Revisit to the Intrinsic Viscosity–Molecular Weight Relationship of Ionic Polymers. 5. Further Studies on Solution Viscosity of Sodium Poly(styrenesulfonates)

Junpei Yamanaka,[†] Hidemasa Araie,[†] Hideki Matsuoka,[‡] Hiromi Kitano,[‡] Norio Ise,[*,‡] Takuji Yamaguchi,[†] Susumu Saeki,[†] and Masakazu Tsubokawa[†]

Department of Materials Science and Engineering, Fukui University, Fukui 910, Japan, and Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan

Received January 31, 1991; Revised Manuscript Received June 24, 1991

ABSTRACT: The shear-rate dependence of the intrinsic viscosity ($[\eta]$) and the concentration (C in g/dL) dependence of the reduced viscosity (η_{sp}/C) were investigated for aqueous solutions of sodium poly(styrenesulfonate) (NaPSS). The $[\eta]$ of salt-free aqueous solutions of NaPSS ($M_w = 1.7 \times 10^6$ and 1.1×10^6) was always larger than the Kirkwood–Plock theoretical value for the nonionic rigid rod in the shear-rate range investigated (0–300 s^{-1}). The viscosity of aqueous solutions of NaPSS ($M_w = 1.7 \times 10^6$) was measured in a wider concentration region than that we reported previously. There existed a distinct maximum at C_m in the η_{sp}/C vs C plot. The shear-thinning behavior was clearly observed throughout the C range investigated. The plot was approximated by the equation $\eta_{sp}/C_p = AC_p^{\beta}$ (C_p in molar concentration) below and above C_m. Since a similar maximum was observed also for suspensions of an ionic polymer latex whose conformational change can be ignored, the maximum is suggested to be due to electroviscous effects (not due to the conformational factor of macroions).

Introduction

We have already reported the viscosity behavior of ionic polymers in water and in binary systems: aqueous suspensions of ionic polymer latex (part 1[1]) and aqueous solutions of sodium poly(styrenesulfonates) (NaPSS) (part 2[2]), and ethylene glycol/water suspensions of ionic polymer latex (part 3[3]) and ethylene glycol/water solutions of sodium poly(styrenesulfonate) (part 4[4]).

We revealed in part 2 that the reduced viscosity (η_{sp}/C) of salt-free aqueous solutions of NaPSS increased with increasing polymer concentration (C) below $C = 5 \times 10^{-4}$ g/dL. The intrinsic viscosity ($[\eta]$) was evaluated by extrapolations of the reduced viscosity to $C = 0$ and rate of shear (q) = 0. When these extrapolations were performed, the exponent α of the relation $[\eta] = KM^{\alpha}$ was found to be 1.2–1.6 for salt-free aqueous solutions of NaPSS in contrast with the results reported earlier. This suggests that the macroions are not fully stretched out like a rod even at the infinite dilution, if the intrinsic viscosity–molecular weight relationship is valid for ionic polymers. When macromolecules are coiled, the intrinsic viscosity is expected to be smaller than that of a rodlike polymer solution. However, the experimental value was always larger than the theoretical value proposed for rodlike nonionic macromolecules by Kirkwood and Auer.[5] This discrepancy seems to be due to the electroviscous effect, which exceeded the decrease of viscosity owing to the shrinkage of the molecule.

Since both hydrodynamic and electroviscous effects have to be considered, it is difficult to reach a reliable conclusion on the conformation of a flexible ionic polymer at infinite dilution by investigating only the viscosity behavior. Nonetheless, the viscosity data we obtained are valuable because the experiments were performed with the utmost care to prevent impurity effects and the lowest concentration studied was quite small (4×10^{-5} g/dL). Furthermore, there are only a few reports on the viscosity behavior of salt-free dilute aqueous solutions of ionic polymers in which the shear-rate dependence was carefully measured. We first discuss the shear-rate dependence of the intrinsic viscosity by using the data obtained in our previous measurements.

A maximum is known to exist in the η_{sp}/C vs C curve of linear ionic polymers.[2,6–8] In our previous work,[2] however, the viscosity around the maximum was not measured. In the present paper, the viscosity data are accumulated for a high molecular weight poly(styrenesulfonate) sample (designated NaPSS-H) in a much wider concentration region at various shear rates. The influence of NaCl concentration on the η_{sp}/C vs C curve is also examined.

