Dilute Solution Behavior and Mark-Houwink Constants for a Non-linear Cationic Polyelectrolyte

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Synopsis

Mark-Houwink coefficients and radius of gyration dimensions are presented for six unfractionated cationic polyelectrolytes of the poly(dimethylamine-epichlorohydrin-ethylenediamine) type. The copolymer system was studied in .05M, .10M, and 1.0M NaCl, and .12M $NaClO_4$ aqueous solutions. Their solution behavior, as studied by intrinsic viscosity and light-scattering technique, suggests these polymers adopt a somewhat spherical or star-like conformation in aqueous salt solutions.

INTRODUCTION

The dilute solution behavior of 1,2-ethanediamine polymer with (chloromethyl) oxirane and *N*-methylmethanamine was studied by intrinsic viscosity and light-scattering techniques. This cationic polyelectrolyte is commercially described as a copolymer of dimethylamine (DMA) and epichlorohydrin (EPI) cross-linked with ethylene diamine (EDA). The compound is a water-soluble polymeric flocculant used in numerous waste water operations such as API separators, induced and dissolved air flotation, sludge thickening and dewatering, and media filtration.

The unusual dilute solution characteristics and magnitude of the Mark-Houwink constant ($0 < a < .5$) for this polymer in the presence of electrolytes suggests that it adopts a somewhat spherical or star-like configuration and not a linear random coil. Because of this configuration, many relationships such as the Stockmayer-Fixman equations which are traditionally used to describe the behavior of linear coiled polymers are inapplicable. This paper presents the Mark-Houwink-Sakurada constants for this polyelectrolyte in .05M, .10M, and 1.0M NaCl, and .12M $NaClO_4$, and describes its behavior in these salt solutions.

There are no previous referenced studies in the literature that pertain to the solution characteristics or Mark-Houwink constants for this particular type of polyelectrolyte.

EXPERIMENTAL

Structure Elucidation

Six unfractionated solution copolymers of the poly(dimethylamine-epichlorohydrin-ethylenediamine) type were studied in this investigation. The com-

pounds were synthesized by our laboratories and CPS Chemical Co. The synthesis of ionenes through condensation-addition polymerization is well understood.[1-6] The molar ratios of dimethylamine (DMA) to epichlorohydrin (EPI) were approximately 1 : 1 with 1.25 to 6.0 mole percent ethylene diamine (EDA). The major product formed in the 1 : 1 reaction of DMA with EPI is the 2-hydroxy-3-ionene chloride. There are small amounts of azetidinium salt as a reaction byproduct. The addition of EDA to the dimethylamine causes an increase in molecular weight and appears to be incorporated in the polymer backbone as a possible crosslinking agent. A generalized reaction sequence and structure for this alternating copolymer system with some crosslinking would be:

DMA   EPI   2-hydroxy-3-ionene   azetidinium salt
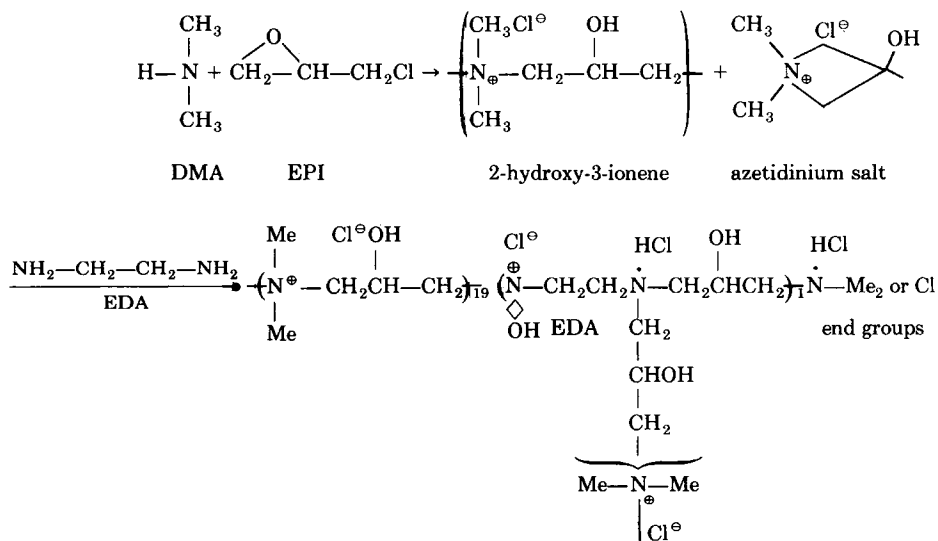
The condensation of dimethylamine with epichlorohydrin and crosslinked with ethylene diamine gave an almost quantitative yield of 1,2-ethanediamine polymer with (chloromethyl) oxirane and N-methylmethanamine. The samples were 98–99% quaternized. The nitrogens of the ethylene diamine can constitute part of an azetidinium ring or if involved in a crosslink they may be tertiary or quaternized. ^{13}C (NMR) nuclear magnetic resonance has identified trace amounts of azetidinium salt and dimethylamino and chloromethyl polymer chain end groups. As the polymerization proceeds, the azetidinium salt concentration decreases, indicating eventual incorporation into the polymer molecules. The amount of azetidinium salt is dependent on the epichlorohydrin addition rate and reaction temperature.

