Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Solution Behavior of an Alternating Anionic-Zwitterionic Copolymer

J. C. Salamone[a]; W. C. Rice[a]; A. C. Watterson[a]
[a] Polymer Science Program Department of Chemistry, University of Lowell, Lowell, Massachusetts

To cite this Article Salamone, J. C. , Rice, W. C. and Watterson, A. C.(1991) 'Solution Behavior of an Alternating Anionic-Zwitterionic Copolymer', Journal of Macromolecular Science, Part A, 28: 9, 885 — 895
To link to this Article: DOI: 10.1080/00222339108054066
URL: http://dx.doi.org/10.1080/00222339108054066

J. MACROMOL. SCI.—CHEM., A28(9), pp. 885–895 (1991)

SOLUTION BEHAVIOR OF AN ALTERNATING ANIONIC-ZWITTERIONIC COPOLYMER

J. C. SALAMONE, W. C. RICE, and A. C. WATTERSON

Polymer Science Program
Department of Chemistry
University of Lowell
Lowell, Massachusetts 01854

ABSTRACT

In this paper the dilute solution properties of a novel alternating anionic-zwitterionic copolymer are discussed. The copolymer, synthesized through a spontaneous route, exhibited contrasting polyampholytic and polyelectrolytic behavior in aqueous salt solution. Intrinsic viscosity and light-scattering studies as a function of simple electrolyte added are presented to illustrate the unique solution characteristics. An explanation of the effect of salt on the molecular dimensions of the polymer is offered.

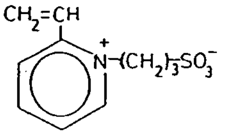
INTRODUCTION

Recently, considerable interest has been generated in the preparation of ionic polymers to meet the current demand for new water-compatible materials [1-4]. These studies have involved the areas of cationic, anionic, and ampholytic polymers, since all classes possess unique chemical and physical properties.

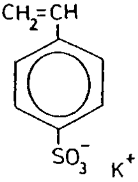
Our research group has conducted extensive studies into the preparation of high-charge-density, ion-containing macromolecules, in particular, ampholytic polymers [1, 2, 4–10]. Two types of monomers have been employed in the synthesis of these polyampholytes: ion-pair comonomers and vinyl monomers derived from 1,3-sultones, the sulfobetaines [9, 10]. Vinyl sulfobetaines contain both cationic and anionic units on the same pendent group, wherein each charge is a counterion to an oppositely charged site and there are no mobile gegenions. Ion-pair comonomers can be considered to consist of two individually polymerizable vinyl monomeric ions, where one anionic vinyl moiety is a gegenion to an oppositely charged cationic vinyl counterpart and no nonpolymerizable ions are present. The presence of ionic units along the polymer backbone has a distinct effect on the solution properties of this class of polymeric material. In the absence of simple electrolyte in aqueous solution, ampholytic polymers exhibit behavior ranging from highly water-swollen, insoluble hydrogels to water-soluble substances.

Relative to these ampholytic monomers mentioned, all systems that contain a 2-, 4-, or 5-vinylpyridinium moiety are subject to spontaneous polymerization [11]. This facile polymerization has yielded a new method for the formation of ampholytic polymers of high molecular weight. In general, monomer pairs of differing polarity, based on the above-mentioned vinylpyridinium ion, have been found to spontaneously polymerize, presumably to an alternating structure through a charge transfer complex [3].

In this investigation it was of interest to prepare an alternating anionic-zwitterionic copolymer from the charge-transfer, spontaneous polymerization of electron accepting 1(3-sulfopropyl)-2-vinylpyridinium inner salt (I) (SVP) and electron-donating potassium *p*-styrenesulfonate (II) (PSS).



I



II

Viscosity measurements in conjunction with light-scattering data have shown that this novel polymer possesses unique and interesting behavior in aqueous salt solution.

EXPERIMENTAL

Polymer Preparation

Poly [*p*-styrenesulfonate-co-1(3-sulfopropyl)-2-vinylpyridinium betaine] [poly(SVP/PSS)] was prepared by spontaneous polymerization of a 0.5 *M* solution of the corresponding vinyl monomeric salts in distilled water at room temperature. After an approximate polymerization period of 5 days, the polymer was dialyzed (MWCO: 12,000–14,000) exhaustively against distilled water to remove low-molecular-weight fractions. The purified product was then obtained through lyophilization.