Experimental Section

A. Materials. The characteristics of the NaPSS samples investigated were reported in part 2. The concentration of the polymer in the viscosity measurements was evaluated spectrophotometrically by using the extinction coefficient at the peak top near 262 nm of NaPSS (ϵ_{262}). The determination of the weight-averaged molecular weight M_w, degree of sulfonation, and ϵ_{262} were described in part 2. Preparation of the sample solution and determination of the solution concentration were performed as described in parts 1 and 2. Polyethylene bottles used as containers were filled with nitrogen gas during solution preparation, and nitrogen gas was further blown into the bottles after the preparation.

The water used was purified by the same procedure as described in part 3. The specific conductivity of the water obtained was (0.5–0.6) × 10^{-6} S cm^{-1}, practically the same as that of the water used in the previous papers.

A "suprapur" grade sodium chloride was purchased from Merck Co. (Darmstadt, Germany). After the sodium chloride was dried at 130 °C for at least 24 h, a stock 0.1 M aqueous solution was prepared.

B. Methods. A variable-shear capillary viscometer described in previous papers was used for measurements when the specific viscosity (η_{sp}) was less than 1. The viscometer was cleaned by using sulfuric acid and rinsed with purified water. The viscometer and other apparatus were washed with purified water just prior to use, whose conductivity was measured to examine whether the cleaning was satisfactory. The air inside the viscometer was replaced by nitrogen gas. For solutions having higher viscosities, a precision rotational viscometer (Haake Rotovisco RV20 system) was used. The details of the measurement and the determination of the viscosity were as described in part 1. In the present paper, the accuracy of the viscosity data obtained with the RV20

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[*] To whom correspondence should be addressed.
[†] Fukui University.
[‡] Kyoto University.

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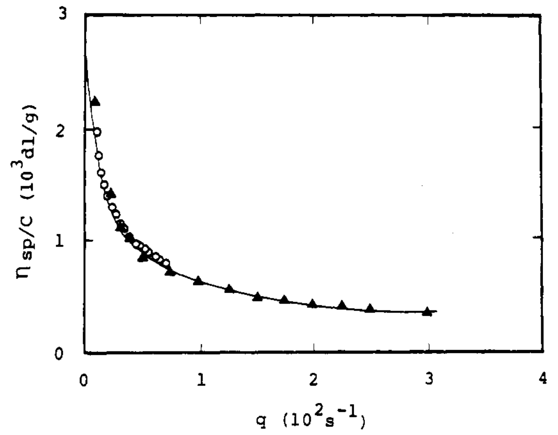

Figure 1. Comparison of the reduced viscosities determined by the variable shear capillary viscometer (open circles) and by the rotational viscometer (filled triangles): salt-free aqueous solution of NaPSS-H, 9.0×10^{-3} g/dL, at 25 °C.

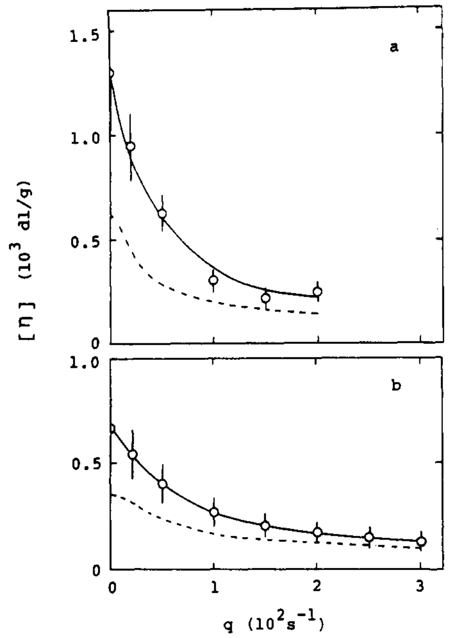

Figure 2. Shear-rate dependence of the intrinsic viscosity for salt-free aqueous solutions of NaPSS: (a) NaPSS-H; (b) NaPSS no. 17. Broken line represents the Kirkwood–Plock theoretical curve.

system was improved by using a digitizer (Model K-510 mk2, Logitec Co., Tokyo) and computer devices for analysis of raw data, and consequently the data at low shear rates became sufficiently reliable that zero-shear extrapolation of the viscosity could be performed with almost the same accuracy as by the variable-shear viscometer. Figure 1 shows the η_{sp}/C vs q plot for an aqueous solution of NaPSS-H measured by the variable-shear viscometer and by the rotational viscometer. The agreement of the data by the two viscometers was satisfactory even at low shear rates.