The structure and composition of the final product was characterized by ^{13}C NMR, gas chromatography-mass spectroscopy (GC-MS), total and basic nitrogen analysis, % quaternization, and Schöniger and ionic chloride determination. The gas chromatography-mass spectroscopy was performed on a DuPont Instruments DP-1 System with methane chemical ionization and single ion monitoring on a SP-2250 column for epichlorohydrin detection and on a four foot 3% OV-1 column for the dimethylamine and ethylene diamine

detection. The ^{13}C NMR spectra were run on a JEOL JNM-FX-60 spectrophotometer. The final product was examined with a Carlo Erba Total Nitrogen Analyzer to aid in the determination of the charge density.

Synthesis

Dimethylamine, epichlorohydrin, and ethylene diamine from Aldrich Chemical Co. were used as obtained. A 40 wt% dimethylamine solution in water and ethylene diamine were charged into a Chemco pressure reactor and pressured to 10 psig. The reactor temperature was adjusted through hot and cold water coils regulated with a thermo watch. The reactor stirring was set at 485 rpm with a mixing intensity of 300 s^{-1} for the initial reaction stages. As the polymer solution viscosity increased to 100–200 cps, the stirrer was increased to 1145 rpm to maintain the same initial mixing intensity. Continuous indirect viscosity measurements of the reactor solution were accomplished with a G. K. Heller torque meter connected to a Heller 1/8 H.P. motor that drives the reactor stirrer. The torque meter made it possible to monitor the rate of polymerization continuously and to add incremental amounts of epichlorohydrin when required based on the viscosity changes rather than at specified time. The addition of epichlorohydrin to the reactor, on a 1:1 molar ratio with dimethylamine, was from a stainless steel pressure cylinder with the reactor temperature maintained at 60–70°C.

The epichlorohydrin was added at 2.7 × 10^{-2} mole per mole dimethylamine per minute to the reactor vessel while maintaining the temperature at 60–70°C with cooling. After the initial bulk portion of epichlorohydrin was added, the reactor vessel was heated to 90–95°C for the remainder of the polymerization. As the rate of viscosity increase leveled off, 0.059 moles of additional epichlorohydrin per mole of epichlorohydrin in the reactor was added. Once the desired viscosity was achieved, the sample was diluted with distilled water and cooled and the pH adjusted to 5.5 with concentrated HCl to prevent further polymerization. The polymer samples were characterized as quickly as possible after synthesis because of product instability upon storage. The polymers may increase in viscosity with time due to further reaction of remaining chlorohydrin groups with any free amines. A pH of 5.5 will help minimize any viscosity change by preventing the conversion of unquaternized amines on the polymer molecules to free amines. The variance in the polymer molecular weights was governed by the amount of ethylene diamine in the system, and by the addition rate of epichlorohydrin.

Sample Preparation

The polymers were placed in Spectrapor #6 membrane tubing with a molecular weight cut off of 1,000 and dialyzed against deionized water for 24 hours. Rotary evaporation and freeze-drying of the dialyzed samples was initially pursued, but later eliminated from the purification procedure due to the great difficulty encountered in removing the glass-like polymer from the freeze-drying flask.

The polymer concentration after dialysis was determined by two methods. The first is a spectrophotometric procedure capable of detecting low levels of cationic polyelectrolytes and depends upon the charge complex formed be-

tween the cationic polymer and the anionic dye Ponceau S.[7] The second method was a nonvolatile activity procedure whereby the water was evaporated at elevated temperatures.