Elemental analysis for ($C_{18}H_{18}O_6NS_2*1.1H_2O$):
Calcd. C:46.07, H:4.73, N:2.99, S:13.65,K:8.30.
Found C:46.11, H:4.77, N:3.00, S:13.62, K:8.27.

Viscosity Measurements

Viscometric properties of the polymer system were studied under dilute (1%) and concentrated (10%) conditions utilizing a variable-shear, four-bulb Ubblehode dilution viscometer for the former and a cone-plate Brookfield digital viscometer for the latter. Quantitative amounts of polymer sample were dissolved in a salt solution of varying concentrations using a volumetric flask. The simple electrolyte employed throughout this investigation was sodium chloride of reagent purity. Dialysis of all polymeric solutions against solvent was omitted because of the large excess of salt present. Viscosities were determined at 25 + 0.1 °C taking precautions to keep all solutions dust free.

Light-Scattering Measurements

The light-scattering measurements were carried out on a laser light-scattering photometer, Dawn model F (Wyatt Technology Corp., Santa Barbara, CA), which employs a He-Ne 5 mW vertically polarized laser (λ = 632.8 nm) as a light source. Measurements were made on solutions that were previously dialyzed against solvent to establish Donnan membrane equilibrium and filtered through a 0.22 μm Millipore filter.

Optical clarity for all solutions was checked by direct observation of the light beam within the solution coupled with constant readings on the channel monitor. Light-scattering intensities were measured from 15 different angles between 35 and 124. The specific refractive index, dn/

dc, was determined on a Brice-Phoenix differential refractometer calibrated with NaCl solutions of known refractive indices. The light source was a mercury vapor lamp fitted with a filter to isolate the 632.8-nm emission line.

Light-scattering intensities were evaluated by the Zimm technique. A computer program was developed in this laboratory to generate the Zimm plot where double extrapolations were required.

RESULTS AND DISCUSSION

Viscosity Studies

Preliminary viscosity results obtained by using an ordinary Ubblehode viscometer showed the polymer was shear dependent even in very dilute solution. Subsequent viscosity measurements were all carried out on a variable-shear, four-bulb Ubblehode dilution viscometer. Results were treated by the well-known Huggins equation:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C$$

which produced a linear plot that fit the data well as observed by good correlation coefficients for a straight line. The limiting viscosity number, $[\eta]$, was obtained from the intercept of the viscosity axis with the Huggins curve. Table 1 is a compilation of the data obtained from this

TABLE 1. Effect of Salt on Intrinsic Viscosity and Huggins Constant for Poly(SVP/PSS)

[NaCl]	$[\eta]$ (dL/g)	k'	Corr. coeff.
0.10	3.7	0.73	0.99
0.25	3.1	0.62	0.99
0.50	3.0	0.47	1.00
1.00	1.5	0.45	0.99
1.50	1.3	0.40	0.99
2.00	1.2	0.38	0.98
3.00	1.1	0.23	0.99
4.00	1.0	0.20	0.99

investigation. In this table the effect of salt on the solution properties of poly(SVP/PSS) is reflected in the concurrent changes in the Huggins constant, *k*′, and intrinsic viscosity values.

Intrinsic viscosity of the anionic-zwitterionic polymer as a function of salt concentration was studied as shown in Fig. 1. It is observed that moderate changes in the ionic strength of the media sharply reduced the intrinsic viscosity. This type of solution behavior is similar to that of polyelectrolytes, where the presence of simple electrolyte causes a screening of like charges on the macromolecule and permits the polymer coil to collapse and sometimes precipitate from solution.

Furthermore, Table 1 shows a decrease in the Huggins constant with a corresponding increase in simple electrolyte concentration. This decrease in the Huggins constant may be associated with an increase in polymer-solvent interaction. It is conceivable that this solubilizing effect can be rationalized on the basis that salt penetrates into the polymer network and disrupts the ionic crosslinks leading to increased solvent segment interaction. Behavior of this type is indicative of polyampholytes in aqueous salt solution.