Results and Discussion

A. Shear-Rate Dependence of Intrinsic Viscosity. In this section we discuss the shear-rate dependence of the intrinsic viscosity by using the data obtained in part 2. Parts a and b of Figure 2 show the intrinsic viscosity[9] vs q plots for aqueous solutions of NaPSS-H ($M_w = 1.7 \times 10^6$, $M_w/M_n = 1.10$, degree of sulfonation = 0.88) and NaPSS no. 17 ($M_w = 1.1 \times 10^6$, $M_w/M_n = 1.10$, degree of sulfonation = 0.81), respectively. The data were obtained by the extrapolation of η_{sp}/C to $C = 0$ by applying the third-order least-squares method for the η_{sp}/C vs C curve. The error bar was determined by averaging the standard deviation of the data points from the least-squares curve. Shear-thinning behavior is clear as we have repeatedly pointed out.[10]

Although some other factors, for example, deformations of macromolecules and of counterion clouds under a velocity gradient, should be taken into consideration, it seems worth comparing the observed data with the theoretical values for a solution of nonionic rigid rods as a first-order approximation. Kirkwood and Plock[11] (K–P) extended the theory of Kirkwood and Auer[5] (K–A) to consider the shear-rate dependence of the intrinsic viscosity of solutions of rodlike rigid nonionic molecules. According to the K–P theory, the intrinsic viscosity at shear rate = q, $[\eta]_q$, is given as

$$[\eta]_q = [4\pi N b L^2/9000 M_0 \ln (L/b)][1 - 0.729(tq)^2 + 1.011(tq)^4 - ...] \quad (1)$$

where N is Avogadro's number, b is the monomer length, L is the rod length, M_0 is the monomer molecule weight, and t is the relaxation time. The K–P theory agrees with the K–A theory at $q = 0$. For NaPSS, b was estimated to be 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 which was calculated by using the degree of substitution. L was obtained from M_0 and the molecular weight of the polymer. The relaxation time was related to the rotational diffusion constant (D_{rot}) by

$$t = 1/6D_{rot} \quad (2)$$

and D_{rot} for the rigid rod is given by

$$D_{rot} = 3kT \ln (L/b)/\eta_0 L^3 \quad (3)$$

where k is the Boltzmann constant, T is the absolute temperature, and η_0 is the solvent viscosity.[11]

The broken curves in Figure 2 show the K–P theoretical intrinsic viscosity. The theoretical value was always smaller than the observed value not only at $q = 0$ but throughout the q range investigated. This deviation may be attributed to the first-order electroviscous effect resulting from the electrostatic interaction between the polyions and counterions, which was not considered in the K–P theory.

From eq 1, it is obvious that the shear-thinning effect in viscosity decreases with decreasing relaxation time of the molecule. When a molecule shrinks from a rod, the relaxation time is expected to be more or less reduced, and therefore the shear-thinning effect in the viscosity of the solution is reduced. However, Figure 2 clearly shows that the shear-thinning effect is more substantial for NaPSS than the theoretical results for the rod, although the PSS molecule was suggested not to be fully stretched.[2]

The molecule is flexible and is expected to be easily deformed from its equilibrium shape by shearing force. The larger degree of deformation, or decrease in the anisotropy of the molecule, with increasing q (probably up to a certain threshold q value) explains why the NaPSS solutions show larger shear-thinning behavior than the (undeformable) rigid rod.