Viscosity, Refractive index Increment, and Light-Scattering Measurements

Solvents and polymer solutions were filtered through .45 μm Millipore cellulose acetate-cellulose nitrate membranes. A 400 mL ultrafiltration cell (Amicon) served as the standard filtration system. For calibration of the light scattering photometer with benzene, a stainless steel cylindrical pressure vessel was used with a .22 μm Millipore teflon filter. All filters were rinsed with 600 mL of distilled water before use in order to remove the glycerol which acts as a preserving agent. Aqueous salt solutions were prepared with distilled water and analytical grade salts.

Viscosity measurements were made at 25 $\pm$ .05°C in a constant temperature water bath with a #75 Cannon-Fenske Viscometer. Intrinsic or limiting viscosities were determined at 25°C in .05M, .10M, and 1.0M NaCl, and in .12M NaClO$_4$ at pH = 5.5 units. Intrinsic viscosities were extrapolated from the linear plots of reduced viscosity versus concentration (Huggins Plot).

The specific refractive index increment (dn/dc) measurements were made with a Brice-Phoenix differential refractometer in 1.0M and .10M NaCl, pH = 5.5, and at ambient temperature. The instrument was calibrated with distilled water solutions of potassium chloride. An additional dialysis against the reference solvent was incorporated at this point in order to get a more accurate assessment of the refractive index increment. This additional dialysis step assures a constant chemical potential between the polymer solution and the reference solvent. Refractive index increment measurements were made with and without equilibrium dialysis.

Light-scattering measurements were also carried out in 1.0M and .10M NaCl at pH = 5.5 with a Brice-Phoenix universal light scattering photometer and blue unpolarized light of 4361 Å (in vacuo). Scattering angles evaluated were 30°, 45°, 60°, 75°, 90°, 105°, 120°, and 135°, although only those angles greater than 75° were normally used in constructing the Zimm plots due to poor data at the lower angles. The photometer was calibrated with benzene as a standard. The literature value[8] of 48.5 $\times$ 10^{-6} cm^{-1} for the benzene Rayleigh ratio R (90°) at 436 nm was used as a calibration standard for the photometer. A fluorescein sodium salt solution was used to calculate the angular correction terms. The values of the weight average molecular weight $\overline{M}_w$, second virial coefficient A$_2$, and mean square radius of gyration $\langle \overline{S}^2 \rangle$, were obtained from Zimm plot extrapolations.

RESULTS AND DISCUSSION

The experimental values for the refractive index increments are listed in Table I. Values are given for those measurements taken before equilibrium dialysis at constant molality (dn/dc)$_m$ and after dialysis at constant chemical potential (dn/dc)$_\mu$. The constant chemical potential values were somewhat larger than the constant molality readings. These findings further illustrate the necessity of dialysis against the reference solvent in order to get an

TABLE I
Refractive Index Increments at Constant Molality and Constant Chemical Potential
for Poly (DMA-EPI-EDA) Copolymer System in 1.0M and .10M Aqueous NaCl
at pH = 5.5 Units

.10M NaCl (mL/g)		1.0M NaCl (mL/g)	
$(dn/dc)_m$	$(dn/dc)_\mu$	$(dn/dc)_m$	$(dn/dc)_\mu$
.201	.203	.182	.198

accurate assessment of the refractive index increment as reported by other studies.[9-11] Constant chemical potential refractive index increments were used in all molecular weight determinations. Values are reported for two solvent systems, .10M and 1.0M NaCl, because the highest molecular weight compound exhibited a very pronounced Tyndall effect in 1.0M NaCl with excessive back scattering in the photometer at the lower angles. The .10M NaCl solvent system was more suitable for this compound in the light-scattering studies.

Light-scattering data was examined according to the Zimm plot procedure[12] where double extrapolation of polymer concentration and scattering angle to zero should give a common intercept. All six compounds studied exhibited concentration and/or angular dependence. The concentration curves of the first five polymers had large linear deviations at scattering angles less than 90°. These same compounds also exhibited sharp angular curvature as the concentrations decreased. The deviations from linearity at low scattering angles does not prevent an accurate assessment of the true weight average molecular weight. The linear correlation at angles 90°, 105°, 120°, and 135° was very good and the double extrapolation of the angular and concentration curves to a common intercept was in agreement. The highest molecular weight compound studied had a quite different Zimm plot from the others. As mentioned previously, this compound was run in .1M NaCl instead of 1.0M NaCl due to high back scattering intensities at the lower angles where there was more light scattered at 30° and 45° than at 0°. The sample in 1.0M NaCl had a pronounced haze indicating some insolubility. The .10M NaCl solvent system was satisfactory. The Zimm plot of this compound showed marked angular dependence with the concentration curves bending downward at the higher angles. According to Huglin,[13] this is a general feature of polydispersity.

