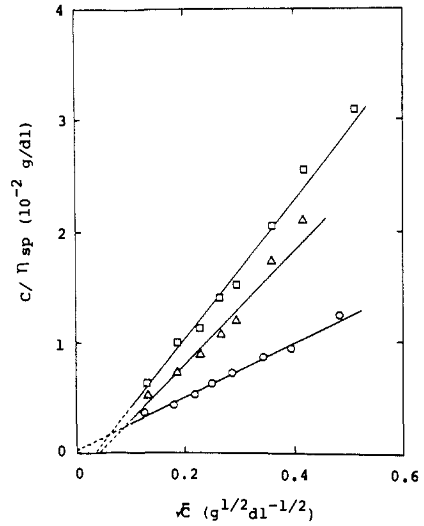

Figure 6. The Fuoss plot at a shear rate of 100 s^{-1} of three samples of various molecular weights. The symbols are the same as in Figure 4.

B. Very Dilute Regions. The viscosity data in very dilute regions are strongly subject to a trace of impurities. This is a widely known phenomenon which the pioneers in the field have successfully demonstrated by the judicious addition of extraneous salts to the solvent.[3,6,8,19,20] Furthermore, Butler et al. noticed that the η_{sp}/C of poly(styrenesulfonate) solutions was quite sensitive to the quality of water used.[8] Thus, in the present paper, the utmost care was taken to prevent or minimize the effects of impurities including carbon dioxide in air. Figure 7 shows the vitiating influence of air on the viscosity measured by the Ubbelohde type viscometer.

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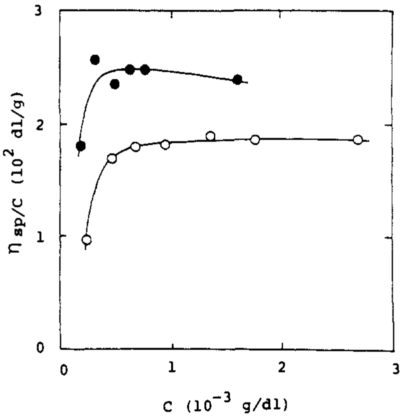

Figure 7. Comparison of the reduced viscosities measured in air and under a nitrogen atmosphere. Both the solution preparation and the viscosity measurement (with the Ubbelohde viscometer) were carried out under the nitrogen atmosphere (filled circles) or in air (open circles): NaPSS, no. 16.

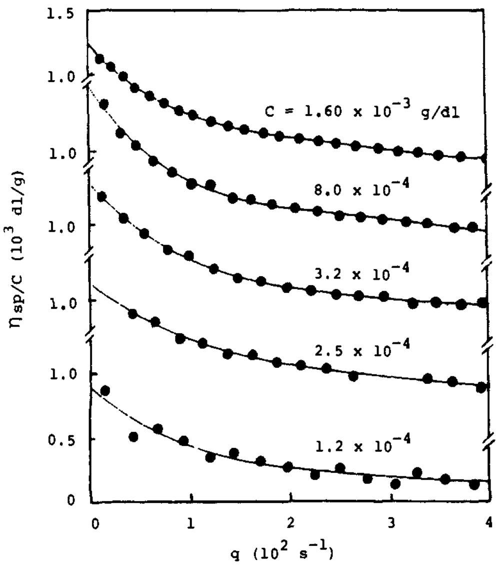

Figure 8. The shear-thinning effects on the reduced viscosity: NaPSS, no. 17.

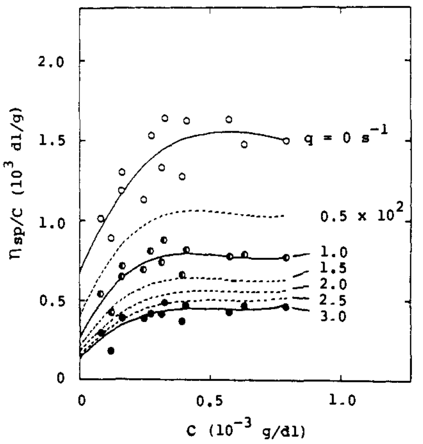

Figure 9. The reduced viscosity–concentration curves at various shear rates in a very dilute region. Except at $q = 0$, 100, and 300 s^{-1}, the data are shown by the third-order least-squares curves. NaPSS, no. 17.