The Brookfield viscosity behavior was investigated to ascertain if the

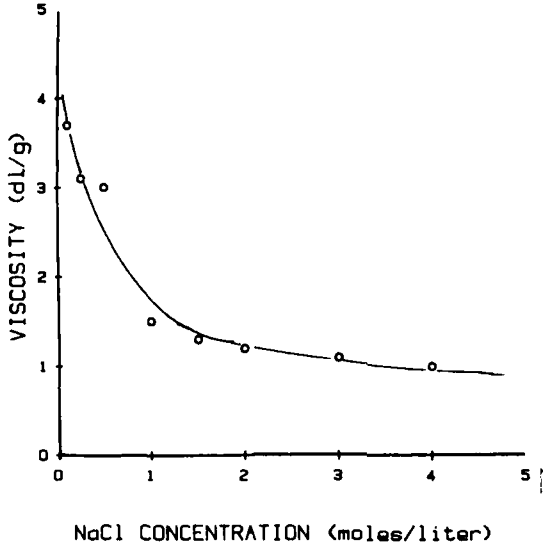


FIG. 1. Effect of NaCl concentration on intrinsic viscosity.

zwitterionic-anionic system was pseudoplastic or thixotropic. Figure 2 represents the results of three 10% solutions in water and in 1.0 *M* and 2.0 *M* sodium chloride solutions. All three solutions behaved similarly; in all three, the viscosity dropped rapidly at lower shear rates, apparently owing to the disentanglement of chains, and then became constant, Newtonian, at higher shear rates, probably owing to the ionic bonding that maintains viscosity. It was observed that the aqueous polymer solution exhibited shear thinning even at higher shear rates. This could be attributed to agglomerization of polymer particles through ionic attractions. In all solutions, with increased salt concentration the viscosity decreased owing to the breaking up of ionic-type bonds between the oppositely charged sites located along the polymer pendent groups. No thixotropic behavior was noted for any of the solutions under the conditions employed.

Light-Scattering Studies

In conjunction with viscosity measurements, light-scattering techniques were utilized to investigate further the increased solvent-segment interaction with increased salt content. The Zimm method, which con-

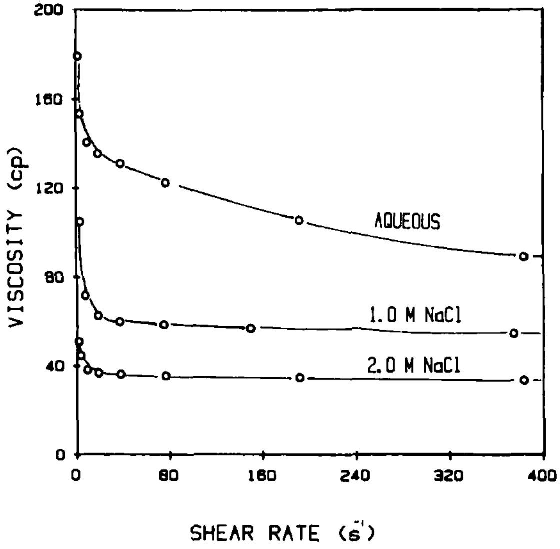


FIG. 2. Effect of shear rate and NaCl concentration on the apparent viscosity of a 5% solution of spontaneous copolymer.

sists of extrapolating to both zero angle and zero concentration, presented a convenient method to determine such molecular dimensions as the radius of gyration, second virial coefficent, and weight average molecular weight, provided that the polymer solution was dialyzed against solvent to achieve similar chemical potential. Figure 3 is an illustration of this technique with respect to the polymer under study. With all Zimm plots obtained in salt solution the data points remained linear even at higher angles, indicating a polymer that possesses a narrow-molecular-weight distribution. This data is consistent with previously found light-scattering experiments and GPC results on other spontaneously formed polymeric systems [8]. The results obtained by the Zimm analysis for the polymer under study in salt solution are given in Table 2. The light-scattering data appear to be consistent with viscosity data.

It is interesting to notice that as salt concentration is increased, both the weight average molecular weight and radius of gyration decreased. The decrease in molecular weight with an increase in added electrolyte may be attributed to the breaking of agglomerated structures that are present due to intermolecular ionic associations at low ionic strength of

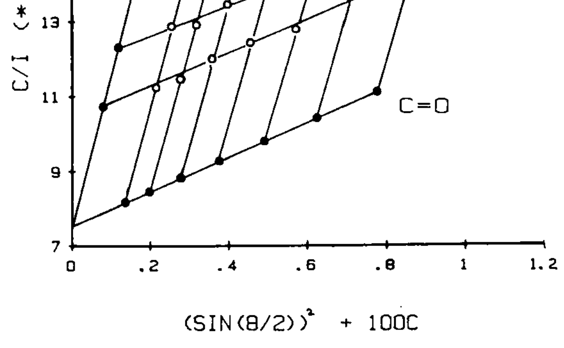


FIG. 3. Zimm plot of spontaneous copolymer in 1.5 *M* aqueous NaCl solution.