The polymer samples were also checked for fluorescence and adsorption of incident light. Fluorescence is easily determined with the photometer because the transversely scattered light is polarized and fluorescent light is largely unpolarized and is also of longer wavelength than the scattered light. The polymer samples were tested for fluorescence with the green wavelength (5460 Å) and the red CF-2 filter. No additional intensity was observed by the detector for the polymer dilutions when compared to the solvent reading; therefore, no adjustments were needed for fluorescence.

Adsorption due to color in the polymer solutions is generally not a problem in determining scattering ratios. However, it was worthwhile to test these compounds because of the yellow color present in the solutions after very

TABLE II
Weight-Average Molecular Weight, Second Virial Coefficient, and Root-Mean-Square Radius of Gyration from Light Scattering Data in 1.0M NaCl and .10M NaCl

| Sample | (For 1.0M NaCl) | | |
	$\overline{M}_w \times 10^{-4}$ (daltons)	$A_2 \times 10^6$ (mol · cm^3 · g^{-2})	$\langle \overline{S}^2 \rangle^{1/2}$ (Å)
1	3.83	19.81	218
2	9.55	4.10	226
3	15.72	3.86	277
4	18.10	3.22	269
5	32.42	3.15	315
	(For .10M NaCl)		
6	102.14	3.68	830

thorough dialysis. The compound with the most color was tested first and each concentration was tested for a transmittance factor and an adsorption coefficient. The corrected scattering intensities for color absorption increased the molecular weight by 2.2%. This was considered a negligible contribution and no further corrections were investigated for the less colored samples.

Table II summarizes the light scattering experimental data. The slope of the $\theta = 0$ curve yields the second virial coefficient A_2 while the initial slope of the C=O curve was instrumental in the calculation of polymer dimensional parameters. As expected, there was the general tendency of the second virial coefficient to decrease with increasing molecular weight. The size of the
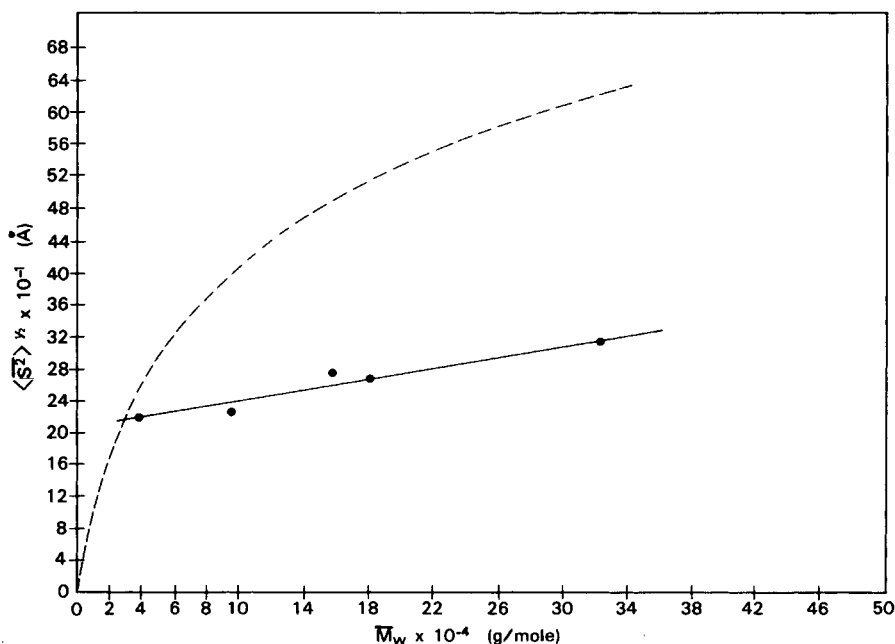

Fig. 1. Plot of root mean square radius of gyration $\langle \overline{S}^2 \rangle^{1/2}$ vs. weight-average molecular weight $\overline{M}_w$ in 1M NaCl. Dashed curve represents typical behavior of linear random coiled polyelectrolyes.