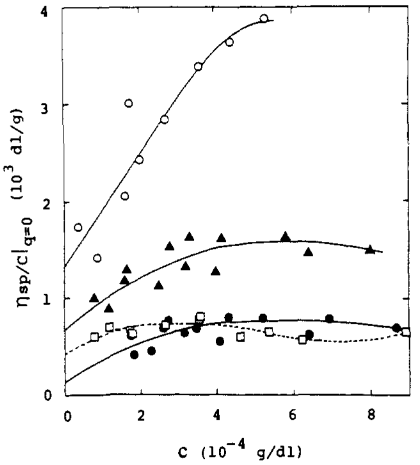

Figure 10. The reduced viscosity at zero shear rate versus concentration: open circles, NaPSS-H; filled triangles, no. 17; open squares, no. 16; filled circles, no. 12.

The viscosity data in air is lower by about 30% than that obtained under nitrogen. Presumably, carbon dioxide in air dissolved into the solutions to produce carbonic acid and its salt, which acted as a foreign salt and lowered the viscosity. For this reason, the following experiments were performed under a nitrogen atmosphere. Figure 7 shows that the reduced viscosity increased with increasing concentration. To obtain more reliable data on the concentration dependence, it was judged necessary to evaluate the shear rate dependence. Thus the variable shear viscometer was used to cover a q range between 10 and 500 s^{-1}.

Figure 8 is the shear-rate dependence of the reduced viscosity at various polymer concentrations. By using the fourth-order least-squares method, the reduced viscosity was extrapolated to $q = 0$ and interpolated to several q values. Figure 9 shows the reduced viscosity at various q values thus obtained. Obviously, the concentration dependence of the viscosity in very dilute regions is quite different from that in dilute regions. An increasing tendency of the reduced viscosity with increasing concentration is seen. Furthermore, the shear-thinning effect is more than obvious. The curves in Figure 9 were obtained by using the third-order least-squares method, by which the extrapolation of the reduced viscosity to $C = 0$ was effected to evaluate the intrinsic viscosity ($[\eta]$).

The reduced viscosity we obtained for no. 16 at $q = 600$ s^{-1} was about 230 dL/g at a concentration of 10^{-3} g/dL, whereas that reported by Cohen et al.[11] on presumably the same material was 170 dL/g. There was no serious discrepancy. However, we note that our viscosity data extrapolated to zero shear rate was about 580 dL/g, whereas they considered the shear rate dependence unimportant.

Figure 10 gives the reduced viscosity extrapolated to the zero shear rate ($\eta_{sp}/C]_{q=0}$) as a function of concentration. For all samples, the viscosity is seen to increase with increasing concentration. The curves in the figure were drawn by the third-order least-squares method and used to determine the intrinsic viscosity at zero shear rate ($[\eta]_{q=0}$).

C. On Adsorption of Sodium Poly(styrenesulfonate) onto Glass Surface. It has been frequently pointed out that the observed increase of the η_{sp}/C with increasing C in very dilute regions might be due to adsorption of polymer molecules to the glass wall of viscometer, which would cause lowering of polymer concentration in the solution. To examine this problem, the extent of the adsorption of NaPSS was determined by using the method described in the Experimental Section. The glass beads column was saturated by 50 injections of an NaPSS solution. The amount of adsorption was 5×10^{-5} g/cm^2 for the sample with a molecular weight of 1.7×10^6.

By using this information, the adsorption by the capillary of the variable shear viscometer (inner diameter, 0.0618 cm, and length, 49.18 cm) was concluded to decrease the NaPSS concentration (1.2×10^{-4} g/dL) at the most only by 0.1%. For the sample with a molecular weight of 3×10^5, the corresponding concentration decrease was found to be 0.2%. In light of these experimental data, the adsorption could be excluded from further consideration.

D. Intrinsic Viscosity–Molecular Weight Relationship. In Figure 11 is plotted the $[\eta]_{q=0}$ determined in the preceding section against the molecular weight. Line A was drawn by using the

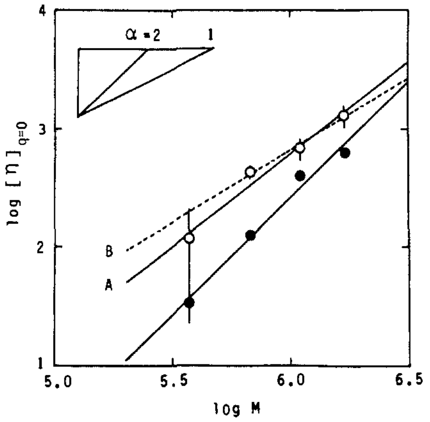

Figure 11. The intrinsic viscosity versus molecular weight plot: open circles, observed data; filled circles, Kirkwood–Auer theory. Line A is drawn by the linear first-order least-squares method through the observed points for the four samples, whereas line B was drawn for the three higher molecular weight sample with a slope of 1.2. The error bar was determined by taking the average of the standard deviation of the data points from the least-squares curve of Figure 10.

first-order least-squares method. The slope of this line was 1.6.