The flexibility of the molecule determines the molecular conformation at zero shear (and hence zero-shear intrinsic viscosity). Schmitz referred to this problem in his recent article.[12] He pointed out that the intrinsic viscosity of our lowest molecular weight sample ($M_w = 3.7 \times 10^5$) was significantly lower than those of the other samples. According to his theoretical analysis, this

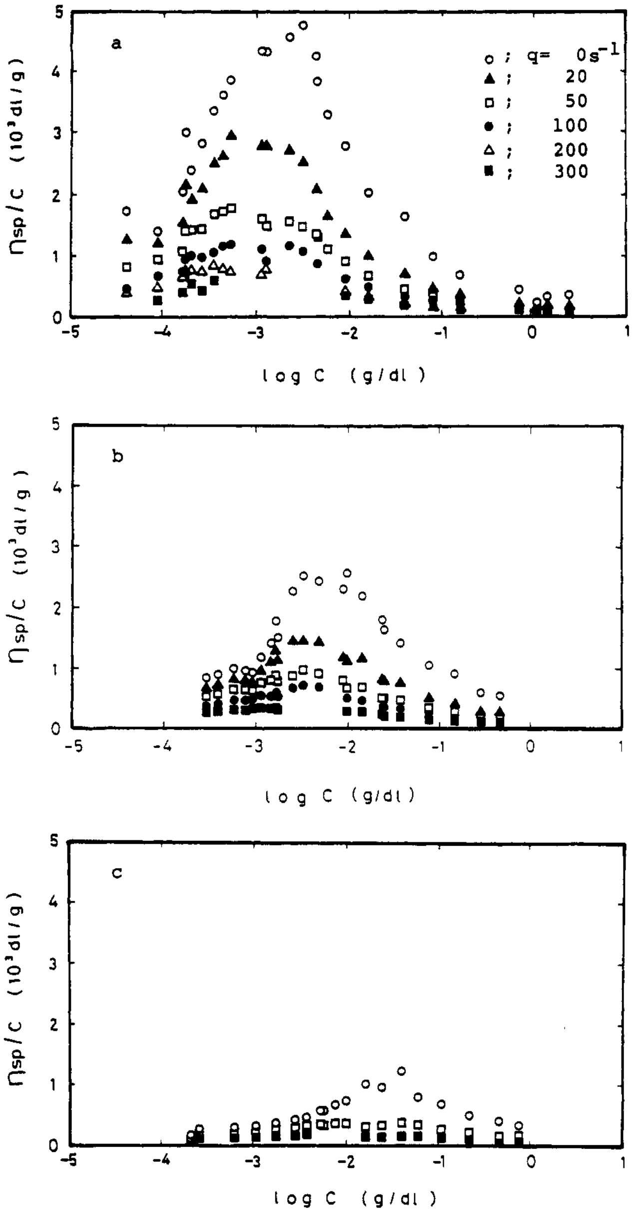

Figure 3. Reduced viscosity–concentration plot for aqueous solutions of NaPSS-H at various shear rates: (a) [NaCl] = 0 M; (b) 10^{-5} M; (c), 10^{-4} M.

observation can be explained if the lowest molecular weight sample was more flexible than the other samples having higher molecular weights.

B. Concentration Dependence of Reduced Viscosity. Figure 3 shows η_{sp}/C vs C plots for aqueous solutions of NaPSS at three NaCl concentrations. The data for the salt-free aqueous solution (Figure 3a) below $C = 10^{-3}$ g/dL were reproduced from the previous paper.[2] The data at zero shear are plotted in Figure 4 to make comparison easier. Obviously, there exists a distinct maximum in the η_{sp}/C vs C plots, and the polymer concentration at the maximum (C_m) becomes larger with increasing NaCl concentration. Furthermore, the shear-thinning behavior of the reduced viscosity was obvious throughout the concentration range investigated.

Cohen et al.[6-8] also reported the presence of the maximum in the η_{sp}/C vs C curve for aqueous solutions of NaPSS. They claimed that the viscosity was independent of the shear rate, and the viscosity measurements were performed by a precision Ubbelohde viscometer without changing the shear rate. As mentioned in part 2, the absence of the shear-rate dependence reported by these authors is contradictory to a large body of experimental data and would be due to the narrow range of shear rate (300–600 s^{-1}) covered by Cohen et al. When conventional capillary viscometers, including the Ubbelohde-type one, are used for non-Newtonian fluids, not only the viscosity value itself but also its concentration dependence may be different from those at zero shear, since the rate of shear generated by the viscometer becomes larger with decreasing viscosity (consequently, with decreasing polymer concentration). Thus the extrapolation of the reduced viscosity to zero shear rate is essentially important.