root-mean-square radius of gyration relative to the molecular weight of the samples is quite unusual. There is very little increase in the dimensions of the polymer as the molecular weight increases. The dimensions of sample six cannot be evaluated relative to the other five because of the different solvent system for the light-scattering study. Figure 1 is a plot of the root-mean-square radius of gyration vs the weight-average molecular weight of the first five compounds in 1M NaCl and pH = 5.5 units. This plot is quite different from linear random coiled polyelectrolyte plots as approximated by the dashed curve. Normally the curve will intercept the axis at zero as expected for a compound with zero molecular weight and then it will increase initially in a near logarithmic fashion before leveling off somewhat at the very high molecular weights. In contrast, as the molecular weight of these DMA/EPI/EDA polyelectrolytes increased by an order of magnitude (900%), the radius of gyration increased only 41%. This behavior is best explained if these compounds exist not as linear random coils, but rather, possess spherical star-like configurations. Then large increases in the molar mass or volume could be achieved with very little increase in the radius of gyration. The radius of gyration dimension was also examined through the relationship.

$$\langle \bar{S}^2 \rangle^{1/2} \propto \bar{M}_w^{\text{slope}} \qquad (1)$$

where the exponent is the slope of the double logarithmic plot of the root-mean-square radius of gyration vs the weight-average molecular weight as illustrated in Figure 2. The slope is .177 and the proportionality constant is 32.3 if Eq. (1) is treated as an equality.

The intrinsic viscosity was determined in four different solvent systems in an attempt to study the polymer's behavior in near theta conditions. The sodium perchlorate system was included because of its excellent counterion efficiency and specific ion effects such as the polarizability of the anion and the strength of the protonic acid in water.[14] In .21M and .17M $NaClO_4$, the polymer precipitated from solution. However, in .12M $NaCl_4$, successful runs
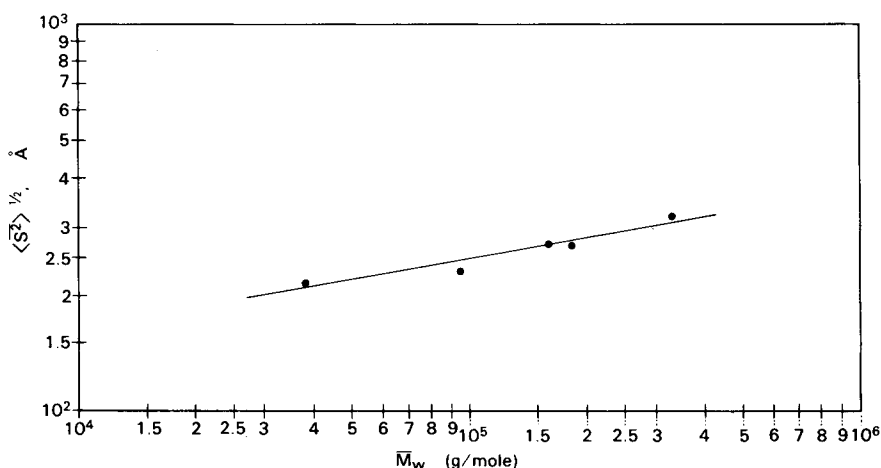

Fig. 2. Double logarithmic plot of the root-mean-square radius of gyration vs. the weight-average molecular weight in 1.0M aqueous NaCl.

TABLE III

Intrinsic Viscosities in .05M, .10M, and 1.0M NaCl, and .12M NaClO$_4$ at 25°C and
pH = 5.5 units for DMA/EPI/EDA Copolymer System ([η], in dL/g)

Sample	.05M NaCl	.10M NaCl	1.0M NaCl	.12M NaClO$_4$
1	.488	.386	.190	.085
2	.663	.490	.226	.089
3	.858	.628	.275	.087
4	.876	.661	.250	.087
5	.992	.802	.323	.091
6	1.733	1.324	.536	---

TABLE IV

Huggin's Coefficient (K') in .05M, .10M, and 1.0M, NaCl, and .12M NaClO$_4$ at 25°C and pH = 5.5 units
(From Plots of Reduced Viscosity vs Polymer Concentration)

Sample	.05M NaCl	.10M NaCl	1.0M NaCl	.12M NaClO$_4$
1	.164	.118	.190	13.76
2	.077	.162	.333	11.55
3	.196	.274	.472	25.63
4	.069	.169	.334	21.23
5	.319	.218	.489	29.46
6	.650	.598	1.027	---

were made on the first five compounds, but the highest molecular weight compound precipitated. This solvent system is certainly extremely close to representative theta conditions.

Tables III and IV list the intrinsic viscosity experimental data and Huggin's Coefficients (K') for .05M, .10M, and 1.0M NaCl, and .12M NaClO$_4$ at pH = 5.5 units and 25°C.