TABLE 2. Effect of Salt Concentration on the Molecular Parameters of Poly(SVP/PSS)

[NaCl]	$\overline{M}_w \times 10^{-6}$	$A_2 \times 10^6$	R_g(Å)
0.10	4.0	0.5	856
0.25	3.8	0.6	597
0.50	3.9	0.7	507
1.00	2.5	1.3	566
1.50	2.1	1.9	677
2.00	1.5	1.8	573
3.00	1.3	3.3	439
4.00	0.8	4.9	478

the media. This also explains the large drop in viscosity at low salt strength of solvent, since molecular weight and intrinsic viscosity have been empirically related. In addition, a least-squares treatment of the molecular-weight data versus NaCl concentration gives an apparent molecular weight of 4.3 × 10^6 in the absence of salt.

Figure 4 gives a plot of the second virial coefficient, A_2, as function of salt concentration, where A_2 is a measure of the total excluded volume effect. It can be seen that the value of A_2 increased with corresponding increases in salt concentration. A comparison of the experimentally determined Huggins constants (Table 1) and second virial coefficients (Table 2) appears to confirm the idea that the reduction in molecular dimensions of the spontaneous polymer is primarily due to some type of solubilizing and dissociation effect caused by the presence of salt.

From Fig. 5 it can be noted that the effect of salt on the radius of gyration of poly(SVP/PSS) is not as pronounced as with the other molecular dimensions, i.e., $\overline{M}_w$, A_2, k', $[\eta]$. It has been known that the radius of gyration is more susceptible to intramolecular changes than other molecular parameters. To account for this sensitivity in our results, it is conceivable that two opposing forces are in action, both caused by the dissociative power of simple salt to disrupt ionic attractions between oppositely charged sites located along the macromolecule. In one case, particle size is diminished through the breaking of intermolecular bonding and the elimination of polymer aggregates. On the other hand, expansion occurs at the intramolecular site of the zwitterionic sulfopropyl substituent.

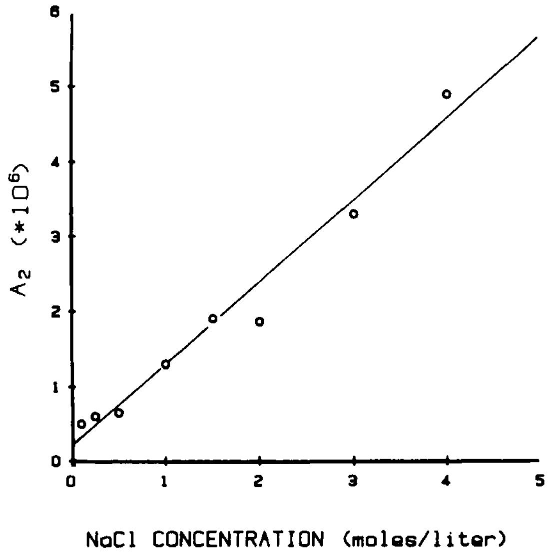


FIG. 4. Second virial coefficient versus NaCl concentration.

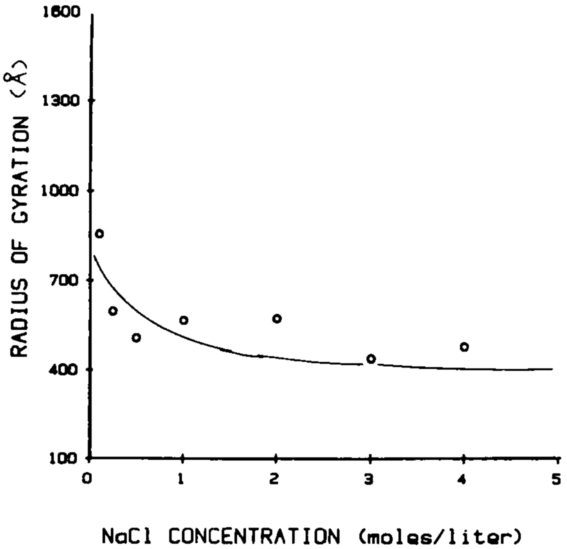


FIG. 5. Radius of gyration versus NaCl concentration.

In deionized water, a twisted Zimm plot is obtained, as shown in Fig. 6. This Figure graphically represents the effect of large macromolecular aggregates on the scattering intensities in solution. Light-scattering data were inconsistent even for very dilute aqueous solutions and did not permit interpretation of the data by the Zimm technique. Even though our light-scattering data was not able to allow determination of the desired molecular parameters, in deionized water it can be seen that the zero-angle line possesses a negative slope, which indicates a negative second virial coefficient. This suggests that water is a poor solvent for the system. Presumably the structural feature responsible for this behavior is the ionic interaction between the charged groups, which leads to the exclusion of solvent.