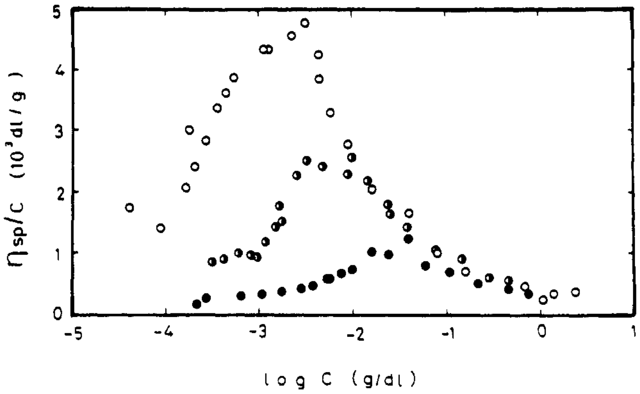

Figure 4. Zero-shear reduced viscosity–concentraton plot for aqueous solutions of NaPSS-H: open circles, [NaCl] = 0 M; half-filled circles, 10^{-5} M; filled circles, 10^{-4} M.

According to Cohen et al.,[6] the C_m for a salt-free aqueous solution of NaPSS was about 10^{-4} g/dL, independent of molecular weight ($M_w = 1.6 \times 10^3$ to 6.9×10^5). At [NaCl] $\simeq 10^{-5}$ and 10^{-4} M, C_m was about 5×10^{-3} and 5×10^{-2} g/dL, respectively, according to our measurements (Figure 4). There is no serious discrepancy between the C_m value Cohen et al. reported and that which we reported.

The maximum has also been observed for aqueous suspensions of an ionic polymer latex whose conformational change can be safely ignored. Furthermore, the decreasing tendency of the reduced viscosity with increasing polymer concentration was also noticed for a halato-telechelic ionomer,[13] which has only one ionic end group in the polymer chain so that intramolecular interaction is ruled out. Thus the conformation of the macroion and intramolecular interaction are not the main factors in determining the reduced viscosity vs concentration curve. On the basis of our study on latex suspensions, we can claim that the electroviscous effect is important.

Without knowing the physical meaning, we would like to point out that there exists an empirical relation $\eta_{sp}/C_p = AC_p^{\beta}$ (C_p is molar concentration; A and β are constants) below and above C_m.[14] Figure 5 is a replot of Figure 3a, showing a double-logarithmic reduced viscosity–polymer concentration plot for salt-free aqueous solutions of NaPSS-H at three shear rates. The C_p value was calculated from the C value and the average monomer molecular weight obtained by taking the degree of sulfonation into consideration. The linearity of the plot was satisfactory both below and above C_m. Figure 6 shows the same plot for NaPSS no. 12 ($M_w = 3.7 \times 10^5$, $M_w/M_n = 1.10$, degree of sulfonation = 0.85), no. 16 ($M_w = 6.7 \times 10^5$, $M_w/M_n = 1.10$, degree of sulfonation = 0.73), and no. 17, which were measured in part 2. The data in the log $C_p < -4$ region were obtained by the variable-shear capillary viscometer and extrapolated to zero shear, whereas the data at higher C_p's were obtained by the rotational viscometer at $q = 100$ s^{-1}. The plot also showed a good linearity. The slopes of the plot, namely, the exponent β of the relation $\eta_{sp}/C_p =$

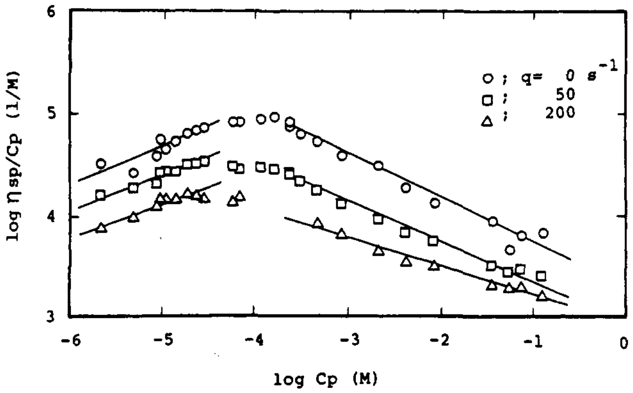

Figure 5. Double-logarithmic reduced viscosity–concentration plot for salt-free aqueous solutions of NaPSS-H at three shear rates. Polymer concentration is represented by monomer moles per liter (C_p).