A very interesting phenomenon was observed with the theta solvent intrinsic viscosity determinations that is contrary to coiled polyelectrolyte behavior. It has been reasoned that random coiled polyelectrolytes in near theta conditions would tend to precipitate when more concentrated due to higher collision and aggregation probabilities. This same reasoning has applied to molecular weight where the higher molecular weight species tends to precipitate more readily in high specific ion environments. However, some of this behavior was not observed with the DMA/EPI copolymer system where the polymer solution showed definite signs of turbidity and polymer precipitation as the polymer was diluted in a near theta solution. This was verified by the relative viscosity readings where the polymer flow times approximated the solvent flow time. Figure 3 illustrates this behavior in a plot of reduced viscosity versus polymer concentration in .17M NaClO$_4$. Initially, an attempt was made to explain this behavior from the intrinsic viscosity procedure where successive dilutions are made from the first polymer concentration. It seemed plausible that if there was some entrainment of additional counterion along with the polymer upon dilution that each successive concentration could conceivably have a higher specific ion concentration. Therefore, if the polymer is near theta solvent conditions, this slightly higher chemical potential could
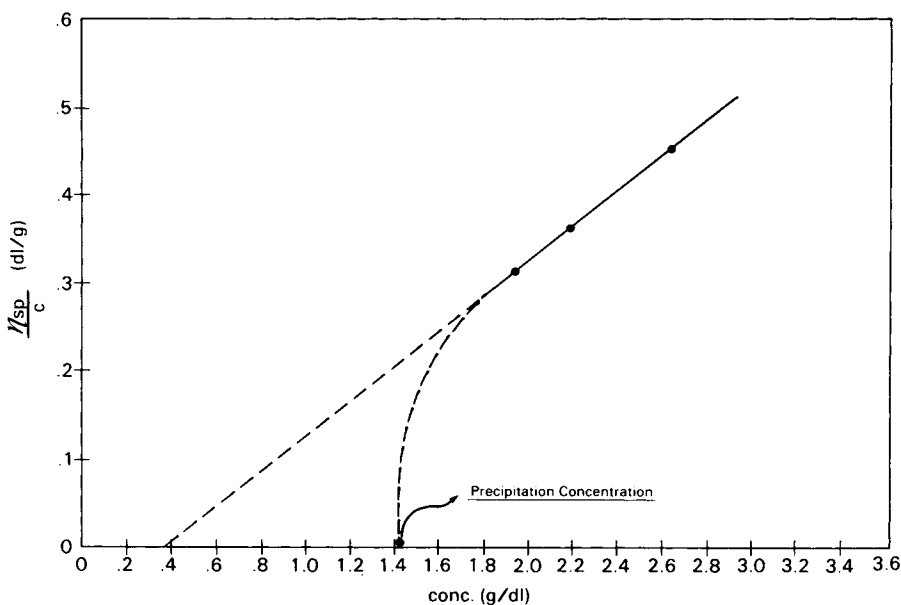
Fig. 3. Plot of reduced viscosity vs. polymer concentration in .17M NaClO₄ at 25°C.

induce polymer precipitation. We eliminated the successive dilutions method and prepared each polymer concentration individually from the stock solution and still the polymer precipitated upon dilution. It is possible from a charge ratio perspective that as the polymer concentration decreases, and consequently the number of cationic charges decreases per unit volume, the specific anion to polymer cation charge ratio per unit volume will increase, indicative of a more effective charge neutralization and possible polymer precipitation.

The Mark-Houwink-Sakurada equation expresses the empirical relation between the intrinsic viscosity of a polymer and its weight average or viscosity average molecular weight. The Mark-Houwink constants (K) and (a) for this copolymer system were determined in .05M, .10M, and 1.0M NaCl, and .12M NaClO₄ at pH5.5 and 25°C. Below are listed the Mark-Houwink equations for each solvent system.

$$[\eta] = 8.75 \times 10^{-3}\overline{M}_v^{.38} \quad (.05\text{M NaCl})$$

$$[\eta] = 6.61 \times 10^{-3}\overline{M}_v^{.38} \quad (.10\text{M NaCl})$$

$$[\eta] = 6.20 \times 10^{-3}\overline{M}_v^{.32} \quad (1.0\text{M NaCl})$$

$$[\eta] = 6.57 \times 10^{-2}\overline{M}_v^{.02} \quad (.12\text{M NaClO}_4)$$

Figure 4 shows the viscosity-molecular weight relationship for the DMA/EPI copolymer system in the various solvent systems studied.