CONCLUSION

From the data obtained it seems apparent that the presence of salt promotes the dissolution of this alternating polymer in aqueous media due to the disruption of ionic-type interactions. Addition of small

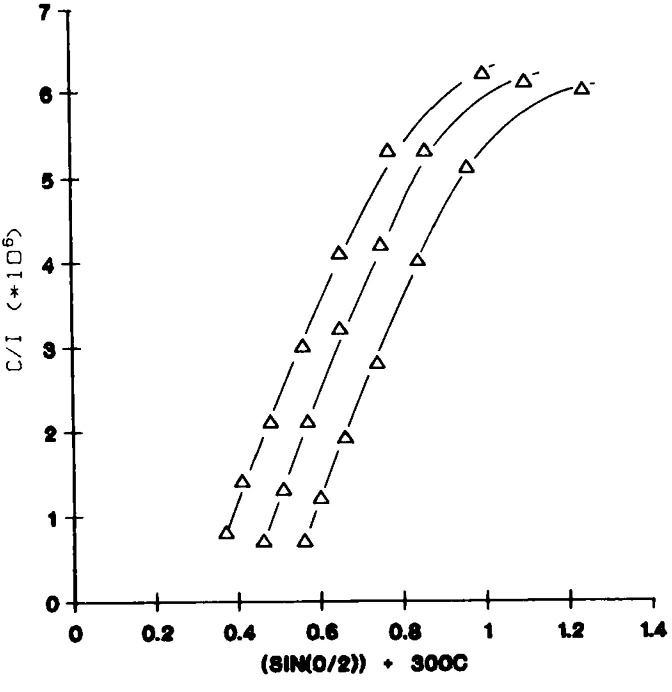


FIG. 6. Twisted Zimm plot of spontaneous copolymer in water.

amounts of salt dissipates large polymer aggregates, as noted by sharp reductions in viscosity, molecular weight, and radius of gyration. It appears that on further addition of simple electrolyte, the solubilizing effect of salt is slowed, which is reflected in smaller changes in the values of the experimentally determined quantities. The leveling effect can be explained through the disappearance of aggregated structures. Once the large structures have been broken, only the intramolecular attractions, such as those between the zwitterionic sites of the sulfopropyl betaine moiety, are present for the simple electrolyte to neutralize.

Thus, light-scattering studies together with viscosity determinations, in water as well as in salt solution of varying concentrations, have revealed the existence of a contrasting polyampholyte/polyelectrolyte behavior for this novel copolymer in dilute aqueous salt solution.

REFERENCES

[1] J. C. Salamone, W. C. Rice, and A. C. Watterson, *Polym. Prep., 1*(29), 279 (1988).

[2] J. C. Salamone and W. C. Rice, in *Encyclopedia of Polymer Science and Engineering,* Vol. 11, 2nd ed., Wiley, New York, 1988, pp. 513-530.

[3] J. C. Salamone, C. C. Tsai, and A. C. Watterson, *J. Macromol. Sci. – Chem., A13*(5), 665 (1979).

[4] J. C. Salamone, M. U. Mahmud, A. C. Watterson, A. P. Olson, and E. J. Ellis, *J. Polym. Sci. Polym. Chem. Ed., 20,* 1153 (1982).

[5] J. C. Salamone, B. Snider, and W. Fitch, *Macromolecules, 3,* 707 (1970).

[6] J. C. Salamone, B. Snider, and W. Fitch, *J. Polym. Sci., Part A., 9,* 1493 (1971).

[7] J. C. Salamone, E. J. Ellis, and S. C. Israel, *J. Polym. Sci., Part B, 10,* 605 (1972).

[8] J. C. Salamone, E. J. Ellis, and D. F. Bardoliwalla, *J. Polym. Sci., Part C, 45,* 51 (1974).

[9] J. C. Salamone, A. C. Watterson, T. D. Hsu, C. C. Tsai, and M. U. Mahmud, *J. Polym. Sci., Polym. Lett. Ed., 15,* 487 (1977).

[10] J. C. Salamone, W. Volksen, A. P. Olson, and S. C. Israel, *Polymer, 19,* 1157 (1978).

[11] J. C. Salamone and W. C. Rice, in *Encyclopedia of Polymer Science and Engineering,* Vol. 17, 2nd ed., Wiley, New York, 1988, pp. 578-586.