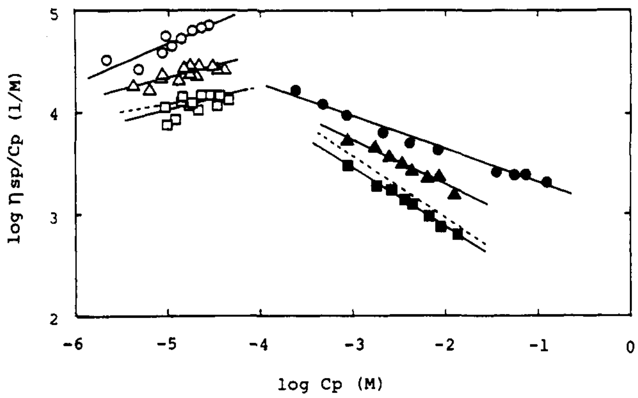

Figure 6. Double-logarithmic reduced viscosity–concentration plot for salt-free aqueous solutions of NaPSS: circles, NaPSS-H; triangles, no. 17; squares, no. 12; broken line, no. 16. $q = 0$ s^{-1} for log $C_p < -4$ (open symbols) and 100 s^{-1} for log $C_p > -4$ (filled symbols). The data of NaPSS-H at $q = 0$ s^{-1} are shown for comparison.

AC_p^{β}, was determined by a first-order least-squares method. β values below C_m ranged between 0.3 and 0.2, decreasing with increasing shear rate, while those above C_m were about −0.3. It would be interesting to dissect the nature of the linearity and the slope values.

Recently, Witten and Pincus (W–P) developed a theory[15] on the basis of a rodlike model of polyions. They claimed that the empirical Fuoss law[16] can thereby be reproduced at $C_p > C^*$ (C^* = overlap concentration of the rodlike polyion). We point out that our previous work (part 2) and the present one clearly showed the invalidity of the Fuoss law. In addition, part 2 cast strong doubt on the rodlike conformation of poly(styrenesulfonate) ions on the basis of the exponent of the Mark–Houwink–Sakurada equation not being 2.

Concluding Remarks

The viscosity behavior of aqueous solutions of sodium poly(styrenesulfonates) was carefully studied. The intrinsic viscosity of salt-free aqueous solutions of NaPSS was determined at various shear rates by extrapolation of the reduced viscosity–concentration plots to infinite dilution. The intrinsic viscosity thus obtained was larger than the Kirkwood–Plock theoretical value for the nonionic rigid rod at any shear rate investigated. This deviation was ascribed to a first-order electroviscous effect which was not considered in the theory. The intrinsic viscosity decreased markedly with increasing shear rate (shear-thinning behavior). The Kirkwood–Plock theory predicts shear-thinning behavior as a result of molecular orientation by a shearing force. However, the shear-thinning behavior was more substantial for the present system than the theoretical result.

We examined the concentration dependence of the reduced viscosity in a higher polymer concentration range than we did previously. A distinct maximum was confirmed in the η_{sp}/C vs C plot. The maximum concentration shifted to a higher C with increasing concentration of a simple salt. Since a similar maximum was observed for suspensions of ionic polymer latices, the presence of a maximum was attributed to the electroviscous effect. The double-logarithmic plot for η_{sp}/C vs C showed a good linearity below and above the maximum.

Acknowledgment. J.Y. is grateful to Professor T. Takahashi and Associate Professor K. Sakurai, Fukui University, for their permission to use the spectrophotometer. We are grateful to Professor N. Imai, Nagoya University, for his helpful discussion on the electroviscous effect. This work was supported by a Grant-in-Aid for Specially Promoted Research of the Ministry of Education, Culture, and Science (No. 63060003).

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