The Mark-Houwink constant (a) varied from .02 to .38. These values are very close to the upper and lower limits for this constant in the DMA/EPI/EDA copolymer system. It was difficult to produce a solvent system which exceeded this range. Linear extrapolation to zero concentration for the intrinsic viscosity was impossible at lower salt concentrations due to
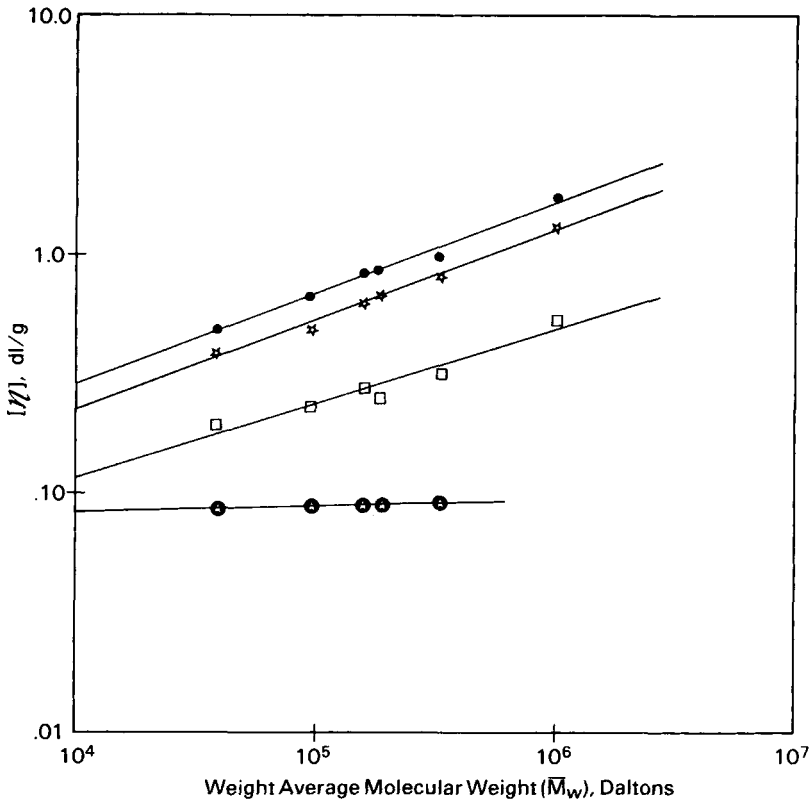
Fig. 4.   Double logarithmic plot of intrinsic viscosity vs. weight-average molecular weight in .05M, .10M, and 1.0M NaCl, and .12M NaClO$_4$ at 25° and pH = 5.5. ● = .05M NaCl; ☆ = .10M NaCl; □ = 1.0M NaCl; (☆) = .12M NaClO$_4$.

the increase in reduced viscosity as the polymer concentration decreased. This is typical behavior for a polyelectrolyte in very low counterion solutions where the polymer molecule will continue to expand upon dilution due to lack of charge neutralization of like charges on the polymer. This behavior was seen in .01M NaCl solutions. At the lower limit of constant (a), the problem of polymer precipitation is encountered as near theta conditions are approached. As mentioned earlier, .21M and .17M NaClO$_4$ solutions precipitated the polymer solutions.

Table V lists the variations in the Mark-Houwink constant (a) with changes in polymer conformation. These are very general guidelines.

TABLE V
Variations in the Mark-Houwink Constant (a) with Changes in Polymer Conformation

Mark-Houwink constant (a)	Polymer conformation
0	sphere
.5	theta solvent (poor solvent) for soft coiled polymer (tightly coiled-compact)
.65–.85	good solvent for soft coiled polymer (coil is expanded)
> .85	indicates molecular stiffness or asymmetry
1.80	rigid rod

The Mark-Houwink constant (a) fluctuated from .02 to .38 under the highest and lowest specific counterion conditions. From Table V, this would suggest that the DMA/EPI/EDA copolymer system assumes a somewhat spherical or star-like configuration in solution regardless of the salt concentration. The branching of side chains probably imparts some star-like character to the spherical mass. The fact that the Mark-Houwink exponent "a" approaches zero indicates that the crosslinked polymer molecules closely resemble spheres in shape. This conclusion is supported by Einstein's law of viscosity.[15] For a dilute suspension of spherical particles

$$\frac{(\eta/\eta_0 - 1)}{\phi} = 2.5 + K_1\phi + \cdots$$

where ϕ is the volume fraction for the spheres and K_n are expansion coefficients. For infinite dilution, which is in essence the intrinsic viscosity, the value of the reduced viscosity is equal to a constant regardless of the particle size. Thus a plot of log $[\eta]$ vs log $\overline{M}_w$ for spherical-like polymer molecules will give a line having a slope of zero, and therefore, a Mark-Houwink constant $a = 0$.