In regards to the value of 1.6 it is reminded that all the samples used do not have the same degree of substitution (DS). It might be possible to find an α value smaller than 1.6, if the small value of DS for no. 16 and the large one for NaPSS-H are corrected. Although this point has to be studied in more detail by using a more well-defined ionic polymer with a narrow molecular weight distribution, Figure 11 seems to exclude the possibility that the α is 2. Furthermore, it is feared that the $[\eta]$ data for no. 12 (lowest molecular weight) is less reliable since the experimentally attainable lowest concentration was higher for this sample (about 2×10^{-4} g/dL) as a result of a small relative viscosity than for other samples, so that the extrapolation to $C = 0$ would be less reliable. Taking this factor into consideration and using only three data points for other higher molecular weight samples, we have a straight line (B in Figure 11) with a slope of 1.2.

From the above discussion, it seems reasonable to state that the exponent α is 1.6–1.2 for sodium poly(styrenesulfonate) in the molecular weight range covered. In this respect, it is reminded that Vink obtained $\alpha = 1.1$ for sodium carboxymethylcellulose of a relatively low degree of substitution by extrapolation of viscosity data at various ionic strengths.[9] The difference in the α values of the two samples is interesting, but we cannot give quantitative discussion until further data have been accumulated.

The fact that the α takes a value smaller than two at zero ionic strength indicates that the earlier reasoning on the conformation of macroions needs reconsideration. One of the simplest counterinterpretations is that the ionic macromolecules are not fully extended even at the infinite dilution. This view was advanced by Butler et al.[8] based on the sedimentation coefficients that even at the observed maximum of the reduced viscosity poly(styrenesulfonate) ions have a maximum end-to-end distance less than half the contour length required by the molecular weight. Also Vink reached the same conclusion.

Another important factor is the electroviscous effect. As was demonstrated in part 1, the first-order effect could be estimated by viscosity measurements in salt-containing polymer latex suspensions, whereas it was not possible in the salt-free cases because of the difficulty in extrapolating the viscosity data to zero latex concentration and shear rate in the salt-free suspension. Booth's theory of the first-order electroviscous effect predicts, however, that the effect becomes larger with decreasing salt concentration, and the experimentally determined effect showed a tendency to increase. If this is really the case and if the effect is substantial with soluble macroions such as poly(styrenesulfonate), we should dissociate ourselves from applying the relation $[\eta] = KM^{\alpha}$ for consideration of the conformation of *macroions*, since this relation has been derived without taking the electroviscous effect into consideration.

The substantial contribution of the effect appears to be exhibited by comparison of the observed data with a viscosity theory of solutions of rod-like nonionic macromolecules proposed by Kirkwood and Auer.[22] According to the theory, the intrinsic viscosity is given by

$$[\eta] = 4\pi N b L^2 / 9000 M_0 \ln (L/b) \qquad (1)$$

where N is Avogadro's number, L the length of the rod, M_0 the molecular weight of the monomer, and b the length of the monomer. For NaPSS, b is 2.515×10^{-8} cm from the bond angle and the length of the C–C bond. M_0 was obtained from the average molecular weight of the monomer calculated from the degree of substitution. L was obtained from M_0 and the molecular weight of polymer. The theoretical results were shown by the filled circles in Figure 11. The observed values were of the same order of magnitude as the theoretical ones, but the former was always larger than the latter. Accepting the theory as a criterion in the argument, this difference between the two values might testify to the contribution of the electroviscous effect, which was not considered in the theory: the difference indicates a fairly large effect even when the macroions are rods as was assumed in the theory. If the macroions are coiled, the energy dissipation would be lowered so that the observed viscosity would be smaller. Then a much larger electroviscous effect would exist for this conformation than for rods. In the absence of a satisfactory theory for viscosity of ionic macromolecules, however, quantitative discussion is formidable for the time being. Even then, the earlier reasoning based on $[\eta] = KM^{\alpha}$, that the macroions are fully stretched, would be claimed to be unwarranted.

IV. Concluding Remarks

In the present paper, the viscosity behavior of aqueous solutions of sodium poly(styrenesulfonates) was investigated. The measurements were done with the utmost care to prevent the impurity effect. The adsorption problem of polymers onto the capillary wall was examined by a chromatographic method and found to be unimportant. The reduced viscosity showed a marked shear-thinning effect as was found by most previous authors. The reduced viscosity extrapolated to zero shear rate increased first with increasing concentration in a very dilute region and, passing a maximum, decreased in a dilute region. The presence of the viscosity maximum indicated that the so-called Fuoss plot is not universally justifiable. In other words, the earlier reasoning that the macroions are stretched out like rods needs reconsideration. The intrinsic viscosity determined after having taken the maximum into consideration displayed a different molecular weight dependence: the exponent α of the relation $[\eta] = KM^{\alpha}$ was in the range between 1.6 and 1.2. Taking this at face value and assuming that $[\eta] = KM^{\alpha}$ holds not only for nonionic macromolecules but also for ionic flexible macromolecules, the macroions were concluded not to be stretched out even at the infinite dilution.