Unperturbed Dimensions

Due to this polymer's conformational characteristics in dilute solution, the unperturbed dimensional parameters could not be calculated with any certainty or validity. The quantities in the empirical Mark-Houwink equation describe a compact branched star-like configuration, and consequently, the pertinent hydrodynamic theories of Kirkwood-Riseman[16] and Flory[17] for
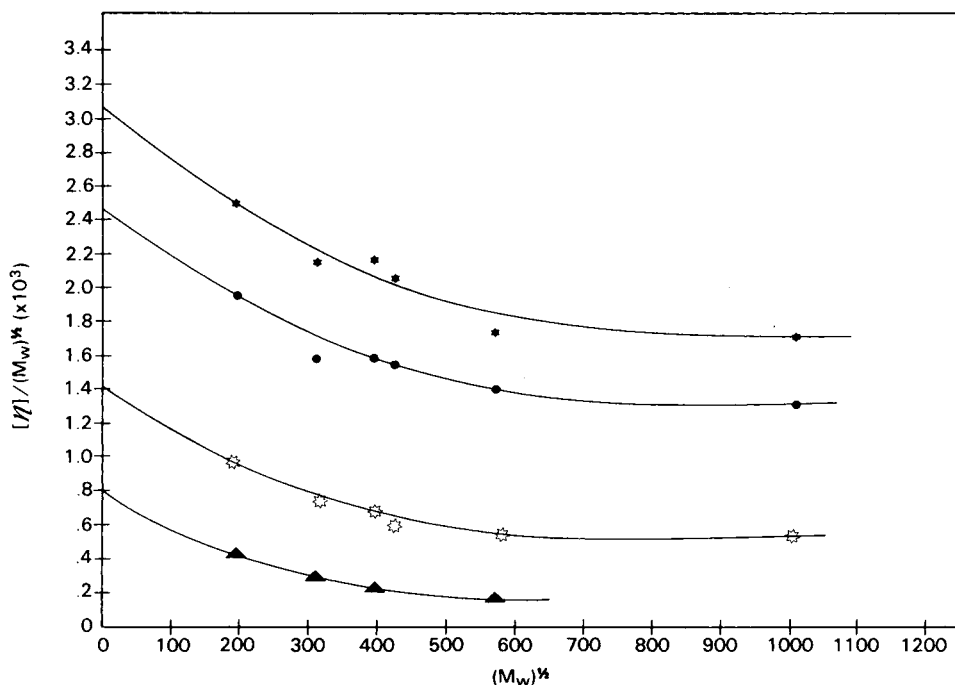

Fig. 5. Stockmayer-Fixman plot for DMA/EPI/EDA Copolymer in various aqueous salt solutions. (★) 0.05M NaCl; (●) 0.10M NaCl; (☆) 01.0M NaCl; (▲) 0.12M NaClO$_4$.

flexible linear macromolecules is inapplicable. This became very apparent when the Stockmayer-Fixman extrapolation technique was used to obtain the unperturbed dimensions. Figure 5 shows the plots of $[\eta]/M^{1/2}$ versus $M^{1/2}$ according to equation[18]

$$[\eta]/M^{1/2} = K_0 + 0.51\phi BM^{1/2} \tag{2}$$

where ϕ is Flory's universal constant, B is a parameter related to the second virial coefficient, and K_0 is expressed by the following equations.

$$[\eta]_\theta = K_0 M^{1/2} \tag{3}$$

$$K_0 = \phi_0 \left(\frac{\bar{r}_0^2}{M} \right)^{3/2} \tag{4}$$

The Stockmayer-Fixman plots of Figure 5 have negative slopes, and therefore, negative second virial coefficients, and there is no convergence to a common ordinate intercept (K_0) as predicted by the relationship.

CONCLUSIONS

The Mark-Houwink constants and the relationship between molecular weight and polymer dimensions suggests that the dimethylamine-epichlorohy-drin-ethylenediamine copolymer system assumes a spherical or star-like conformation in aqueous solution. Reliable values of the viscosity average molecular weight may be obtained from their intrinsic viscosities in .05M and .10M NaCl using the reported constants. There are limitations to the 1.0M NaCl system for high molecular weight species and the .12M $NaClO_4$ solvent system approximates near theta conditions for this compound.

Since there are no published results on the Mark-Houwink constants and dilute solution behavior of this compound, this paper will serve as a basis for future studies of the characteristics of this novel polyelectrolyte.

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