Furthermore, in the present paper, a problem was raised whether the intrinsic viscosity–molecular weight relationship can be ultimately applicable to flexible ionic macromolecules. One factor is the electroviscous effect, which was not considered in the derivation of the relation. As we have seen in part 1, the first-order electroviscous effect is not negligible for polymer latex suspensions. If this is the case also for linear ionic macromolecules, the use of the intrinsic viscosity–molecular weight relationship would be questioned.

As we already mentioned in part 1, the macroion domain corresponds to highly concentrated simple ionic solutions: for vinylic polymers the distance between ionized groups would be in the order of magnitude of 2.5 Å, whereas the average interionic distance in 10 M of 1–1 electrolyte solutions is about 4 Å. It would be justifying to claim that the formation of ionic aggregates such as triple ions and quadruple ions cannot be ruled out. When even a very small number of these aggregates are produced intramolecularly,—although this is highly plausible in such concentrated

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states,—the macroions would immediately deviate from fully stretched conformation. The positive proof for aggregation phenomena inside the macroion domain remains to be obtained, but at the same time there must be required likewise positive proof for the lack of the aggregation almost completely disregarded in previous arguments.

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Microscopic Observation and Quasielastic Light-Scattering Measurements of Colloid Crystals. Determination of the Radial Distribution Function and Structure Factor for the Two-State Structure

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Abstract: Direct observation by fluorescence microscopy and quasielastic light-scattering (QELS) measurements have been carried out to study particle distributions in polymer latex suspensions. Special attention was paid to the scattering profiles from the two-state structure, in which localized ordered, non-space-filling structures coexisted with disordered regions. From the direct observation, the radial distribution function (RDF) was determined for 35000 particles by an image data analyzer and further Fourier transformed to the structure factor $S(Q)$. The 2D Fourier analysis (2D FT) of the micrographs was also carried out. The interference function (D_0/D_{eff}), which corresponds to $S(Q)$, was determined by the QELS measurement. The interparticle spacings ($2D_{\mathrm{exp}}$) determined from RDF, 2D FT, and QELS measurements were in good agreement and were smaller than those calculated with the assumption of a homogeneous distribution of particles ($2D_0$). Furthermore, $S(Q)$ determined from the direct observation and D_0/D_{eff} determined from the QELS measurement agreed well in both number and position of the peaks. Thus the particle distributions obtained from the microscopic measurements were essentially the same as those obtained by QELS measurements, ruling out the possible vitiating influence of the container wall on the microscopic observation.

I. Introduction

Polymer latex suspensions (particularly polystyrene-based latices) have been intensively studied by microscopic observation and both elastic and quasielastic light-scattering (QELS) measurements.[1-8] By the direct observation technique, the distributions of the particles can be easily photographed,[3,6] although the information derived is on the local, but not global, situation. On the other hand, the scattering techniques are essentially indirect, providing averaged information on the particle distribution. By the direct observation of the suspensions, the coexistence of the ordered structure of a high number density and disordered region having a lower density was confirmed as was shown in Figures 1, 2, and 11 of our previous paper.[9] Such an inhomogeneity in the suspension, which we call the two-state structure, suggests the existence of an (electrostatic) attraction between the particles.[2] Although the ordered structure can be easily distinguished from the disordered region on the bases of the average displacement of the particles, the regularity in the particle distribution, and the number density of the particles, the interference functions determined by the scattering measurements showed only one or two broad peaks. This data has led many authors to the conclusion that there exist no ordered arrangements.

In this report, we determined the particle distribution from the direct observation and concurrently from the QELS measurements for the same sample. The direct observation method is feasible only for relatively large particles, say about 0.2×10^{-6} m in diameter, because of a resolving power of an optical ultramicroscope and of the difference in the refractive indices of the latex and solvent. On the other hand, such large particles cannot be studied by the QELS measurements due to the limitation of Rayleigh–Debye–Gans scattering[10] and the possible disturbance by multiple scattering. Previously,[8] we reported the agreement in the interparticle spacings obtained from the two methods performed independently. To study the same sample by these two methods, a rather small fluorescent latex was used. Although the particles were small (0.14×10^{-6} m in diameter), they could be seen under the fluorescence microscope and micrographs could be taken.

In the present paper, special attention was paid to the two-state structure in the latex suspension. It is attractive to dissect the

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